

Biogenic nitric oxide emission from saline sodic soils in a semiarid region, northeastern China: A laboratory study

Junbao Yu,^{1,2,3} Franz X. Meixner,² Weidong Sun,⁴ Zhengwei Liang,³ Yuan Chen,³ Buhalgem Mamtimin,² Guoping Wang,³ and Zhigao Sun¹

Received 23 August 2007; revised 24 June 2008; accepted 24 July 2008; published 10 October 2008.

[1] It is well-known that nitric oxide (NO) is an important component in nitrogen biogeochemical cycling produced through biological process of nitrification and denitrification in soils, but the production and the consumption processes of NO in sodic saline soil are less understood. Through a series of laboratory experiments focusing on NO biogenic emissions from four kinds of saline sodic soils of different land use in western Songnen Plain northeastern China, we found that the optimum soil moisture for the maximum NO production and emission were 14.0%, 9.0%, 9.5%, and 18% water-filled pore space (WFPS) for soil samples from natural pasture, man-made pasture, paddy field of saline sodic soil mixed sandy soil, and paddy field of pure saline sodic soil, respectively. For a given moisture, NO fluxes increased exponentially with soil temperature at any given soil moisture. The optimum soil moisture for the maximum NO emission for a certain soil type, however, was constant and independent of soil temperature. The NO consumption processes for different land uses were similar in all studied saline sodic soils since the difference of NO consumption rate constant in these soils was small (ranged from 1.07×10^{-6} to $7.45 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$). The NO emission potential for paddy field soils was about 1.2–2-fold higher than pasture soils. On the basis of laboratory results and field monitoring data of soil water content and soil temperature, the average NO fluxes from these saline sodic soils in the region were estimated to be 1.3–4.9 $\text{ng m}^{-2} \text{ s}^{-1}$ for an entire plant growth period. NO fluxes for pastures mainly occurred in the dry season and were about threefold higher than that for paddy fields, which was strongly influenced by field management.

Citation: Yu, J. B., F. X. Meixner, W. D. Sun, Z. W. Liang, Y. Chen, B. Mamtimin, G. P. Wang, and Z. G. Sun (2008), Biogenic nitric oxide emission from saline sodic soils in a semiarid region, northeastern China: A laboratory study, *J. Geophys. Res.*, 113, G04005, doi:10.1029/2007JG000576.

1. Introduction

[2] Saline soils cover about 380–995 million hectares, ~2.55–6.86% of the Earth's land surface [International Atomic Energy Agency (IAEA), 1995; Szabolcs, 1994] and of these, 62% are saline sodic or sodic. There are about 3.73 million hectares of saline sodic land in northeastern China, distributed mainly in western Songnen Plain. Saline sodic land area in western Jilin province, northeastern China, increased to 1.43 million hectares at an average rate

of about $0.6\% \text{ a}^{-1}$ during the last 50 years, occupying more than 28% total area of the province [Wang and Qiu, 2002].

[3] The typical characteristics of saline sodic soil is accumulation of excess sodium (Na^+) and high pH in soil surface, causing imbalances of plant-available nutrients [Qadir and Schubert, 2002]. In addition, changes of land use in saline sodic soil are accompanied by changes in biogeochemical cycles of nutrients, especially the air-surface exchanges of trace gas such as nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$).

[4] Nitric oxide in soil is produced through biological process of nitrification and denitrification, as well as chemical decomposition of HNO_2 [Firestone and Davidson, 1989; Remde and Conrad, 1991]. Temperature, soil moisture, soil texture, wetting of dry soil, fertilization and land use category have all been shown to be key factors controlling NO emission from soils [Barger et al., 2005; Gut et al., 2002; Keller et al., 2005; Martin et al., 1998; Pilegaard et al., 1999; Williams et al., 1992; Yu et al., 2007]. Generally, NO flux observed from dry arid and semiarid soils ($<1.5 \text{ ng m}^{-2} \text{ s}^{-1}$), is about 10 to 100-fold lower than those from temperate grassland and forests, as well as rain

¹Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, Yantai, Shandong, China.

²Biogeochemistry Department, Max Planck Institute for Chemistry, Mainz, Germany.

³Da'an Experimental Station of Sodic Soil Ecology, Northeast Institute of Geography and Agricultural Ecology, Chinese Academy of Sciences, Changchun, China.

⁴Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou, China.

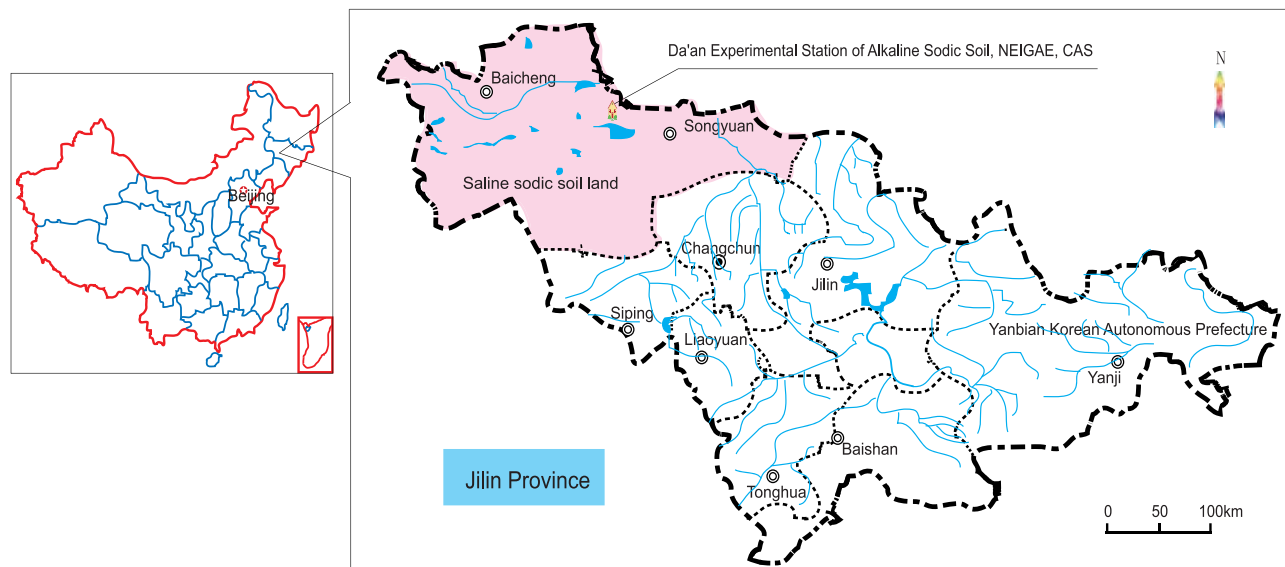


Figure 1. Map of Jilin province showing the location of the studied region.

forest soils [Kirkman *et al.*, 2002; Ludwig *et al.*, 2001; Meixner and Yang, 2006; van Dijk *et al.*, 2002; Verchot *et al.*, 1999]. Biogenic NO emission pulses have been observed in rainy season for semiarid or arid soils [Meixner *et al.*, 1997; Otter *et al.*, 1999]. Dramatically increased NO emission has even been observed within only 10 min after a 20 mm artificial rainfall [Hartley and Schlesinger, 2000].

[5] Generally, only the net flux of NO from soil is measured in the field, while NO production and consumption can be measured separately on soil samples under controlled conditions in laboratories. However, some scientists found that net fluxes of NO, which derive from soil samples in the laboratory agreed well with dynamic chamber measurements at corresponding field sites [Ludwig *et al.*, 2001; Otter *et al.*, 1999; van Dijk *et al.*, 2002]. Unfortunately, few laboratory and field results about net NO fluxes from the saline sodic soil have been reported so far. In this study, we present results of NO emission from laboratory studies on sodic saline soil samples of different land use from semiarid land in western Jilin province, northeastern China. Our purposes were (1) to study NO production, NO consumption and NO emission in saline sodic soils from four types of land use as functions of soil temperature and soil moisture, and (2) to predict seasonal variation of biogenic NO emission from saline sodic soil in the region based on results obtained using a laboratory incubation technique.

