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# Diurnal and spatial variations of soil NO<sub>x</sub> fluxes in the northern steppe of China

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## ABSTRACT

NO<sub>x</sub> emissions from biogenic sources in soils play a significant role in the gaseous loss of soil nitrogen and consequent changes in tropospheric chemistry. In order to investigate the characteristics of NO<sub>x</sub> fluxes and factors influencing these fluxes in degraded sandy grasslands in northern China, diurnal and spatial variations of NO<sub>x</sub> fluxes were measured in situ. A dynamic flux chamber method was used at eight sites with various vegetation coverages and soil types in the northern steppe of China in the summer season of 2010. Fluxes of NO<sub>x</sub> from soils with plant covers were generally higher than those in the corresponding bare vegetation-free soils, indicating that the canopy plays an important role in the exchange of NO<sub>x</sub> between soil and air. The fluxes of NO<sub>x</sub> increased in the daytime, and decreased during the nighttime, with peak emissions occurring between 12:00 and 14:00. The results of multiple linear regression analysis indicated that the diurnal variation of NO<sub>x</sub> fluxes was positively correlated with soil temperature ( $P < 0.05$ ) and negatively with soil moisture content ( $P < 0.05$ ). Based on measurement over a season, the overall variation in NO<sub>x</sub> flux was lower than that of soil nitrogen contents, suggesting that the gaseous loss of N from the grasslands of northern China was not a significant contributor to the high C/N in the northern steppe of China. The concentration of NO<sub>x</sub> emitted from soils in the region did not exceed the 1-hr National Ambient Air Quality Standard (0.25 mg/m<sup>3</sup>).

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## Introduction

Nitrogen oxides (NO<sub>x</sub>), comprising NO and NO<sub>2</sub>, play a key role in the photochemical synthesis of ozone (O<sub>3</sub>) in the troposphere. They also contribute to the photochemical formation of secondary pollutants, as well as to acidification of clouds and precipitation (Atkinson, 2000; Delmas et al., 1997; Li and Wang, 2007). NO can be oxidized to NO<sub>2</sub> by O<sub>3</sub> during daylight, while NO<sub>2</sub> is converted back to NO as a result of photolysis.

Both gases are primarily derived from combustion of fossil fuel and biomass burning. The former accounts for about ~50% of the total flux, while the latter about 20%, and the remaining 30% comes from natural processes such as lightning and soil respiration (Delmas et al., 1997). Soil emits NO<sub>x</sub> primarily through microbial activities, and thus is subject to a set of environmental variables, including soil water content, soil temperature and the availability of soil inorganic nitrogen (Ludwig et al., 2001). Early studies regarded the soil

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emission as unimportant. Recent studies, however, indicate that the flux can be on a par with fossil fuel combustion (Delmas et al., 1997; Passianoto et al., 2004; Zheng et al., 2003). This is especially the case in rural and/or arid areas, where the soil emission often dominates the total flux (Atkins and Lee, 1995; Hall et al., 2008; Yienger and Levy, 1995). The emission of NO<sub>x</sub> gases from soils is so significant that can lead to a reduction in plant-available nitrogen (N) while affecting regional air quality. Currently, most of the studies have focused on agricultural and forest soils with or without fertilization (Aneja et al., 1995; Christensen et al., 1996; Das et al., 2008; Davidson et al., 1993; Fang and Mu, 2006, 2007; Li and Wang, 2007, 2008; Mei et al., 2009; Pang et al., 2009; Passianoto et al., 2004; Roelle et al., 2001; Sullivan et al., 1996; Yamulki et al., 1995; Zhang et al., 2011). Despite the importance of soil emission in the arid rural area, few studies have been done in arid and semi-arid land (Galbally et al., 2008; Holst et al., 2007; Lee et al., 2005; Su et al., 2004), and even fewer on degraded soils of different taxonomy and plant coverage in arid grassland, the steppe (Xu et al., 2003).

The northern steppe of China covers an area of 1.5 million km<sup>2</sup>, providing livelihood to the majority of inhabitants that depend on animal husbandry. The soil quality and productivity are fundamental to the living standard of the people as well as to the regional economic development. Over-grazing in the past decades has left 90% of the steppe in degraded state, which is characterized by loss of organic carbon and nitrogen as well as in clay and silt.

