Biogenic Nitric Oxide Emission of Mountain Soils Sampled from Different Vertical Landscape Zones in the Changbai Mountains, Northeastern China

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Nitric oxide (NO) is an important component in nitrogen biogeochemical cycling produced through biological processes of nitrification and denitrification in soils, but the production and the consumption processes of NO in temperate mountain soil are less understood. Through laboratory experiments focusing on NO biogenic emissions from six kinds of mountain soils sampled from different vertical landscape zones, that is, coniferous and broadleaf mixed forest (CBF), fir forest (FF), spruce (SP), Erman’s birch forest (EBF), alpine tundra (AT), and volcanic ash (VA), in the Changbai Mountains, northeastern China, we found that the optimum water-filled pore space (WFPS) for NO production varies between 22.5% and 35% for a range of mountain soils. The optimal soil moisture for the maximum NO emission for a certain soil type, however, was constant and independent of soil temperature. The NO emission potential for forest soils was about 7–50-fold higher than tundra soil and volcanic ash, indicating that it is strongly influenced by nutrient contents in soils. On the basis of laboratory results and field monitoring data, the average NO fluxes from these mountain soils were estimated to be 0.14–29.56 ng N m−2 s−1 for an entire plant growth period. NO emissions mainly occur in wet season for CBF and FF, but in dry season for other soil types.

Introduction

Nitric oxide (NO) is a highly reactive atmospheric trace gas, which is of importance for atmospheric chemistry (1, 2). In the stratosphere, nitrogen oxides (NOx = NO + NO2), mainly from the oxidation of nitrous oxide there, could mediate the production and the destruction of ozone (O3) (2). They also influence the formation of the hydroxyl radical (OH), which in turn regulates the lifetime of numerous compounds in the atmosphere (3). NOx are precursors in the photochemical formation of gaseous nitric acid (HNO3) and thus contribute to the acidity of clouds and precipitation (3).

Soils are a major source of atmospheric NOx (4, 5). On the global scale, the budget of NOx source from soils is around 8.9 Tg N yr−1, about 20% of total global source (6). Generally soils contribute to the global budgets of NO sources, although its contribution as sinks is also likely but considered to be small (7). According to present knowledge, NO is produced in soils nearly ubiquitously; therefore, soil emissions constitute a continuous background flux of NO to the atmosphere. Even in industrialized regions, there is substantial evidence that soil emissions make a significant contribution to the tropospheric NO burden (8, 9).

Nitric oxide in soil is produced through biological processes of nitrification and denitrification, as well as chemical decomposition of HNO3 (10). Temperature, soil moisture, soil texture, atmospheric concentration of NO, wetting of dry soil, fertilization and land use category have all been shown to be key factors controlling NO emission from soils (8, 11–13). The rough ranking of NO emission levels (fertilized agricultural fields > grasslands > forests > other natural systems) is in broad accordance with the nitrogen status of corresponding soils (14). Generally, forest soils may be regarded as minor sources of NO, except those forest soils in temperate regions, which receive considerable nitrogen inputs (NH3, HNO3, NH4+, NO3−) by wet and dry deposition. Recent studies found that the NO flux observed from temperate forests and rainforest soils is about 10 to 100-fold higher than that from dry arid and semiarid soils (12, 15, 16).

Although soils are a major source of atmospheric NOx, there still exists huge uncertainty and disagreement about the source strength. A probable cause of this huge uncertainty is that previous studies of NO emissions are imbalanced in regions under investigation. As to the forests, for example, most studies about NO fluxes were carried out in Europe, U.S.A., tropical America, and Africa (8, 11, 17). Only two reports on soil NO emission from Asian forests, to our knowledge, are available to date (18). However, the mentioned problems are not necessarily solved by integration of fluxes over larger areas and longer time periods, since most of observed uncertainties and problems with NO flux data can be traced (15). 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 (14, 16, 19). Unfortunately, few laboratory and field results about net NO fluxes from the Asian temperate forest soil have been reported so far. In this study, we present results of NO emission from laboratory studies on mountain soil samples of different vertical landscape zones in the Changbai Mountains, northeastern China. Our purposes are (a) to study NO production, NO consumption, and NO emission in mountain soils from 6 landscape zones as functions of soil temperature and soil moisture, and (b) to estimate the biogenic NO emission from temperate forest soils in the
studied region based on results obtained using a laboratory incubation technique.