2. Materials and Methods

2.1. Site Description

[6] The study region is located in western Jilin province (N40°52′–46°18′, E121°38′–131°19′). Based on satellite image interpretation and field surveys, about 28% of the total area of Jilin province is saline sodic land, which mainly distributes in western Jilin province. The climate of this region is classified as semiarid. Based on 30 years (1971–2000) monitoring data of Qianguoerluosi meteorological station (N45°05′, E124°52′), the average annual

rainfall in this region is 350–450 mm, with 70–80% of the total rainfall concentrated in July to September. The average annual evaporation (1600–1800 mm) exceeds 4–5 times of the mean annual precipitation. The monthly mean air temperature in this area ranges from about –16.2°C in January to about 23.5°C in July, with an annual mean temperature of 4.5°C.

[7] The studied site is located at Da'an Experimental Station of Sodic Soil Ecology, Northeast Institute of Geography and Agricultural Ecology, Chinese Academy of Sciences, at approximately N45°35′58″–N45°36′28″, E123°50′27″–123°51′31″ (Figure 1), in Baicheng city, where the soil salinity and alkalization are the heaviest in western Jilin province, with about 74.1% of total saline sodic land classified as serious grade (salt content: 0.5–0.7%; ESP: 30–45%; pH: ≥ 9.0) [Wang and Qiu, 2002]. The topography is flat with relative height differences of no more than 0.5 m in the studied region. The predominant land use types are pasture and paddy field in this area.

[8] The soil is characterized by low nutrients, high sodicity and salinity, and poor infiltration [Wang and Qiu, 2002]. Nutrient concentrations in soil layer at depths of 0–30 cm are 4.3–5.8 g kg^{−1} for TOC, 0.43–0.65 g kg^{−1} for TN, 1.46–6.63 mg kg^{−1} for NH₄–N, 11.69–32.11 mg kg^{−1} for NO₃–N and 0.15–0.24 g kg^{−1} for TP. The average total dissolved salt concentration of the topsoil (0–30 cm) ranges from 0.5% to 1.1% with NaHCO₃ as the main components. Soil pH ranges from 8.7 to 10.7, and ESP up to 45% (occasionally can be as high as >70%).

2.2. Laboratory Experiments for NO Measurement

2.2.1. Description of Dynamic Laboratory Incubation System

[9] The NO production and consumption were measured under 15°C and 25°C in laboratory using a fully automatic laboratory dynamic incubation system (Figure 2). The system includes four sub-systems, i.e., air purification system, gas dilution system, dynamic chamber system and measurement system. The purification system consists of a

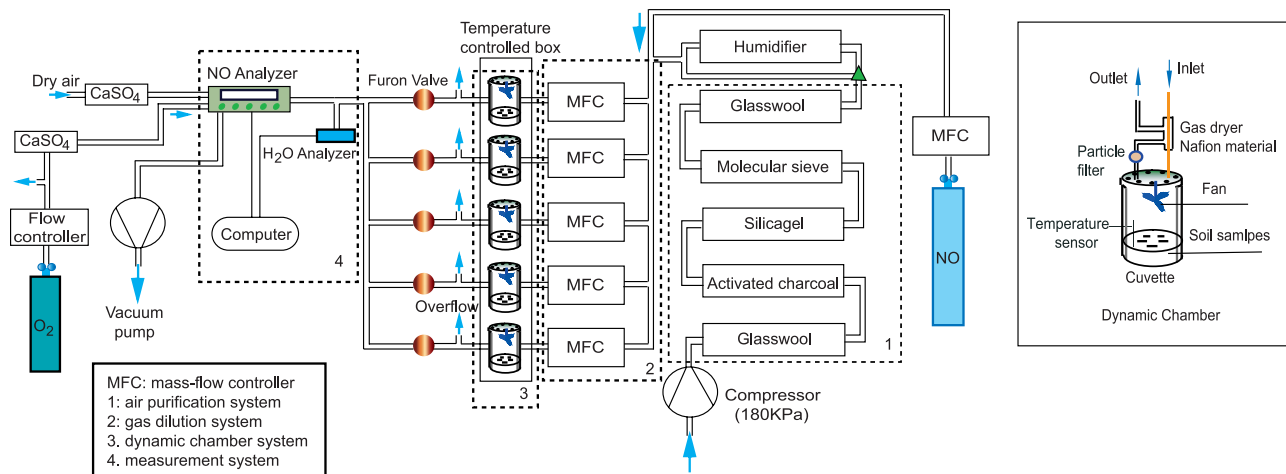


Figure 2. Laboratory dynamic incubation system for laboratory investigation of NO production and consumption in soil samples.

particle filter, two glass wool traps (one at the beginning of the scrubbing process and one at the end) to remove dust particles, an activated charcoal (1.5 mm) trap to remove CO, NO_x and O₃, and two silica gel traps as well as one molecular sieve (0.4 nm, 2 mm beads) trap to remove water vapor and NO_x (Figure 2). Plexiglas scrubbing traps containing glass wool, activated charcoal, silica gel and molecular sieve were approximately 13 cm in diameter and 47 cm in height. One inch (dia.) PTFE tubing connected all the traps in series. Pressurized air was supplied at 180 kPa to the gas purification system. Purified air entered the gas dilution system at multiple points to aid mixing (Figure 2). The flow of NO standard gas (200 ppm in N₂; Messer-Griesheim, Germany) was controlled by a Mass Flow Controller (MFC-NO) (0–50 ml min⁻¹; High Tech, MKS). The NO mixing ratio flowing through the chambers were controlled by changing the flow rate of the NO standard gas into the dilution system. This procedure is required for the measurement of NO consumption rates and for the calibration of the chemiluminescence NO analyzer. The dynamic chamber system is shown in Figure 2. The chambers and lids were made of Plexiglas with a diameter and height of 9.2 cm and 13.6 cm, respectively. A rubber O-ring was placed between the chamber and the lid to obtain a gas-tight seal. A PTFE-coated fan attached to the lid of the chamber to mix the air inside the chamber. A thermocouple, temperature sensor, for measuring the soil temperature, was installed on the inner side of the chamber. A Teflon particle filter was attached to the chamber outlet to prevent any particles from flowing into the analyzers. In order to reduce the water vapor losses from the dynamic chamber thus keeping soil moisture constant during measurements, a water-selective system (Gas Dryer MD, Perma Pure Inc.) was connected. The Gas Dryer consists of an inner tube (Nafion[®] polymer, 0.0032 m diameter) and a concentric surrounding outer tube (Teflon, 0.0064 m diameter). Nafion[®] polymer is a hygroscopic ion exchange membrane, which enables the diffusion of water vapor only. The Gas Dryer set up to lead dry air through the outer tube and moist air (sample air) in the opposite direction through the inner tube. When dry air and moist airflow

through the outer and the inner tubes of the Gas Dryer, respectively, water vapor diffuses from the moist air through the Nafion[®] membrane to the dry air stream. The flow rate through the chambers was maintained at 2.5 L min⁻¹ by MFCs (High Tech, MKS; range 0–5 L min⁻¹). All MFC were controlled by a Multi Gas Controller (High Tech, MKS, model 647B). Measurement system includes CLD 780TR Chemiluminescence NO Analyzer (detection limit 0.052ppb and precision ±0.026 ppb, Eco Physics AG., Switzerland) for NO measurement and Binos (Rosemount, Germany) for vapor signal capture. All measurements are stored into computer automatically.

2.2.2. Treatment of Soil Samples and Experimental Layout for NO Measurements

[10] Four kinds of saline sodic soil samples for different land use, i.e., natural pasture (NP), man-made pasture (MP), paddy field mixed with sandy soil (750 m³ ha⁻¹ a⁻¹) and fertilized with nitrogen fertilizer (100–150 kg ha⁻¹ a⁻¹) (SP), paddy field fertilized with about 180 kg ha⁻¹ a⁻¹ nitrogen fertilizer (PP), respectively, were collected from the surface soil (0–20 cm depth) in early October, 2005 for NO production measurements. Soil temperature, air temperature, soil bulk density and soil water content were measured in situ when soil samples were collected. The dry soils were kept in sealed plastic bags at 5°C to limit the microorganism activities until the time of the NO emission analysis after sieved through a 2 mm coarse stainless steel sieve. Roots as well as other organic matters were removed to homogenize the sample, and soil water content was determined.

[11] About 80-g soil sample was weighed into the chamber, and evenly spread across the bottom of the chamber. Soil samples were incubated three days after saturation. The soil moisture was measured before NO analysis.