Our previous studies have demonstrated that the C/N ratio of soil organic matter is systematically higher in the steppe compared with other grasslands, and hypothesized that the relative deficiency of N might be a result of its faster loss than carbon due to significant emission of NO<sub>x</sub> gases during soil degradation. Based on this notion, we measured the fluxes of NO<sub>x</sub> in degraded land of the steppe so as to understand (1) the diurnal and spatial variations of the NO<sub>x</sub> fluxes; (2) the influence of soil type and vegetative covers; and (3) the influence of soil temperature, soil water content and pH.

## 1. Methods and materials

### 1.1. Site description

The study area is located in the southern edge of the steppe, bordering the Loess Plateau to the south. The southern part of the area is in the center-and-east Ningxia Hui Autonomous Region, while the northern part is in central Inner Mongolia (Latitude 35°1′–38°52′N, Longitude 105°52′E–107°34′E) (Fig. 1). The climate is temperate with annual air temperature 15.3°C. The annual precipitation is about 300 mm, half of which falls between June and August.

*In-situ* measurement of the NO<sub>x</sub> fluxes was carried out from August to September in 2010, along a transect about 450 km long. It crossed a variety of vegetation types such as *Stipa*, *K. squarrosa* (Trin.) Packer, *Lespedeza*, *Caragana*, *Peganum harmala* L., *Salsola* and *A. scopauia* Waldstein et Kitaibel. A total of 8 sites were studied, 3 of which were located in pasture land, and 5 in a typical agri-pasture transitional zone. To curb land degradation, the Chinese government implemented

No-Grazing and Rotating-Grazing policies in recent decades. As a result, the study sites were either located in fenced pastures, or in farmland that has lain fallow for decades. Thus, the topsoil is free from fresh disturbance. Details on the vegetation and soil on the study sites are listed in Table 1.

### 1.2. Measurements of NO<sub>x</sub> fluxes

NO<sub>x</sub> fluxes were measured using a dynamic flux chamber (DFC) method. The chambers were made of fluorinated ethylene propylene (FEP) lined with an inner Teflon membrane to reduce the possible adsorption of NO<sub>x</sub>. Each chamber had an inlet port on one side (5 mm), and an exhaust port (5 mm) and outlet port (5 mm) on the opposite side. A thermometer and an electronic fan were installed tightly in the top side. The fan was 0.15 m<sup>2</sup> in size and powered by a 12 V Direct Current rechargeable battery. It was used to stir the air so as to make the concentration of NO<sub>x</sub> uniform in the chamber. The chamber (30 Length × 30 Width × 20 Height, 18 L) was placed tightly on a pre-installed stainless steel tetragonal base, which was inserted into the soil 1 hr before measurement. The experiment was conducted one site after another along the transection line.

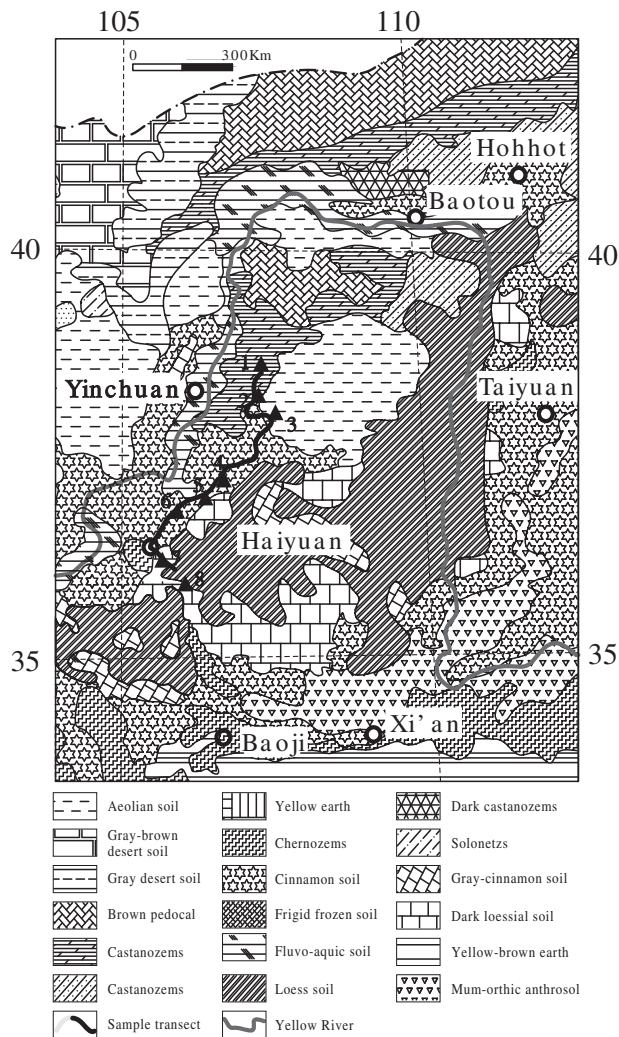
Four chambers were applied at each studying site, two covering soil with vegetation, while the other two were without vegetation. To conduct a blank measurement for the chamber, a reference chamber was used in the field. It was made the same as the sampling chambers but sealed at the bottom with a Teflon sheet, and placed on the same environment as the sampling chambers.