Materials and Methods

Site Description. The studied region is located in the Changbai Mountain Biosphere Reserve (CMBR) at 41°41', 49°42'-55°25', 127°18'-128°16', 1706.48' E (720-2691 m above sea level) in northeastern China. From the bottom to the mountain peaks, the CMBR has clear vertical zones of ecosystems, and the soils are dark brown forest soil, brown coniferous forest soil, subalpine open forest and meadow soil, alpine tundra soil and volcanic soil (see Figure S1 and Section 1 for detail introduction, Supporting Information). Nutrient concentrations in soil layer at depths of 0-20 cm are 2.83-98.52 g kg\(^{-1}\) for TOC, 0.51-5.34 g k g\(^{-1}\) for TN, 1.02-1.52 g kg\(^{-1}\) for TS and 0.52-1.61 g kg\(^{-1}\) for TP. Soil pH ranges from 4.5 to 6.2, and bulk density ranges from 0.2-0.96 g cm\(^{-3}\) (20-22).

Laboratory Experiments for NO Measurement. The NO production and consumption were measured under 15 and 25 °C in the laboratory using a fully automatic laboratory dynamic incubation system. The system includes four subsystems, that is, air purification system, gas dilution system, dynamic chamber system and measurement system (described in detail by reference (13)). The CLD 780TR Chemiluminescence NO Analyzer (detection limit 0.052 ppb and precision ±0.026 ppb, Eco Physics AG., Switzerland) was used for NO measurement and Binos (Rosemount, Germany) for vapor signal capture. All measurements are stored into a computer automatically.

Six kinds of soil samples for different vertical landscape zones, that is, coniferous and broadleaf mixed forest (CBF), fir forest (FF), spruce forest (SF), Erman’s birch forest (EBF), alpine tundra (AT) and volcanic ash at top of mountain (approximately 2650 above sea level) (VA), respectively, were collected from the surface soil (0-20 cm depth) in early October, 2005 for NO production measurements (see Figure S1, Supporting Information). 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 being sieved through a 2 mm coarse stainless steel sieve. Roots as well as other organic matter were removed to homogenize the sample, and the soil-water content was determined.

During experiment, the dynamic chambers were kept in a thermostatted cabinet to maintain certain soil temperatures. 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 in reference (13)). Before the measurements were made, the gas in the headspace was allowed to equilibrate (overnight). The NO analyzer

![Figure 1](https://example.com/figure1.png)  
**FIGURE 1.** Initial estimate and fitted relations of NO release from soil samples in volcanic ash (A), alpine tundra (B), Erman’s birch forest (C), spruce forest (D), fir forest (E), and coniferous and broadleaf mixed forest (F) and soil moisture at a constant soil temperature of 25 °C.
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 9 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).

Data Calculation. The NO release rate \( J \) was calculated using the difference of the NO mixing ratio between outlet and inlet of each dynamic chamber, and the modified model of Galbally and Johannson (23) as eq 1 was used to transform the laboratory-derived NO release into a net NO flux (see Section 2 for detail description, Supporting Information).