[12] All the chambers were kept in a thermostat cabinet to maintain certain soil temperatures during experiment. The purified air with or without NO standard gas flowed from the gas dilution system into a main Teflon tube with 5 T-connections to supply air, via 5 MFCs, to each chamber at a flow rate of 2.5 L min⁻¹ (Figure 2). Once the air passed through a chamber and the Inverted Gas Dryer, it was directed

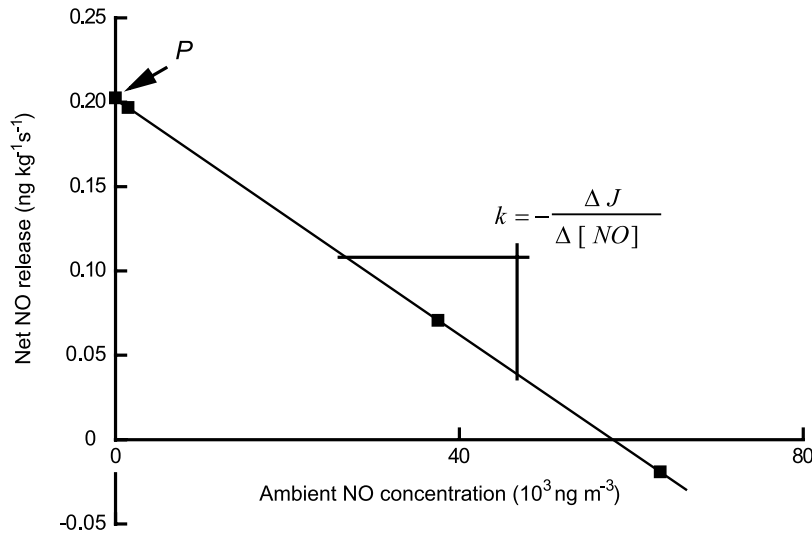


Figure 3. General relationship between NO release (or uptake) and ambient NO concentration.

to a Furon valve, before which there is a T-connection for vapor measurement with Binos and the overflow. The NO analyzer is installed at end of this Teflon tube. Thereafter all of the Furon valves are connected to one main Teflon tube. Airflowed through all the chambers at the same time. The Furon valves were controlled by a computer program, allowing the sample air from one of the chambers to go to the analyzer at a time. The NO analyzer was set to measure the NO mixing ratio in the headspace of the chambers every 10 s. The measuring process for one chamber was 1.5 min. The average value of nine measurements within 1.5 min was used for data analysis. The NO mixing ratios in the headspace of the chambers were determined by a chemiluminescence NO analyzer. Calibrations were performed once a week with a NO standard (200 ppm NO in N₂, Messer-Griessheim Germany).

2.3 Data Calculation

2.3.1. Calculation of NO Release Rate J

[13] The NO release rate J was calculated using the difference of the NO mixing ratio between outlet and inlet of each dynamic chamber described in equation (1).

$$J = \frac{Q}{m_{sdx}} \times (NO_{outlet} - NO_{inlet}) \times \frac{M_N}{V_N} \quad (1)$$

where J is the release rate of NO (ng kg⁻¹ s⁻¹), Q is gas flow rate through chambers (m³ s⁻¹), m_{sdx} is the soil dry weight (kg), NO_{outlet} and NO_{inlet} are NO mixing ratios at chamber outlet and inlet, respectively, M_N is the molecular weight of nitrogen (14.0067 kg kmol⁻¹) and V_N is the molecular normal volume (22.4 m³ kmol⁻¹).

2.3.2. Calculation of Volumetric NO Uptake Rate k

[14] To determine the NO uptake by the soil, the dynamic chambers were flushed with air mixed with NO standard gas. The obtained inlet NO mixing ratios using the gas dilution system range from 0 to 200 ppbv. The NO release rates at inlet NO mixing ratios of 0 ppbv and 60 ppbv

were measured, respectively. To obtain the volumetric NO uptake rate k , a linear regression is used (Figure 3). The volumetric NO uptake rate k , NO production rate P and NO compensation mixing ratio NO_c were calculated as equations (2)–(4).

$$J = P - k \times NO_{amb} \quad (2)$$

$$k = -\frac{J_{[0ppbNO]} - J_{[60ppbNO]}}{(0_{ppb} - 60ppb)} \times \frac{M_A \times 0.001}{\rho_A \times M_N} \quad (3)$$

$$NO_c = \frac{P}{k} \quad (4)$$

where J is the release rate of NO (ng kg⁻¹ s⁻¹), P is the NO production (ng kg⁻¹ s⁻¹), k is the volumetric NO uptake rate (m³ kg⁻¹ s⁻¹), NO_{amb} is the ambient NO concentration (ng m⁻³), M_A is the molecular weight of dry air (28.9644 kg kmol⁻¹), ρ_A the air density at certain temperature (kg m⁻³) and M_N is the molecular weight of nitrogen (kg kmol⁻¹). NO_c is compensation mixing ratio (ng m⁻³). The intercept of the linear regression with the y axis expresses the compensation point or the compensation concentration, where NO uptake is equal to NO production, which results in a NO release rate $J = 0$. The algorithm used to fit the laboratory data was described by Meixner and Yang [2006] in detail.

2.3.3. Calculation of NO Production Rate

[15] As shown in Figure 3, NO production can be expressed as the intercept of the linear regression. This value represents the emission of NO by the soil under the condition that the NO mixing ratio in the headspace of the chamber is zero, assuming no NO uptake by the soil.

2.3.4 Determination of NO Fluxes

[16] The model of Galbally and Johansson [1989] shows an algorithm of transforming the laboratory-derived NO release into a net NO flux. The model considers only

3 variables for NO production and NO consumption in soils, which are (1) the soil bulk density, (2) the NO concentration and diffusive or net gaseous flow through the soil, and (3) two unknown parameters representing NO production and uptake in the soil. We measured the NO flux from soil in the laboratory under 15°C and 25°C, thus the NO flux was determined from equation (5). A detailed description of the determination of NO fluxes for laboratory measurements is given by *van Dijk et al.* [2002].

$$F_{NO}(WFPS, T) = \sqrt{BD \times k(WFPS, T) \times D} \times \left[\left(\frac{P(WFPS, T)}{k(WFPS, T)} \right) - [NO]_{amb} \right] \quad (5)$$

where $F_{NO}(WFPS, T)$ is NO flux ($\text{ng m}^{-2} \text{s}^{-1}$), BD is soil bulk density (kg m^{-3}), $k(WFPS, T)$ is the volumetric NO uptake rate under different water filling pore space (WFPS) ($\text{m}^3 \text{N kg}^{-1} \text{s}^{-1}$) and temperature (°C), D is NO diffusion coefficient in soil ($\text{m}^2 \text{s}^{-1}$), $P(WFPS, T)$ is the NO production under different WFPS ($\text{ng kg}^{-1} \text{s}^{-1}$) and temperature. NO diffusion coefficient in soil and WFPS were calculated as equations (6) and (7), respectively.

$$\frac{D}{D_0} = \frac{\varepsilon^{2.5}}{\Phi} \quad (6)$$

$$WFPS = \frac{\theta_g \times BD}{1 - (BD/PD)} \times 100\% \quad (7)$$

where D_0 is NO diffusion coefficient in free air ($0.0000199 \text{ m}^2 \text{s}^{-1}$), ε is the soil air-filled porosity (%), Φ is the soil total porosity (%) [Moldrup et al., 2000], θ_g is gravimetric soil moisture ($\text{kg H}_2\text{O kg}^{-1}$ oven-dried soil) and PD is particle density (assumed to be 2650 kg m^{-3}) [Davidson and Schimel, 1995]. An algorithm has been developed to fit observed values from the laboratory flux [Meixner and Yang, 2006], as a function of the WFPS, as shown in equations (8)–(11).

$$F_{NO}(WFPS) = aWFPS^b \exp(-cWFPS) \quad (8)$$

$$a = \frac{F_{NO}(WFPS_{opt})}{[WFPS_{opt}^b \exp(-b)]} \quad (9)$$

$$b = \frac{\ln \left[\frac{F_{NO}(WFPS_{opt})}{F_{NO}(WFPS_{upp})} \right]}{\ln \left(\frac{WFPS_{opt}}{WFPS_{upp}} \right) + \frac{WFPS_{upp}}{WFPS_{opt}} - 1} \quad (10)$$

$$c = \frac{-b}{WFPS_{opt}} \quad (11)$$

where $WFPS_{opt}$ is the soil moisture at which the maximum NO flux is observed, $F_{NO}(WFPS_{opt})$ equals the max F_{NO}

(WFPS), and $WFPS_{upp}$ is the soil moisture at which $F_{NO}(WFPS) = F_{NO}(WFPS_{upp}) \approx 0$ for $WFPS > WFPS_{opt}$. The NO fluxes at different temperature were calculated as equations (12) and (13) [Williams et al., 1992].

$$F_{NO}(T2) = F_{NO}(T1) \times \exp[-q \times (T2 - T1)] \quad (12)$$

$$q = -\frac{\ln(Q_{10})}{10} \quad (13)$$

where $F_{NO}(T2)$ and $F_{NO}(T1)$ are NO fluxes ($\text{ng m}^{-2} \text{s}^{-1}$) at different temperature at certain WFPS, q is exponential factor, $T2$ and $T1$ are different temperature (°C). When $T2 - T1 = 10$, $Q_{10} = F_{NO}(T2)/F_{NO}(T1)$.