Measurement of NO<sub>x</sub> was done by a Model 17i chemiluminescence NO<sub>x</sub>-NH<sub>3</sub> analyzer (Thermo Environmental Instruments Inc., USA). The minimum detection limit was 1 ppbV (parts per billion by volume) for an integration time of 120 sec. Ammonia (NH<sub>3</sub>) flux data were previously published (Zhou et al., 2011). The analyzer was calibrated seasonally using standard gases supplied by the National Research Center for Certified Reference Materials (Beijing, China). Before measurement, the instrument was calibrated using a 146i-Multi-gas Calibrator (Thermo Environmental Instruments Inc., USA) and 1160 Zero Air Supply Calibrator (Thermo Environmental Instruments Inc., USA).

Ambient air was used as the carrier gas. It was drawn through a Teflon FEP (fluorinated ethylene propylene) sample line into the chamber and then into the instrument by suction applied by an external vacuum pump. The flow rate was monitored by a mass flow controller (GFC-17 Aalborg, New York, USA). Flux measurement was started after steady-state was achieved within the chamber. This took about 30 min after setup of the chamber. Net fluxes from the soils were obtained by comparing the flux in the sampling chamber with that in the reference chamber. NO<sub>x</sub> fluxes ( $F$ , ng N/(m<sup>2</sup>·sec)), were calculated using the following equation:

$$F = (C - C_0) \times Q/A \quad (1)$$

where,  $C$  (μg/m<sup>3</sup>) is the NO<sub>x</sub> concentration in the outflow air of the chamber,  $C_0$  (μg/m<sup>3</sup>) is the NO<sub>x</sub> concentration in the inflow air, which is drawn at the height 1.5 m above the ground,  $Q$  (m<sup>3</sup>/sec) is the flow rate of the inflow air, and  $A$  (m<sup>2</sup>) is the area covered by the chamber.  $C$  was determined using the average concentration



**Fig. 1 – Sampling site of the research along the sampling transect on the geographical background of the arid and semi-arid areas of northern China.**

measured during a 20-min period after the NO<sub>x</sub> concentration had reached dynamic equilibrium in the chamber.

### 1.3. Determination of environmental variables

Mercury thermometers were used to measure the temperature inside the chambers and at 5 cm depth in the soil near

the chamber, as well as the temperature of ambient air 1.5 m above the ground, shielded from direct solar radiation. Soil samples were taken from the top 10 cm of the soil profile near the chamber using a cylinder ring sampler (100 cm<sup>3</sup>).

Soil water content was calculated from the difference between the fresh soil weight and the oven-dried (105°C) soil weight divided by the oven-dried soil weight. The soil ammonium (NH<sub>4</sub><sup>+</sup>) content was determined using a colorimetric analysis method after extraction by 2 mol/L KCl solution (Page, 1982).