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F_{\text{NO}}(\text{WFPS}, T) = \sqrt{BD} \times \left( \frac{k(\text{WFPS}, T) \times D \times [NO]}{[\text{WFPS}, T]} - [NO]_{\text{amb}} \right) \quad (1)
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Results and Discussion

NO Release Rate \( J \) and Production \( P \). Figure 1 presents NO release at a constant soil temperature of 25 °C versus soil moisture for all six types of soils studied. A modified algorithm (15) was applied to fit the laboratory results (Figure 1). The initial estimate curve is estimate results because the parameters of \( a, b, \) and \( c \) were calculated from three laboratory measurement data of \( F_{\text{NO}}(\text{WFPS}_\text{opt}), \text{WFPS}_\text{opt}, \) and \( \text{WFPS}_\text{upp} \) based on eqs 9–11 in Section 2, Supporting Information. The fitted results showed that the algorithm was well fitted with the laboratory data \((R > 0.98**) \). The ** and * means relation significant at the 0.01 and 0.05 level, respectively, sum of square for corresponding value difference ranges from 0.02 to 15.53). According to eqs 1 and 2, the production \( P \) (i.e., NO release \( J \) at NO\text{amb} is nearly zero) in soils from different landscapes was evaluated (Figure 2A). 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 1.051 (SD < 0.193). Many studies showed that optimum soil moisture existed for soil NO emissions (19, 24, 25), but the value varied according to soils. For example, a laboratory study showed the optimum soil moisture of about 20% water-filled pore space (WFPS) by Yang and Meixner (24), but in another study conducted in a seasonally dry forest of the eastern Amazon, maximum NO fluxes were observed at approximately 50% WFPS (25). In our study, optimum soil moisture was approximately 13.10%, 25.81%, 36.31%, 53.41%, 54.38%, and 50.77%, which is equivalent to 26.0%, 25.0%, 32.5%, and 35.0% WFPS for soil samples from VA, AT, EBF, SF, FF, and CBF, respectively. The maximum NO production (in terms of mass of N) at optimum soil moisture was 0.24, 0.48, 1.91, 7.64, 12.59, and 18.55 ng N kg\(^{-1}\) s\(^{-1}\) in soils from landscapes of VA, AT, EBF, SF, FF, and CBF, respectively. The NO production results at soil temperature of 15 and 25 °C in the laboratory showed that the optimum soil moisture for NO production did not change significantly with soil temperature. This phenomenon can be plausibly interpreted by that diffusion of NO through pore spaces to the atmosphere is limited under high soil moisture (26), while substrate diffusion through water films to microbial active cells is limited under low soil moisture (27). For all soils, we observed that the relationship of NO production and soil temperature at a given soil moisture (results not shown) was similar to previous results (16, 28). The peak of NO production in the bottom soil (CBF) was about 77-fold of that in top soils (VA) (Figure 2A). This can be plausibly explained by poor nitrogen conditions in volcanic ash soils. The total nitrogen in a 0–20 cm soil layer was 4.31–7.22 g kg\(^{-1}\) CBF soils, more than 10 times higher than that in the VA soil (21, 22). Compared with NO production in pasture soil (maximum

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\text{value of } 0.26 \text{ ng N kg}^{-1} \text{s}^{-1} \quad (28), \text{our results in forest soils are much higher, but the values in VA and AT soils are similar. }
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NO Consumption Rate Constant \( k \) and Compensation Mixing Ratio \( NO_\text{C} \). NO consumption rate constant \( k \) is largely determined by the type of microbial consumption that takes place in a different soil. Our results show that \( k \) values range 4.03 \times 10^{-6}–11.13 \times 10^{-6}, 4.11 \times 10^{-6}–29.11 \times 10^{-6}, 3.37 \times 10^{-5}–33.95 \times 10^{-5}, 29.11 \times 10^{-6}–93.36 \times 10^{-6}, 15.24 \times 10^{-5}–166.22 \times 10^{-5}, \) and \( 5.82 \times 10^{-6}–242.86 \times 10^{-6} \text{ m}^3 \text{kg}^{-1} \text{s}^{-1} \) for soil in VA, AT, EBF, SF, FF, and CBF, respectively. We observe low \( k \) values in VA and AT soils and high \( k \) values in FF and CBF soils (Figure 2B). The different \( k \) value suggests that the consumption processes in our experiment were dramatically different in the six kinds of soils. Our results are higher than that of the range of \( k \) values so far published (ranging from 0.5 \times 10^{-6} to 60 \times 10^{-6} \text{ m}^3 \text{kg}^{-1} \text{s}^{-1} \) (28–30). van Dijk et al. (28) found that the value of the NO consumption rate constant, \( k \), evidently depends on soil moisture and soil temperature, that is, the \( k \) 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 (31) and through oxidation (32). We observed that the soil moisture for not only the highest point of \( k \) in EBF, SF, FF, and CBF with high content of soil N and TOC, but also the
lowest point of $k$ in VA and AT with low content of soil N and TOC was similar with optimum soil moisture for NO production (Figure 2B). 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, respectively, as reported (32–34).