3. Results and Discussion

3.1. NO Release Rate J and Production P

[17] Figure 4 presents NO release at a constant soil temperature of 25°C versus soil moisture for all four types of soils studied. A modified algorithm [Meixner and Yang, 2006] was applied to fit the results of laboratory studies on soil samples (Figure 4). The results showed that the algorithm was well fitted with the laboratory data ($R > 0.92^{**}$ at the 0.01 level, sum of square for corresponding value difference less than 0.09). According to equations (1) and (2), the production P (i.e., NO release J at NO_{amb} is nearly zero) in sodic soils of different land use was evaluated (Figure 5a). Within the range of soil moisture in favor of NO production, the slope of the average ratio of NO production versus NO release is about 1.007 ($SD < 0.006$). The maximum NO production (in terms of mass of N) was 0.11, 0.16, 0.27, 0.28 $\text{ng kg}^{-1} \text{s}^{-1}$ in soils from land use of NP, MP, PP and SP, respectively. NO production peaked at a soil moisture of approximately 4.5%, 2.8%, 3.4% and 8.2%, which is equivalent to 14.0%, 9.0%, 9.5%, and 18% WFPS (water-filled pore space) for soil samples from NP, MP, PP and SP, respectively. The NO production measurement results at soil temperature of 15°C and 25°C in laboratory showed that NO production peaked at certain soil moisture, which did not change significantly with soil temperature. This phenomenon can be plausibly interpreted by that diffusion of NO through pore spaces to atmosphere is limited under high soil moisture [Skopp et al., 1990], while substrate diffusion through water films to microbial active cells is limited under low soil moisture [Linn and Doran, 1984]. For all soils, we observed that the relationship of NO productions and soil temperature at a given soil moisture was similar to previous results [van Dijk et al., 2002; van Dijk and Meixner, 2001]. The peak of NO productions in paddy soils were about twofold of that in pasture soils (Figure 5a). This can be explained by poor nitrogen conditions in pasture soils. The total nitrogen in 0–20 cm soil layer was 1.0–2.1 g kg^{-1} in paddy soils, because of nitrogen fertilizer input of 100–180 $\text{kg ha}^{-1} \text{a}^{-1}$ (in term of N), more than three times higher than that in pasture soils. Compared with NO production in other pasture soil (maximum value of 0.26 $\text{ng kg}^{-1} \text{s}^{-1}$) [van Dijk and

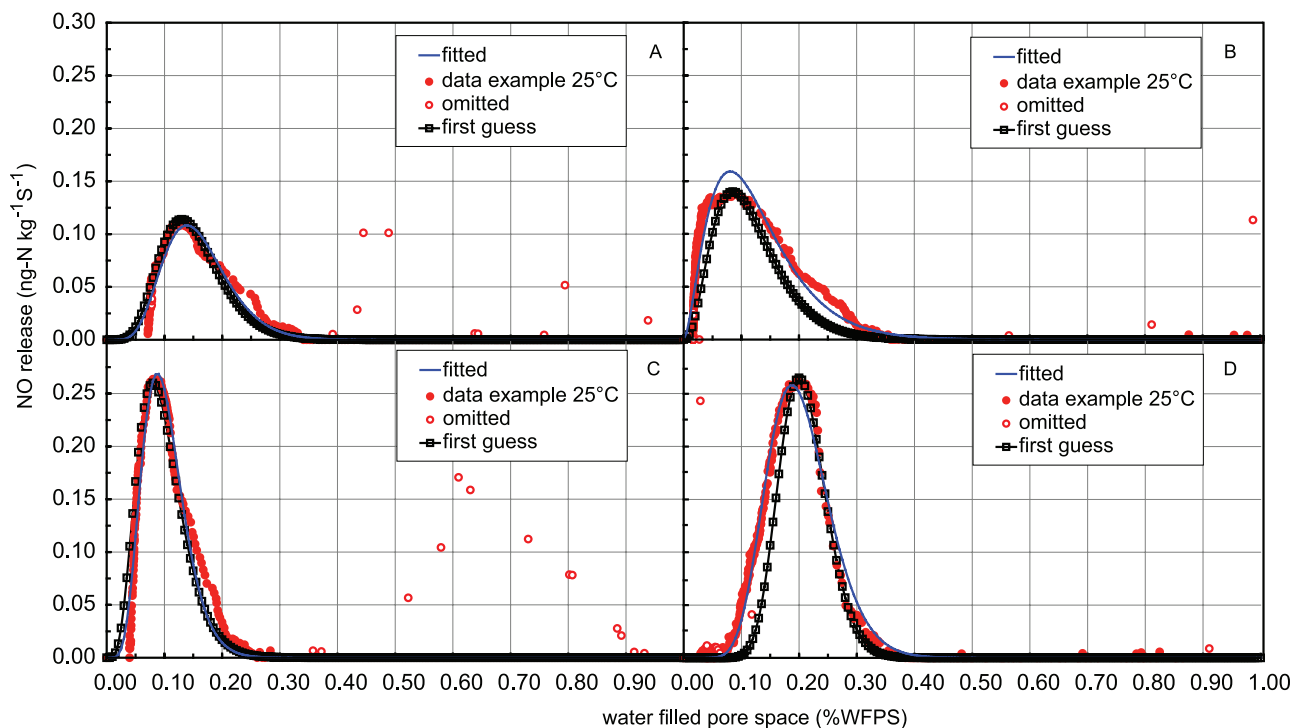


Figure 4. NO release from soil samples in (a) natural pasture, (b) man-made pasture, (c) paddy field which was pure sodic soil, and (d) paddy field which was the sodic soil mixed with sandy soil as a function of soil moisture at a constant soil temperature of 25°C.

Meixner, 2001], our results in pasture soils are slightly lower, but the values in paddy soils are similar.

3.2. NO Consumption Rate Constant k and Compensation Mixing Ratio NO_c

[18] NO consumption rate constant k is largely determined by what type of microbial consumption takes place in different soil. Our results show that k values are similar for saline sodic soils in different land use, ranging 1.37×10^{-6} – 2.91×10^{-6} , 2.05×10^{-6} – 7.10×10^{-6} , 1.07×10^{-6} – 6.99×10^{-6} $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$ and 2.05×10^{-6} – 7.45×10^{-6} $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$ for soil in NP, MP, PP and SP, respectively. The similar k values so far published, ranging from 0.5×10^{-6} to 60×10^{-6} $\text{m}^3 \text{kg}^{-1} \text{s}^{-1}$ [Baumgartner and Conrad, 1992; Bollmann and Conrad, 1997; Saad and Conrad, 1993; van Dijk and Meixner, 2001]. van Dijk and Meixner [2001] found that the value of the NO consumption rate constant, k , evidently depends on soil moisture and soil temperature, i.e., k value decreased with soil moisture and increased with soil temperature. In agreement with those findings, our data showed that the average k value at soil temperature of 25°C is higher than that at 15°C within range of soil moisture in favor of NO production. The dependence on soil temperature can be explained by the microbial nature of the consumption processes both through reduction [Bender and Conrad, 1994] and through oxidation [Godde and Conrad, 1999]. We observed that the soil moisture for the lowest point of k was similar with optimum soil moisture for NO production. The results suggested that NO consumption processes in the soils can be carried out under both aerobic and anaerobic conditions by denitrification and by heterotrophic and methanotropic bacteria, res-

spectively, as reported [Baumgartner et al., 1996; Bender and Conrad, 1994; Godde and Conrad, 1999; Koschorreck and Conrad, 1997].