### 1.4. Statistics and data analysis

The statistical software package SPSS 13.0 (SPSS Inc., Chicago, IL, US) was used for analysis of variance (ANOVA) (post-hoc LSD analysis) between NO and NO<sub>2</sub> fluxes at different sites, and for sample-independent t-tests between NO and NO<sub>2</sub> fluxes for different soil types and vegetative covers. The statistical software package Sigma Plot 10.0 (Systat Software, Inc., Point Richmond, CA, USA) was used for regression analysis.

## 2. Results and discussions

### 2.1. Diurnal and spatial variations of NO, NO<sub>2</sub> and NO<sub>x</sub> fluxes from different soil and vegetation types

The variation in NO<sub>x</sub> fluxes for the eight sites is shown in Fig. 2. For soils with plant cover, the fluxes ranged from 0.274 to 7.32 ng N/(m<sup>2</sup>-sec) for NO, from -11.29 to 0.371 ng N/(m<sup>2</sup>-sec) for NO<sub>2</sub>, and from -3.98 to -3.07 ng N/(m<sup>2</sup>-sec) for NO<sub>x</sub>, with averages of 2.34 ± 1.62 ng N/(m<sup>2</sup>-sec) for NO, -2.32 ± 2.28 ng N/(m<sup>2</sup>-sec) for NO<sub>2</sub>, and 0.019 ± 1.64 ng N/(m<sup>2</sup>-sec) for NO<sub>x</sub> (mean ± SD), respectively. For soils without a vegetative cover, the fluxes ranged from 0.103 to 1.15 ng N/(m<sup>2</sup>-sec) for NO, from -2.465 to 0.111 ng N/(m<sup>2</sup>-sec) for NO<sub>2</sub>, and from -2.35 to 0.816 ng N/(m<sup>2</sup>-sec) for NO<sub>x</sub>, with averages of 0.452 ± 0.356 ng N/(m<sup>2</sup>-sec) for NO, -0.647 ± 0.769 ng N/(m<sup>2</sup>-sec) for NO<sub>2</sub>, and -0.202 ± 0.945 ng N/(m<sup>2</sup>-sec) for NO<sub>x</sub>, respectively. All field sites acted as sources of atmospheric NO and sinks of NO<sub>2</sub>. Large differences occurred for the average NO fluxes among the 8 sites due to different vegetation types.

Temporally, the highest NO flux occurred between noon and 14:00. Spatially, the highest NO flux (averaging 7.32 ng N/(m<sup>2</sup>-sec)) was found in the cinnamon soil covered

**Table 1 – Soil physical and chemical characteristics of different desertification soils.**

Sampling site	Longitude	Latitude	Soil type	Plant type	NH <sub>4</sub> <sup>+</sup> -N (mg N/kg)	TN (g/kg)	Elevation (m)	pH
1	107.36°E	38.86°N	Castanozems	<i>Peganum harmala</i> L.	12.45	0.54	1286	8.21
2	107.23°E	38.49°N	Castanozems	<i>Pennisetum centrasiaticum</i> Tzvelev	15.52	0.33	1425	7.91
3	107.56°E	38.36°N	Aeolian soil	<i>Sophora alopecuroides</i> L.	1.63	0.52	1328	8.36
4	106.76°E	37.53°N	Cinnamon soil	<i>Artemisia scoparia</i> Waldst. et Kit	12.39	0.43	1370	8.24
5	106.49°E	37.34°N	Cinnamon soil	<i>Artemisia scoparia</i> Waldst. et Kit	7.04	0.67	1362	7.95
6	106.01°E	37.10°N	Cinnamon soil	<i>Lespedeza bicolor</i> Turcz + <i>Artemisia scoparia</i> Waldst. et Kit	8.10	0.59	1636	7.88
7	105.87°E	36.46°N	Loess soil	<i>Medicago sativa</i> Linn	8.70	0.51	1728	7.98
8	106.23°E	36.02°N	Loess soil	<i>Pennisetum centrasiaticum</i> Tzvelev	19.85	0.57	1719	7.94

with *Artemisia scoparia* Waldst. et Kit at the site 4 (Fig. 2d); while the NO emission flux (averaging 0.103 ng N/(m<sup>2</sup>·sec)) was lowest at site 6 (Fig. 2f), which also had a cinnamon soil covered with *Lespedeza bicolor* Turcz and *Artemisia scoparia* Waldst. et Kit. Despite having the same soil type and closely similar plant cover, sites 4 and 6 showed widely different NO emission fluxes. This difference probably resulted from the difference in precipitation between the two sampling sites. No significant difference in the flux was found between the other seven sampling sites. The overall flux of NOx gases was low in comparison with the spatial variation in soil nitrogen, suggesting that the gaseous loss of nitrogen was not a significant contributing factor in the high C/N in the northern steppe of China.