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 2C 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 56.5, 97.0, 71.7, 86.4, 93.2, and 77.2 ug m$^{-2}$ (45.2, 77.6, 57.4, 69.1, 74.6, and 61.8 ppb) for VA, AT, EBF, SF, FF, and CBF, respectively. Our results show that the optimum soil moisture for NO compensation mixing ratio is similar to that for NO production for a certain landscape soil. The highest and the lowest $NO_c$ at the optimum soil moisture occurred in soil of AT under soil moisture 22%–26.5% WFPS and in soil of VA under soil moisture 27.5%–30% WFPS, respectively. The $NO_c$ in FF soil was slightly higher than that in other forest soil.

**NO Fluxes from Mountain Soils.** We applied the modified algorithm (23) on NO fluxes from mountain soils of vertical landscape zones in the Changbai Mountains. Results are shown in Figure 3A–F. The maximum of NO fluxes for VA, AT, EBF, SF, FF, and CBF soils (at 25°C) were 1.65, 2.41, 16.73, 51.92, 49.96, and 81.89 ng N m$^{-2}$ s$^{-1}$ at %WFPS of 26.0, 22.5, 22.5, 25.0, 32.5, and 35.0, respectively. Compared to previous results obtained from forest soils, NO emissions are much higher than dry tropical forest of México (0.14–1.27 ng N m$^{-2}$ s$^{-1}$) (17), primary rain forest in eastern Amazonia (3.3–5.9 ng N m$^{-2}$ s$^{-1}$) (25) and humid tropical forest in the Brazilian Amazon (1.4–9.2 ng N m$^{-2}$ s$^{-1}$) (35), and are similar to recent report in subtropical humid forests in south China (7.9–45 ng N m$^{-2}$ s$^{-1}$) (18). However, relatively high NO fluxes were observed by other studies in temperate forest with high nitrogen input (36, 37). The NO emission from AT and VA is relatively low in the present study, but also higher than that of dry arid and dry/hot semiarid soils (<0.15 ng N m$^{-2}$ s$^{-1}$) and similar to grassland soils (15, 38, 39).
Figure 3 shows that the NO emissions are strongly affected by soil moisture. The optimum soil moisture at which the maximum NO flux is 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 (40–42). Q₀ is an important parameter to evaluate NO emission dependence on temperature from soil. Our results show that NO emission from mountain soils strongly depends on temperature with Q₀ ranging from 1.39 to 2.32 as soon as soil moisture was no longer limiting (Figure 3). NO fluxes increased exponentially with soil temperature at any given soil moisture (see Figure S5, Supporting Information). Similar results have also been observed in other studies (24, 43–45). 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 other factors (substrate or moisture available) are not limiting.

The significant relations of maximum NO fluxes and nutrients were observed in the study. The correlation coefficients of maximum NO fluxes to TOC, TN, TP, and TS were 0.886*, 0.882*, 0.912*, and 0.910*, respectively. Both NO fluxes and nutrients in the Changbai Mountains decreased with altitude (see Figure S3, Supporting Information). The NO fluxes for forest soils were about 10–50-fold higher than that for VA soils, most likely because of high nitrogen in forest soils. High substrate (NH₄⁺ and NO₃⁻) can serve for nitrifying and denitrifying bacteria, thus enhances NO emissions from soil (46). Simultaneously, high nutrient content of organic carbon, phosphorus, and sulfur are beneficial for the growth of the microorganism community, which accelerate microbial metabolism activities. Therefore nitrification and denitrification rate in soil are increased for enough substrate and energy supplying by organic matter mineralization (47, 48). Although the soil pH is a sensitive factor for nitrification and denitrification (49), the significant relation of NO fluxes and soil pH is not observed in the present study maybe because of different soils with different plant growth and physico-chemical qualities.