[19] The NO compensation concentration, NO_c , is the concentration of ambient NO where the production of NO is equal to the consumption, at this point there is no net uptake or release of NO from the soil. The soil acts as a source for NO only when its NO_c exceeds the atmospheric concentrations of NO. Figure 5b shows that the compensation concentration varies at soil temperature of 25°C. Under optimum soil moisture conditions for NO production, the NO compensation point mixing ratio was about 60.4, 60.7, 115.2, and 74.0 $\mu\text{g m}^{-3}$ (52, 49, 94, and 60 ppb) for NP, MP, PP, and SP, respectively. Our results show that the optimum soil moisture for NO compensation mixing ratio is similar to that for NO production for a certain land use soil. The highest NO_c occurred in soil of PP under soil moisture 11.5–14.5% WFPS. The NO_c in paddy soil was slightly higher than that in pasture.

3.3. NO Fluxes From Saline Sodic Soil

[20] We applied the modified algorithm [Galbally and Johansson, 1989] on NO fluxes from saline sodic soils in different land use. Results are shown in Figures 6a–6d. The maximum of NO fluxes for NP, MP, PP, and SP soils (at 25°C) were 16, 20, 31, and 24 $\text{ng m}^{-2} \text{s}^{-1}$ at %WFPS of 14.0, 9.0, 9.5, and 18, respectively. Compared to the previous results obtained from arid or semiarid soils, NO emissions are much higher than dry arid and dry/hot semiarid soils ($<0.15 \text{ ng m}^{-2} \text{s}^{-1}$) and similar to grassland soils [Davidson and Kingerlee, 1997; Meixner et al., 1997; Meixner and Yang, 2006]. Figure 6 shows that the NO

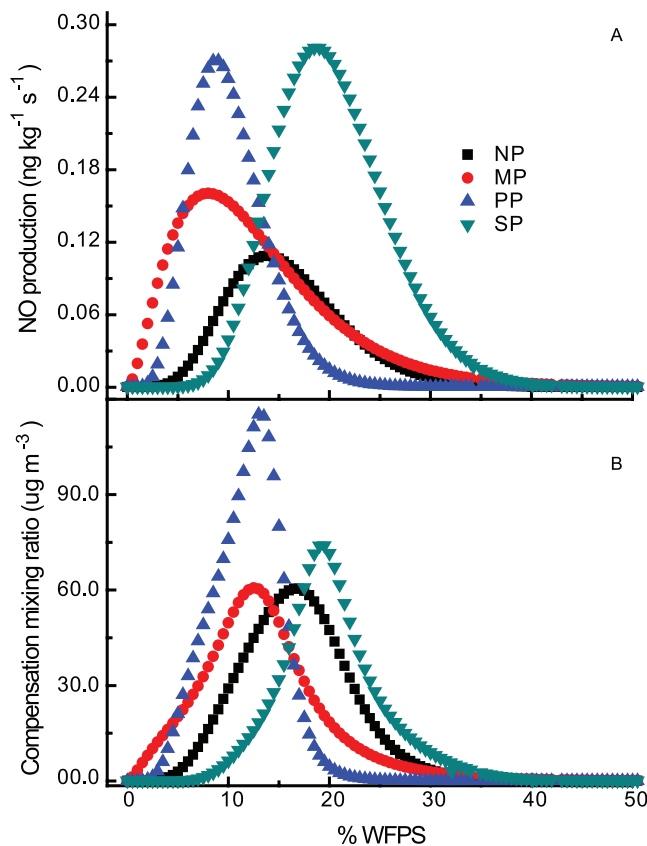


Figure 5. (a) NO production and (b) compensation concentration in saline sodic soils of different land use as a function of soil moisture at a soil temperature of 25°C (NP, natural pasture; MP, man-made pasture; SP, paddy field which was the saline sodic soil mixed with sandy soil; PP, paddy field which was pure saline sodic soil).

emissions are strongly affected by soil moisture. The optimum soil moisture at which maximum NO flux observed is independent of soil temperature. Statistically sound relationships have been observed between NO fluxes and soil moisture (optimum curves). The effects of soil moisture on biological, physical and chemical processes mediating NO emissions have been proposed in previous studies [Bollmann and Conrad, 1998; Davidson, 1993; Davidson and Schimel, 1995]. As soon as soil moisture was no longer limiting (Figure 6), NO emission strongly depends on temperature with Q_{10} ranging from 1.8 to 2.0. NO fluxes increased exponentially with soil temperature at any given soil moisture ($F_{NO}(T) = a \times \text{EXP}(bT)$). Similar results have also been observed in other studies [Hutchinson and Brams, 1992; Maljanen et al., 2007; Martin et al., 1998; Skiba et al., 1992; Yamulki et al., 1995; Yang and Meixner, 1997]. This is due to that the dominance of soil microbial processes in the production of NO anticipates a marked influence of soil temperature on NO emission rates. The rates of chemical and/or enzymatic processes change exponentially with temperature, as long as others factors (substrate or moisture available) are not limiting.

[21] Our results show that the NO fluxes for paddy field soils are about 1.2–2-fold higher than that for pasture soils (Figure 6), most likely due to fertilizer application and thus

increases the substrate (NH_4^+ and NO_3^-), which serve for nitrifying and denitrifying bacteria and thus enhances NO emissions from soil [Vitousek et al., 1997].

[22] The trend of NO emissions in coarser-texture soil greater than fine-texture soil was reported by several studies [Bakwin et al., 1990; McTaggart et al., 2002; Skiba et al., 1992]. The mechanism maintaining high diffusivity through the soil is continuous air-filled porosity [Bakwin et al., 1990]. Therefore, coarser soils tend to be better ventilated, allowing NO to escape more freely [Bakwin et al., 1990; Skiba et al., 1992]. We did not catch the trend (Figures 6c and 6d) probably due to different nitrogen fertilizer application in soils of PP and SP. Nevertheless, the higher soil water content for optimum NO emission from soil of SP than that of PP can be plausibly interpreted by that SP soil is less compacted than the PP soil because of the addition of sand (Table 1). Thus the increasing soil porosity might increase the optimum WFPS for NO emissions, suggesting that the soil texture could be a main factor that affects the relationship of NO emission and soil water moisture.

[23] Based on our laboratory NO flux parameterizations and on field data (soil temperature and soil moisture monitoring data), we estimated net field NO fluxes from these saline sodic soils in different months (Figures 7a–7d). The peaks of NO fluxes from saline sodic NP, MP, PP, and SP soils were 12.3, 14.9, 14.6 and 7.9 $\text{ng m}^{-2} \text{s}^{-1}$. The average NO fluxes in NP, MP, PP, and SP were about 4.9, 3.7, 1.6 and 1.3 $\text{ng m}^{-2} \text{s}^{-1}$, respectively, for an entire plant growth period. Our results in pasture are similar to previous estimates (around 1–5 $\text{ng m}^{-2} \text{s}^{-1}$) in grassland in China [Wang et al., 2005]. In contrast, The NO fluxes from paddy field in this study are more than 10 times less than previous estimates for cropland (20 $\text{ng m}^{-2} \text{s}^{-1}$) in heavily fertilized land in northeastern China [Wang et al., 2005]. Our data indicate that the NO emissions from paddy soils are much lower than that from pasture and dry farming cropland even with more nitrogen fertilizer application, suggesting that field NO emissions are much more dependent on soil moisture than fertilizer.