Previous studies have indicated that NOx emission fluxes are strongly influenced by soil water content (Williams et al., 1992) even without the priming of precipitation. This would explain why the diurnal variation in NOx emission flux from the former four sampling sites was different from that of the latter four sites. In general, maximum NO emissions were measured in the early afternoon when soil temperatures were typically at the maximum. The flux decreased in the late afternoon as soil temperatures declined. The diurnal variation in NOx flux was largely controlled by fluctuations in soil temperature, whereas its spatial variation was influenced by soil type and plant cover. Overall, soil moisture content might be more important than soil pH and soil temperature in affecting the flux of NO. This will be discussed subsequently in more detail.

## 2.2. Factors affecting NOx emission

### 2.2.1. Effect of soil temperature on NO, NO<sub>2</sub> and NOx fluxes

Soil temperature is a major factor affecting NOx emissions because of its effect on microbial activity and gas diffusion rates (Passianoto et al., 2004). To elucidate the influence of soil temperature on NO emissions, the correlation between NO fluxes and soil temperature was assessed for the eight plots. The exponential correlation between NO fluxes and soil temperature was significant ( $P < 0.05$ ).

Within a certain range, an increase in soil temperature promotes soil microbial activity and thus decomposition of soil organic matter, and leads to the soil NOx flux increasing. It was reported, for example, that, in the range of 15 to 35°C, NO emission fluxes were exponentially increased as soil temperatures rose (Aneja et al., 1995). In other cases, NOx emission flux was found to be positively correlated with soil temperature (Hall et al., 1996). When soil temperatures exceeded 35°C, however, NOx gas emission flux tended to decrease with temperature due to a decline in soil microbial activity. In other words, there is a narrow range of temperatures when microbial activity is at an optimum level (Williams and Fehsenfeld, 1991). For nitrification the optimum temperature range is 15–35°C, while for denitrification it is 5–75°C. Passianoto et al. (2004) found that high topsoil temperatures (40–45°C) of conventionally tilled sites caused a reduction in the rate of NO emissions in the Amazon Basin. Soil surface temperature seems to be a good proxy predicting NO emissions, and the two appear to have an inverse relationship.

This relationship, however, was not observed in arid and semi-arid grasslands, although soil surface temperatures were high (Ludwig et al., 2001).

Fig. 2a–d shows that chamber temperatures were significantly related to NOx fluxes when soil water contents were fairly low, while no such relationship was found at high soil water contents (Fig. 2e–h). This finding strongly suggests that NOx emission fluxes are influenced by both soil temperature and soil water content (precipitation).

### 2.2.2. Effect of soil water content on NO and NO<sub>2</sub> fluxes

Soil moisture is an important factor determining the rate of NO emission. A number of studies have shown that NOx flux is negatively correlated with soil moisture content (Feig et al., 2008; Wang et al., 2006). However, NO emissions were also found to increase with soil moisture when the soil moisture content is between 5% (W/W) and 40% (W/W). However, when the soil moisture increases further, the soil aeration and the emission of NOx gases are inhibited because the soil pore space is filled with water. In fact, NO emission from soil can be suppressed under very dry (<5%, W/W) and saturated conditions (Davidson et al., 1991), possibly because soil N is simultaneously lost through mineralization and nitrification. Since soil moisture determines whether nitrification or denitrification is dominant in the soil, it strongly influences the exchange of NO between soil and air.