Several previous studies reported that the trend of NO emissions in coarser-texture soil is greater than in fine-texture soil because of better ventilation in coarser soils (44, 50). In agreement with those studies, we found the NO emissions from different soils increased with total porosity and decreased with bulk density (Figure 3 and Supplementary Table 1, Supporting Information). Moreover, the higher soil–water content for optimum NO emission from soils of SF, FF, and CBF than that of AT and EBF can be plausibly interpreted by that ST, FF, and CBF soils are less compacted than the AT and EBF soils.

On the basis of our laboratory NO flux parametrizations and on field data (soil temperature and soil moisture monitoring data), we applied the eq 14 in Section 2, Supporting Information, to estimate net field NO fluxes from these mountain soils in different months (Figure 4A). The peaks of the NO fluxes from soils of CBF, FF, SF, EBF, AT, and VA were 51.49, 29.85, 23.56, 7.99, 0.69, and 0.31 ng N m⁻² s⁻¹. The average NO fluxes in CBF, FF, SF, EBF, AT, and VA were about 29.56, 18.94, 11.73, 4.85, 0.25, and 0.14 ng N m⁻² s⁻¹, respectively, for an entire plant growth period. Compared to previous reported NO fluxes from forests of different regions (see Supplementary Table 2, Supporting Information), our results in the coniferous and broadleaf mixed forest and the coniferous forest is general higher than those in the tropical forest and other temperate forest, but much lower than that in the temperate spruce forest which received high nitrogen input (37). Peculiarly, the high NO flux (up to 214.9 ng N m⁻² s⁻¹, mean 57.5 ng N m⁻² s⁻¹) was observed from a tropical forest by Butterbach-Bahl et al. (51). In this study, our data indicate that the NO emissions decreased with altitude in the entire growth season, whereas those from forest soils are much higher than that from tundra soil and volcanic soil (Figure 4A), suggesting that field NO emissions are much more dependent on soil nitrogen content and nitrogen input (see Figure S3, Supporting Information). Nitrogen deposition as an important controller of soil NO emissions was clearly indicated by Pilegaard et al. (12), who measured soil NO emissions at 15 European forest sites and found significant positive correlations between nitrogen inputs and NO emissions.

FIGURE 4. Seasonal variation of predicted NO fluxes (A), 5 cm soil temperature and average soil moisture in a year (VA, volcanic ash; AT, alpine tundra; EBF, Erman’s birch forest; SF, spruce forest; FF, fir forest; CBF, coniferous and broadleaf mixed forest, data are mean values, and the standard deviation is indicated by an error bar).
of June. Following this period, the NO flux reached a lowest point abruptly by early July because of heavy precipitation, which leads to much higher soil moisture than at the optimum value, and then increased until the middle September since the field soil moisture was closer to the optimum value, and finally decreased with temperature after the peak observed (Figure 4A, B). Consistently, field studies found that the water–carbon content was a very important factor controlling the seasonal patterns of soil NO emissions from ecosystems. For example, Johansson et al. (1988) observed the large increases in NO emission from savannas after small wetting events (<25 mm) following protracted dry periods (52). However, more intensive (<25 mm) wetting events occurring during the wet season appear to inhibit NO emission (41, 53).

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Supporting Information Available

Details on the Changbai Mountain Biosphere Reserve (CMBR) description, calculation methods for NO release, production, consumption and an algorithm for flux, the physical properties of soils and reported NO fluxes from forests of different regions. This material is available free of charge via the Internet at http://pubs.acs.org.

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