[24] The simulated seasonal variation of NO fluxes from these saline sodic soils showed that NO emissions peaked in early July and late June for NP and MP, respectively (Figures 7a and 7b) and in early October for paddy fields (Figures 7c and 7d), in addition, secondary peaks were observed in the pastures during October (Figures 7a and 7b). The seasonal variation of simulated NO fluxes in pasture depends on field soil moisture, which was related to precipitation. The NO flux in NP decreased with soil moisture during the period of May to mid June, when less than 50 mm monthly precipitation occurred (Figures 7a–7e). As a result, the soil moisture was below the optimum value for NO production (4.5%). Following this dry period, the NO flux reached a peak rapidly by early July, under optimum soil moisture. However, the NO flux in MP increased with decreasing soil moisture until the end of June, when the peak NO flux appeared, since the field soil moisture was closer to the optimum water content for NO production (2.8%) (Figure 7b). Owing to the field soil moisture levels, which were much higher than the optimum for NO emission, the simulation results show very low NO fluxes in both NP and MP during the period from mid July to late September, when 70–80% of the total seasonal

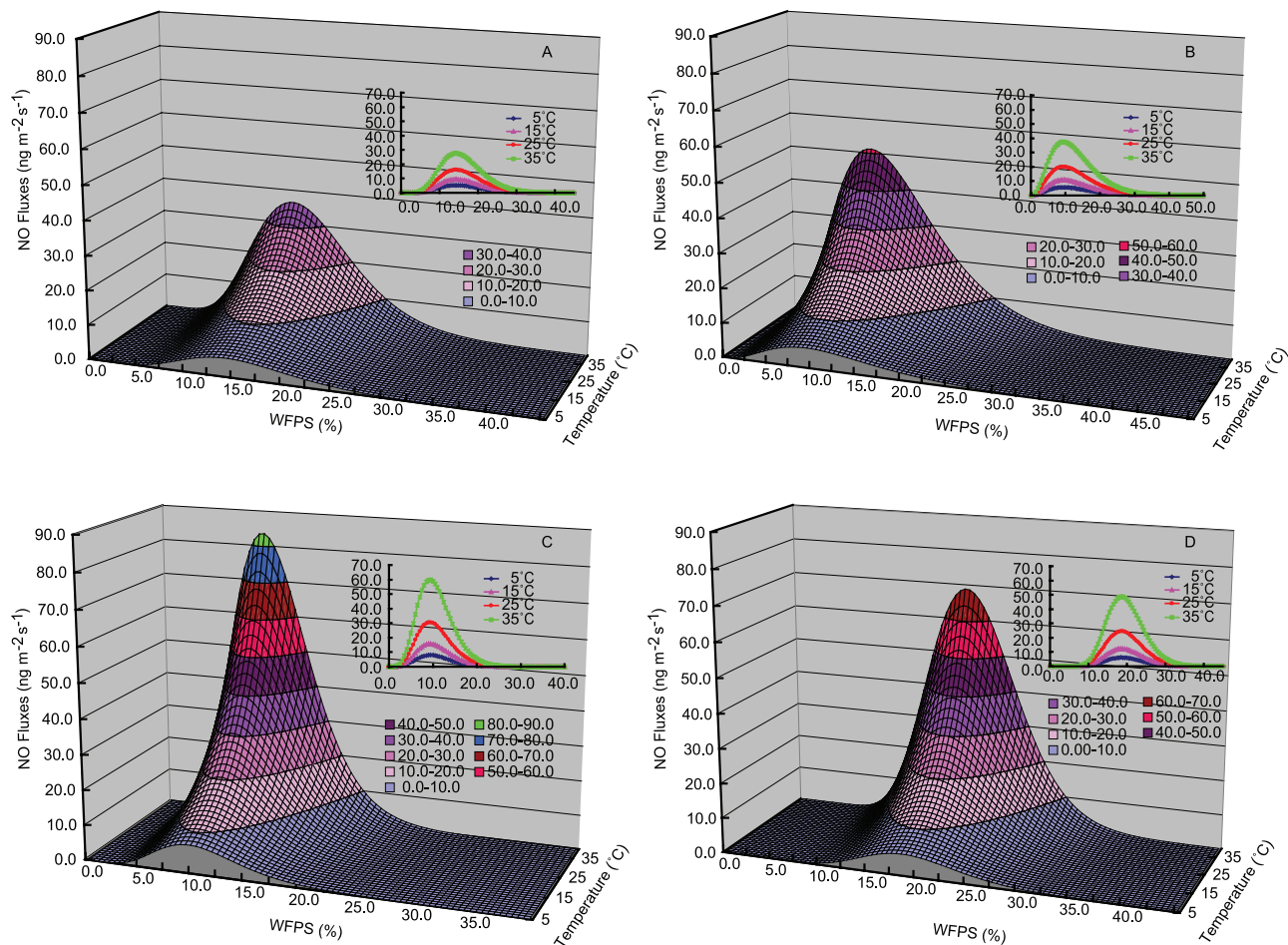


Figure 6. NO fluxes from soil samples in (a) natural pasture, (b) man-made pasture, (c) paddy field which was pure saline sodic soil, and (d) paddy field which was the saline sodic soil mixed with sandy soil versus soil temperature and soil moisture.

precipitation occurs (monthly precipitation was 80–130 mm). Drying of the pasture soil causes the secondary peak in NO flux, which appeared in October. Several studies showed that the relation of NO emissions and wetting events in savannas, i.e., small wetting events (<25 mm) following protracted dry periods result in large increases in NO emission [Johansson *et al.*, 1988]. However, more intensive (>25 mm) wetting events occurring during the wet season appear to inhibit NO emission [Cardenas *et al.*, 1993; Davidson *et al.*, 1993]. Comparing the two peaks of simulated NO fluxes in MP, as well as the NO fluxes from May and June, it suggests that the NO flux increased with temperature at similar soil moisture (Figures 7b and 7e). The seasonal variation of NO emission from paddy field was clearly related to individual agricultural management practices. Simulated NO fluxes from paddy fields were low from May to August for high soil water moisture. These emissions then increased with time after draining the paddy in the mid August, and then decreased, after the peak in October, because of decreasing temperature (Figures 7c–7e).

4. Concluding Remarks

[25] The saline sodic soil region in semiarid region of northeastern China has undergone rapid replacement of

natural pasture by paddy field for food production since the 1950s, leading to more and more serious pasture degradation. For the improvement of poor soil properties, an effective method is to mix sandy soil into paddy field in this region. Our findings of biogenic NO emission from saline sodic soil of pasture and paddy field provide support for a laboratory study by van Dijk and Meixner [2001] for relationship of NO production and soil temperature. Similar value of NO consumption rate constant (1.07×10^{-6} to $7.45 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1} \text{ s}^{-1}$) suggested that the consumption

Table 1. Physical Properties of Saline Sodic Soil From Different Sites^a

| Soil Type | Size Distribution of Individual Particles (μm) | | | | Bulk Density (g cm^{-3}) | Total Porosity |
|-----------|---|-------|-------|-------|-------------------------------------|----------------|
| | 50–2000 | 20–50 | 2–20 | <2 | | |
| NP | 33.89 | 16.53 | 8.26 | 41.32 | 1.4342 | 0.45 |
| MP | 24.40 | 27.30 | 11.55 | 36.75 | 1.4898 | 0.43 |
| SP | 50.07 | 12.48 | 6.24 | 31.20 | 1.2730 | 0.52 |
| PP | 38.68 | 19.03 | 6.34 | 35.95 | 1.3636 | 0.48 |

^aNP, natural pasture; MP, man-made pasture; SP, paddy field which was the saline sodic soil mixed with sandy soil; PP, paddy field which was pure saline sodic soil.