Soil moisture not only affects soil aeration and the rate of the oxygen diffusion but also impacts microbial activity. Thus, dry aerobic conditions are conducive to nitrification, while anaerobic conditions promote denitrification. Within a certain range of moisture content, an increase in soil moisture enhances NOx emissions by increasing soil respiration and carbon–nitrogen mineralization (Hall et al., 1996). Likewise, when the soil temperature exceeds 20°C, soil NO gas emissions and soil moisture are positively correlated (Zheng et al., 2003). A number of studies, summarized by (Li et al., 1999), have indicated that large amounts of NOx are emitted from soils with intermediate moisture contents, but lower quantities are released from dry and wet soils. Thus, no direct correlation of NO flux with soil water content would be expected to exist (Davidson, 1991, 1993; Ludwig et al., 2001). More recently, Cheng et al. (2006) have reported on the relationship between rain pulse size and uptake of summer rainwater by three dominant desert plants in desertified grasslands of northwest China. Increased variability in summer rain event intensity due to climate change would be expected to influence NO emission fluxes. The complex relationship between soil moisture and NO emission needs further investigation.

During the observation period, air temperature and soil temperature decreased from north to south as a result of precipitation, and soil moisture gradually increased accordingly. Soil moisture content changed from <5% (W/W) in the west region of the Mu Us Sandyland to approximately 10% (W/W) in eastern Ningxia and then reached values >18% (W/W) in southern Ningxia. In the northern steppe of China where the climate is dry and rainfall is meager, precipitation is the single most important factor affecting NOx emissions from soil, outweighing pH, temperature, and relative humidity. Precipitation may also promote the release

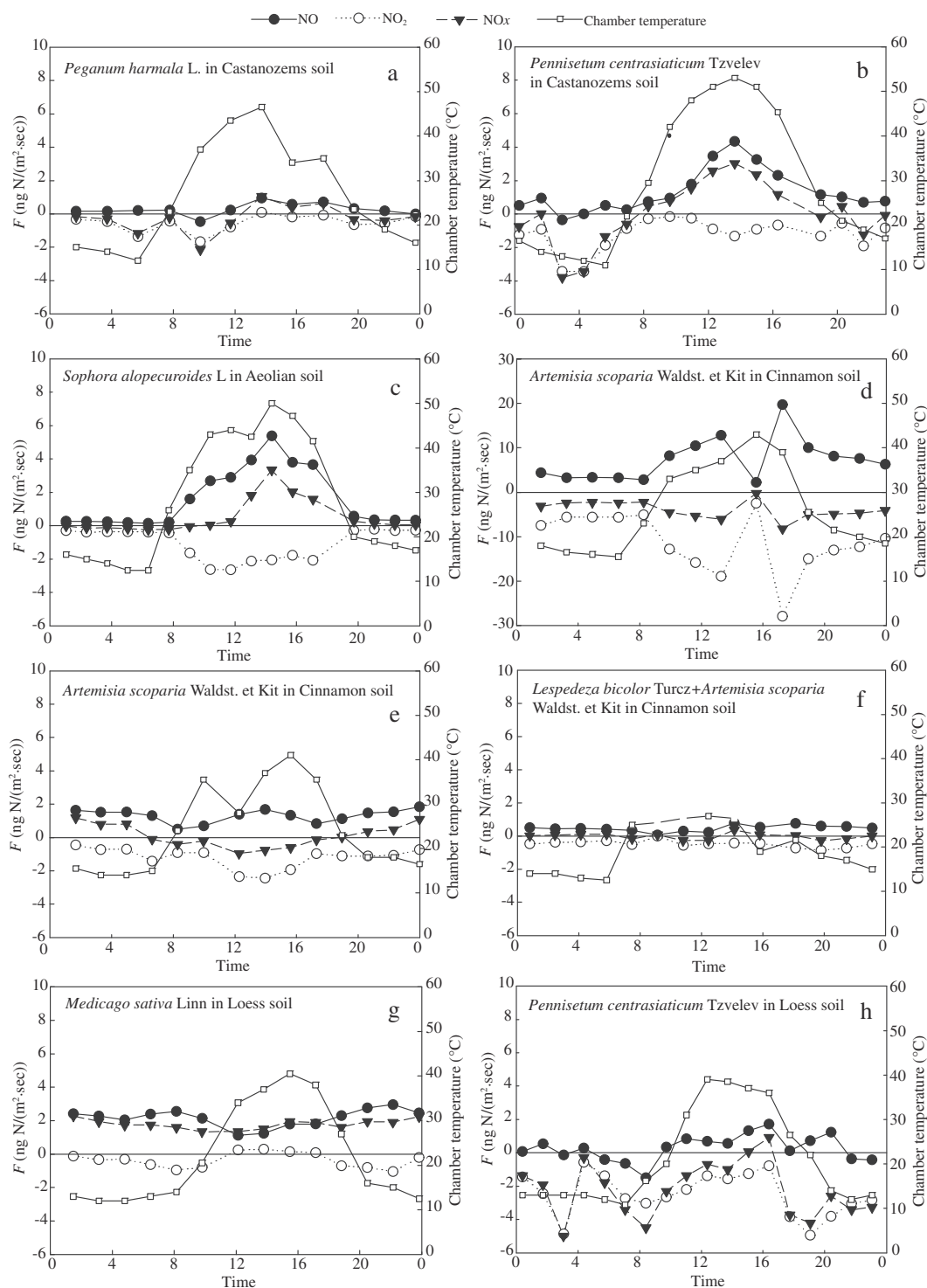


Fig. 2 – Diurnal and spatial variations in NO, NO<sub>2</sub> and NO<sub>x</sub> fluxes from different desertification lands and chambers temperature.

of NO<sub>x</sub>, while droughty conditions tend to inhibit its emission. Since most of the rain in the arid and semi-arid region of northern China falls during the month of August, the NO<sub>x</sub> flux from soil is highest during summertime.

### 2.2.3. Effect of vegetation on NO and NO<sub>2</sub> fluxes

The vegetative cover may directly or indirectly influence NO<sub>x</sub> emissions from the soil underneath (Martin et al., 2003) by (1) competing with soil microbes for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, thus

limiting soil nitrification and denitrification; (2) changing the microclimate of the topsoil; (3) changing soil physical properties, moisture retention, and pH; and (4) providing organic materials (C and N) to the soil, thus affecting microbial biomass and activity. In addition, the vegetative canopy affects the air/soil exchange of NO, and prevents soil-emitted NO from escaping into the ambient atmosphere (Pang et al., 2009).

Our data prove that vegetative cover has a large effect on NO<sub>x</sub> emission flux (Fig. 3). The canopy effect was especially

marked at site 4, where much of the land had been severely over-grazed, and the soil was seriously desertified. We should also mention that >30% of the land in this region is covered with *Artemisia scoparia* Waldst. et Kit, but the significance of this observation is as yet unclear.

The plant canopy may be a sink for  $\text{NO}_2$  because plants are more effective in taking up  $\text{NO}_2$  than  $\text{NO}$  (Hanson and Lindberg, 1991; Hill, 1971). Also, a proportion of the soil-emitted  $\text{NO}$  is converted to  $\text{NO}_2$  within the plant canopy (Bakwin et al., 1990; Pang et al., 2009). As a result, the amount of  $\text{NO}$  that is released to the atmosphere (where it is rapidly oxidized to  $\text{NO}_2$  in the presence of ozone) is reduced.

Interestingly, no significant differences in  $\text{NO}_x$  fluxes were found between the various plant canopies. Thus, the type of vegetative cover does not appear to affect the spatial variation in  $\text{NO}_x$  fluxes between soil and atmosphere. The density and type of plant cover, and its effect on soil-atmosphere exchange of  $\text{NO}_x$ , merit further research.

#### 2.2.4. Effect of soil pH on $\text{NO}$ and $\text{NO}_2$ fluxes

Soil pH is an important factor affecting both nitrification and denitrification (Khan et al., 2011). Although nitrification can take place between pH 5 and pH 9, neutral and slightly acidic conditions are optimum for the process (Ste-Marie and Paré, 1999). Nitrifying bacteria are more sensitive to soil pH than denitrifying bacteria. Although denitrification can occur over a wide range of pH (3.5–11.2), the process is optimal between pH 6 and pH 8 (Šimek et al., 2002; Valera and Alexander, 1961).