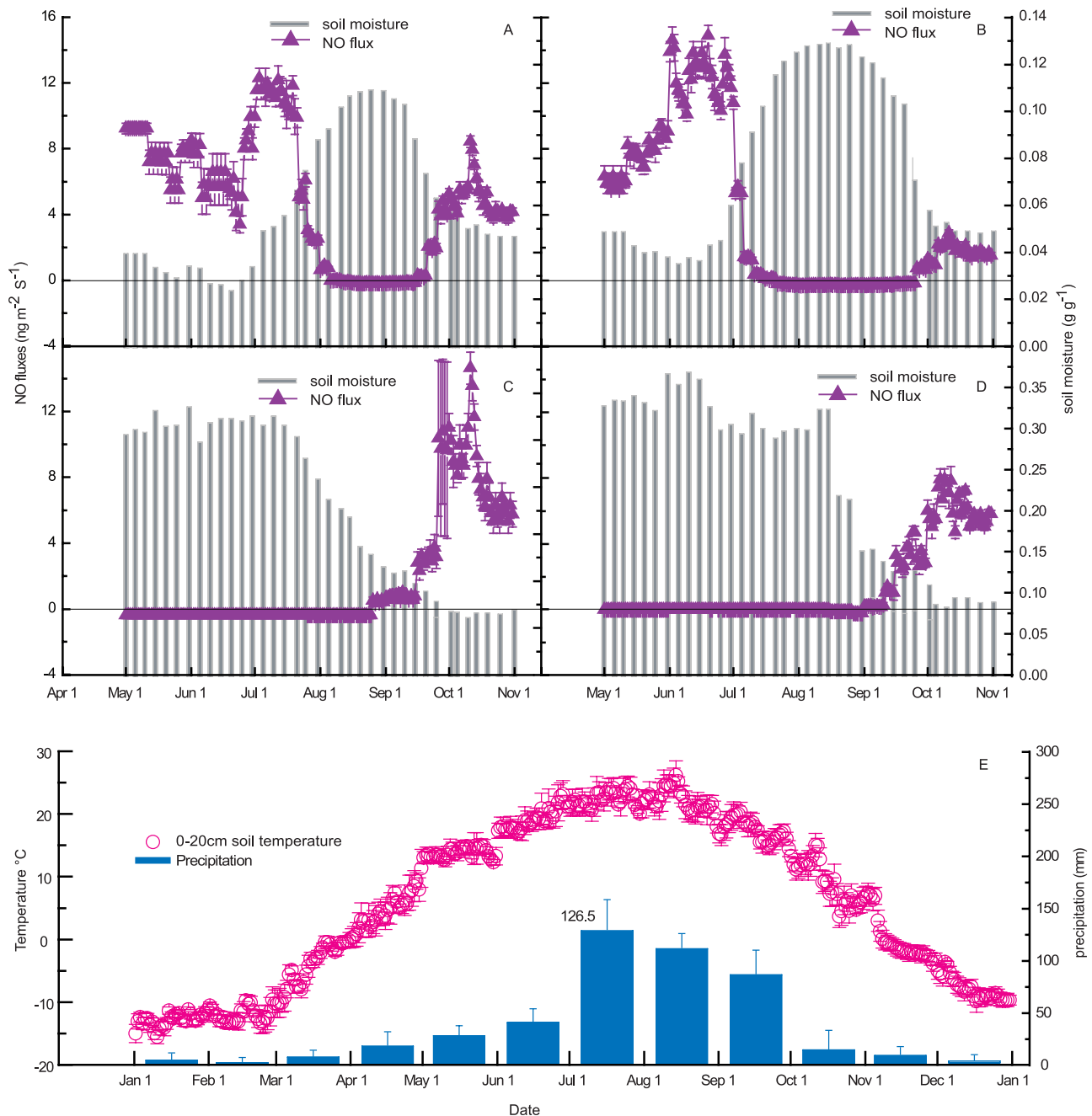


Figure 7. Seasonal variation of predicted NO fluxes and soil moisture in (a) natural pasture, (b) man-made pasture, (c) paddy field which was pure saline sodic soil, (d) paddy field which was the saline sodic soil mixed with sandy soil during a an entire growth period, and (e) soil temperature and precipitation in a year (data are mean values, and the standard deviation is indicated by error bar).

processes were similar in saline sodic soils of different land use. Statistically sound relationships have been observed between NO fluxes and soil moisture and NO fluxes also increased exponentially with soil temperature (Q_{10} ranged from 1.8 to 2.0) at any given soil moisture. The estimated NO fluxes are very low both from the pasture sites during the period from mid July to late September when high precipitation occurred and from the paddy sites before draining in the mid August. More interestingly, the simulated NO fluxes from the pasture sites were about threefold greater than that from paddy sites for the entire growth

period. All these observations indicate that the biogenic NO emissions in the field depend more on rainfall and individual irrigation management practices than fertilizer application.

[26] **Acknowledgments.** This work is financially supported by the Max Planck Society and Max Planck Institute for Chemistry, the 100 Talents Program of the Chinese Academy of Sciences, the Chinese Academy of Sciences–Max Planck Society Exchange Program, and Natural Science Foundation of China (grants 40873062 and 40525010). We thank F. A. Ashuri for assistance in the laboratory. Anonymous referees are thanked for constructive review comments, which are helpful for us to improve our manuscripts.