The relationship between soil pH and  $\text{NO}_x$  emissions is complex. It is reported that in an aerobic soil at pH 7.8,  $\text{NO}$  was largely produced by nitrification of ammonium whereas in an anaerobic, acid soil (pH 4.7), the emitted  $\text{NO}$  was derived exclusively from the reduction of nitrate (denitrification) (Remde and Conrad, 1991). Another report suggested that the microbial community in soil can adjust to low pH conditions, and was responsible for the entire production of  $\text{N}_2\text{O}$  and much of the  $\text{NO}$  emitted (Yamulki et al., 1997). Although the flux of  $\text{N}_2\text{O}$  from soil to atmosphere decreased as soil pH increased, the mean flux of  $\text{NO}$  showed little dependence on soil pH.

Our experiment showed that the flux of  $\text{NO}$  was scarcely influenced by soil pH at all sites (Fig. 4), agreeing with the results of other studies (Yamulki et al., 1997). The pH of the soils ranged from 7.88 to 8.36, under which conditions little  $\text{NO}$  can be produced by chemodenitrification. Therefore, the  $\text{NO}$  flux from arid and semi-arid grasslands in northern China is much lower than that from other regions.

### 3. Conclusions

We measured the diurnal and spatial variations in  $\text{NO}_x$  emission fluxes from different soil types and under different plant covers in the northern steppe of China. Maximum emission fluxes were recorded in the early afternoon (12:00–14:00), showing a positive correlation with temperature and a negative correlation with soil moisture. The diurnal variation in  $\text{NO}_x$  flux is largely controlled by soil temperature, whereas its spatial variation is influenced by soil type and plant cover. Overall, soil moisture content is more important than soil pH and soil temperature in affecting the

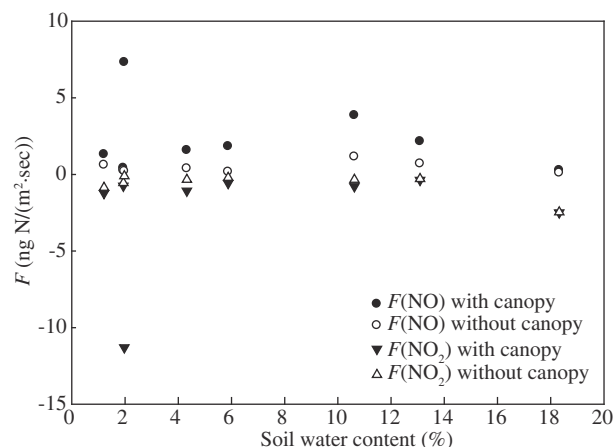


Fig. 3 – Plots showing variations  $\text{NO}$  and  $\text{NO}_2$  fluxes with soil water content under the condition with canopy and without canopy.

flux of  $\text{NO}$ . Therefore,  $\text{NO}$  emission flux would be expected to increase sharply following rainfall or irrigation. The overall flux of  $\text{NO}_x$  gases is low in comparison to the spatial variation in soil nitrogen, suggesting that the gaseous loss of nitrogen is not a significant factor in the high C/N ratio in the northern steppe of China.

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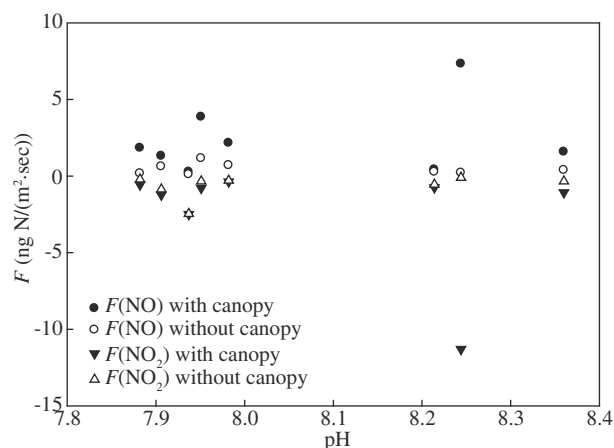


Fig. 4 – Plots showing variations  $\text{NO}$  and  $\text{NO}_2$  fluxes with soil pH under the condition with canopy and without canopy.

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