References

- Bakwin, P. S., S. C. Wofsy, S. M. Fan, M. Keller, S. E. Trumbore, and J. M. Da Costa (1990), Emission of nitric-oxide (NO) from tropical forest soils and exchange of NO between the forest canopy and atmospheric boundary-layers, *J. Geophys. Res.*, 95(D10), 16,755–16,764.
- Barger, N. N., J. Belnap, D. S. Ojima, and A. Mosier (2005), NO gas loss from biologically crusted soils in Canyonlands National Park, Utah, *Biogeochemistry*, 75(3), 373–391.
- Baumgartner, M., and R. Conrad (1992), Effects of soil variables and season on the production and consumption of nitric-oxide in oxic soils, *Biol. Fertil. Soils*, 14(3), 166–174.
- Baumgartner, M., M. Koschorreck, and R. Conrad (1996), Oxidative consumption of nitric oxide by heterotrophic bacteria in soil, *FEMS Microbiol. Ecol.*, 19(3), 165–170.
- Bender, M., and R. Conrad (1994), Microbial oxidation of methane, ammonium and carbon-monoxide, and turnover of nitrous-oxide and nitric-oxide in soils, *Biogeochemistry*, 27(2), 97–112.
- Bollmann, A., and R. Conrad (1997), Enhancement by acetylene of the decomposition of nitric oxide in soil, *Soil Biol. Biochem.*, 29(7), 1057–1066.
- Bollmann, A., and R. Conrad (1998), Influence of O₂ availability on NO and N₂O release by nitrification and denitrification in soils, *Global Change Biol.*, 4(4), 387–396.
- Cardenas, L., A. Rondon, C. Johansson, and E. Sanhueza (1993), Effects of soil-moisture, temperature, and inorganic nitrogen on nitric-oxide emissions from acidic tropical savanna soils, *J. Geophys. Res.*, 98(D8), 14,783–14,790.
- Davidson, E. A. (1993), Soil water content and the ratio of nitrous oxide to nitric oxide emitted from soil, in *Biogeochemistry of Global Change: Radiatively Active Trace Gases*, edited by R. S. Oremland, pp. 369–386, Chapman and Hall, New York.
- Davidson, E. A., and W. Kingerlee (1997), A global inventory of nitric oxide emissions from soils, *Nutr. Cycl. Agroecosyst.*, 48(1–2), 37–50.
- Davidson, E. A., and J. P. Schimel (1995), *Microbial Processes of Production and Consumption of Nitric Oxide, Nitrous Oxide and Methane*, pp. 327–357, Blackwell Sci., Oxford.
- Davidson, E. A., P. M. Matson, R. Vitousek, K. Dunkin, G. Garcia-Mendez, and M. Mass (1993), Processes regulating soil emissions of NO and N₂O in seasonally dry tropical forest, *Ecology*, 74, 130–139.
- Firestone, M. K., and E. A. Davidson (1989), Microbiological basis of NO and N₂O production and consumption in soil, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, edited by M. O. Andreae and D. S. Schimel, pp. 7–21, John Wiley, New York.
- Galbally, I. E., and C. Johansson (1989), A model relating laboratory measurements of rates of nitric-oxide production and field-measurements of nitric-oxide emission from soils, *J. Geophys. Res.*, 94(D5), 6473–6480.
- Godde, M., and R. Conrad (1999), Immediate and adaptational temperature effects on nitric: Oxide production and nitrous oxide release from nitrification and denitrification in two soils, *Biol. Fertil. Soils*, 30(1–2), 33–40.
- Gut, A., M. S. van Dijk, M. Scheibe, U. Rummel, M. Welling, C. Ammann, X. F. Meixner, A. G. Kirkman, O. M. Andreae, and E. B. Lehmann (2002), NO emission from an Amazonian rain forest soil: Continuous measurements of NO flux and soil concentration, *J. Geophys. Res.*, 107(D20), 8057, doi:10.1029/2001JD000521.
- Hartley, A. E., and W. H. Schlesinger (2000), Environmental controls on nitric oxide emission from northern Chihuahuan desert soils, *Biogeochemistry*, 50(3), 279–300.
- Hutchinson, G. L., and E. A. Brams (1992), NO versus N₂O emissions from an NH₄⁺-amended Bermuda grass pasture, *J. Geophys. Res.*, 97(D9), 9889–9896.
- International Atomic Energy Agency (IAEA) (1995), Management strategies to utilize salt-affected soils, *IAEA-TECDOC-814*, Vienna.
- Johansson, C., H. Rodhe, and E. Sanhueza (1988), Emission of NO in a tropical savanna and a cloud forest during the dry Season, *J. Geophys. Res.*, 93(D6), 7180–7192.
- Keller, M., R. Varner, J. D. Dias, H. Silva, P. Crill, and R. C. de Oliveira (2005), Soil-atmosphere exchange of nitrous oxide, nitric oxide, methane, and carbon dioxide in logged and undisturbed forest in the Tapajos National Forest, Brazil, *Earth Interact.*, 9(23), 1–28.
- Kirkman, A. G., A. Gut, C. Ammann, V. L. Gatti, M. A. Cordova, A. L. M. Moura, O. M. Andreae, and F. X. Meixner (2002), Surface exchange of nitric oxide, nitrogen dioxide, and ozone at a cattle pasture in Rondônia, Brazil, *J. Geophys. Res.*, 107(D20), 8083, doi:10.1029/2001JD000523.
- Koschorreck, M., and R. Conrad (1997), Kinetics of nitric oxide consumption in tropical soils under oxic and anoxic conditions, *Biol. Fertil. Soils*, 25(1), 82–88.
- Linn, D. M., and J. W. Doran (1984), Effect of water-filled pore-space on carbon-dioxide and nitrous-oxide production in tilled and nontilled soils, *Soil Sci. Soc. Am. J.*, 48(6), 1267–1272.
- Ludwig, J., F. X. Meixner, B. Vogel, and J. Forstner (2001), Soil-air exchange of nitric oxide: An overview of processes, environmental factors, and modeling studies, *Biogeochemistry*, 52(3), 225–257.
- Maljanen, M., M. Martikala, H. T. Koponen, P. Virkajarvi, and P. J. Martikainen (2007), Fluxes of nitrous oxide and nitric oxide from experimental excreta patches in boreal agricultural soil, *Soil Biol. Biochem.*, 39(4), 914–920.
- Martin, R. E., M. C. Scholes, A. R. Mosier, D. S. Ojima, E. A. Holland, and W. J. Parton (1998), Controls on annual emissions of nitric oxide from soils of the Colorado shortgrass steppe, *Global Biogeochem. Cycles*, 12(1), 81–91.
- McTaggart, I. P., H. Akiyama, H. Tsuruta, and B. C. Ball (2002), Influence of soil physical properties, fertiliser type and moisture tension on N₂O and NO emissions from nearly saturated Japanese upland soils, *Nutr. Cycl. Agroecosyst.*, 63(2–3), 207–217.
- Meixner, F. X., and W. X. Yang (2006), Biogenic emissions of nitric oxide and nitrous oxide from arid and semi-arid land, in *Dryland Ecohydrology*, edited by P. D'Odorico and A. Porporato, pp. 233–256, Springer, Dordrecht, Netherlands.
- Meixner, F. X., T. Fickinger, L. Marufu, D. Serca, F. J. Nathaus, E. Makina, L. Mukumbira, and M. O. Andreae (1997), Preliminary results on nitric oxide emission from a southern African savanna ecosystem, *Nutr. Cycl. Agroecosyst.*, 48(1–2), 123–138.
- Moldrup, P., T. Olesen, J. Gamst, P. Schjonning, T. Yamaguchi, and D. E. Rolston (2000), Predicting the gas diffusion coefficient in repacked soil: Water-induced linear reduction model, *Soil Sci. Soc. Am. J.*, 64(5), 1588–1594.
- Otter, L. B., W. X. Yang, M. C. Scholes, and F. X. Meixner (1999), Nitric oxide emissions from a southern African savanna, *J. Geophys. Res.*, 104(D15), 18,471–18,485.
- Pilegaard, K., P. Hummelshøj, and N. O. Jensen (1999), Nitric oxide emission from a Norway spruce forest floor, *J. Geophys. Res.*, 104(D3), 3433–3445.
- Qadir, M., and S. Schubert (2002), Degradation processes and nutrient constraints in sodic soils, *Land Degrad. Dev.*, 13(4), 275–294.
- Remde, A., and R. Conrad (1991), Metabolism of nitric-oxide in soil and denitrifying bacteria, *FEMS Microbiol. Ecol.*, 85(1), 81–93.
- Saad, O. A. L. O., and R. Conrad (1993), Temperature-dependence of nitrification, denitrification, and turnover of nitric-oxide in different soils, *Biol. Fertil. Soils*, 15(1), 21–27.
- Skiba, U., K. J. Hargreaves, D. Fowler, and K. A. Smith (1992), Fluxes of nitric and nitrous oxides from agricultural soils in a cool temperate climate, *Atmos. Environ. Part A*, 26(14), 2477–2488.
- Skopp, J., M. D. Jawson, and J. W. Doran (1990), Steady-state aerobic microbial activity as a function of soil-water content, *Soil Sci. Soc. Am. J.*, 54(6), 1619–1625.
- Szabolcs, I. (1994), Soils and salinization, in *Handbook of Plant and Crop Stress*, edited by M. Pessarakli, pp. 3–11, Marcel Dekker, New York.
- van Dijk, M. S., and F. X. Meixner (2001), Production and consumption of NO in forest and pasture soils from the Amazon basin: A laboratory study, *Water Air Soil Pollut.*, 1, 119–130.
- van Dijk, M. S., A. Gut, A. G. Kirkman, F. X. Meixner, and O. M. Andreae (2002), Biogenic NO emissions from forest and pasture soils: Relating laboratory studies to field measurements, *J. Geophys. Res.*, 107(D20), 8058, doi:10.1029/2001JD000358.
- Verchot, L. V., E. A. Davidson, J. H. Cattaneo, I. L. Ackerman, H. E. Erickson, and M. Keller (1999), Land use change and biogeochemical controls of nitrogen oxide emissions from soils in eastern Amazonia, *Global Biogeochem. Cycles*, 13(1), 31–46.
- Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, W. H. Schlesinger, and D. G. Tilman (1997), Human alteration of the global nitrogen cycle: Sources and consequences, *Ecol. Appl.*, 7(3), 737–750.
- Wang, Q. G., Z. W. Han, and Y. Higano (2005), An inventory of nitric oxide emissions from soils in China, *Environ. Pollut.*, 135(1), 83–90.
- Wang, Z. C., and S. W. Qiu (2002), Management options of saline-alkali land in west Jilin province, *Agric. Technol.*, 22(5), 6–8, 18.
- Williams, E. J., A. Guenther, and F. C. Fehsenfeld (1992), An inventory of nitric-oxide emissions from soils in the United States, *J. Geophys. Res.*, 97(D7), 7511–7519.
- Yamulki, S., K. W. T. Goulding, C. P. Webster, and R. M. Harrison (1995), Studies on NO and N₂O fluxes from a wheat field, *Atmos. Environ.*, 29(14), 1627–1635.
- Yang, W. X., and F. X. Meixner (1997), Laboratory studies on the release of nitric oxide from subtropical grassland soils: The effect of soil temperature

- and moisture, in *Gaseous Nitrogen Emissions From Grassland*, edited by S. C. Jarvis and B. F. Pain, pp. 67–71, CAB Int, Wallingford, U.K.
- Yu, J. B., W. D. Sun, J. S. Liu, J. D. Wang, J. S. Yang, and F. X. Meixner (2007), Enhanced net formations of nitrous oxide and methane underneath the frozen soil in Sanjiang wetland, northeastern China, *J. Geophys. Res.*, 112, D07111, doi:10.1029/2006JD008025.
- Y. Chen, Z. W. Liang, and G. P. Wang, Da'an Experimental Station of Sodic Soil Ecology, Northeast Institute of Geography and Agricultural Ecology, Chinese Academy of Sciences, Changchun 130012, China.
- B. Mamtimin, F. X. Meixner, and J. B. Yu, Biogeochemistry Department, Max Planck Institute for Chemistry, P.O. Box 3060, D-55020 Mainz, Germany. (meixner@mpch-mainz.mpg.de; junbao.yu@gmail.com; jbyu@mpch-mainz.mpg.de)
- W. D. Sun, Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Wushan, Guangzhou 510640, China.
- Z. G. Sun, Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, Yantai, Shandong 264003, China.