Guest Forum

Nitric Oxide Emissions from Soils
— Field and Laboratory Measurements with HORIBA's APNA

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Nitrogen Oxides (NOx) are climate relevant trace gases in the atmosphere and are involved in acidic precipitation as well as in ozone formation and destruction. NOx originates from natural processes like thunderstorms and especially soil microbial activity next to anthropogenic emissions (mainly combustion processes). The gases play a crucial role in soil-atmosphere feedback processes. Our research aims to investigate NOx-emissions from soils under different land use, geographical and meteorological conditions. Such emissions could be quantified in both field and laboratory experiments with a closed static chamber in combination with HORIBA's NOx-analyser APNA-360. The instrument showed its ability to reliably measure nitrogen oxide soil emissions.

窒素酸化物(NOx)は，酸性雨やオゾンの形成と破壊に関わる重要な大気中の微量ガスである。NOxは人為的な排気ガス(主として燃焼過程から)で大気に放出され，その他には雷雨のような自然過程や，特に土壌中微生物活動が原因となって発生する。これらのガスは，土壌-大気のガス成分の循環に重要な役割を果たす。我々の研究は，様々な利用方法，地理的条件，および気象条件下での土地のNOx排出を調査することを目的としている。このような土壌からの放出は，HORIBAのNOx分析器APNA-360を使った閉鎖系によるフィールドおよび試験室両方での実験により定量化が可能である。この測定装置は土壌からの窒素酸化物放出を確実に測定できることを示した。

Introduction

Nitric Oxide (NOx) emissions play an important role in atmospheric sciences. They contribute to acidic precipitation, global warming, ozone formation and destruction.[1] Next to anthropogenic sources such as the combustion of fossil fuels, natural NO-emissions from soils are very important with a global annual rate of about

13–21 Tg N a^{-1}.[2] Due to the high reactivity of NO, related soil emissions are kept within the troposphere; leading to a short atmospheric life time.[3]

NO-emissions from soils are basically regulated by microbial denitrification and nitrification. NO from denitrification is negligible compared with the produced rate from nitrification.[4] Important parameters, further controlling NO soil emissions, are soil humidity, soil temperature and nutrient availability. Since nitrification is governed by aerobic microbes, soils with low Water-Filled Pore Space (WFPS) show higher NO-emissions and increasing temperatures also lead to higher emissions.[5] To determine NO-soil-emissions in the field, mostly "closed dynamic chambers" or "closed static chambers" are used. These methods can measure hourly emission values.[6] Laboratory experiments have been performed next to field experiments to analyse NO-emissions from soils.[7]

We combined field determinations with laboratory experiments. In the field, emissions from different soils under ambient conditions were analysed. The same soils as in the field determinations were used for laboratory experiments. The key objective was to better understand the behaviour of soil emissions under different temperatures as a contribution to regional climate change research. For this study, we used HORIBA's APNA 360 generation in combination with a closed static chamber system. This report provides some important results from soil NO-emission measurements and details about the measurement set up with APNA-analysers.

Materials and Methods

Site Description

The experimental field sites were situated on grassland and in a spruce forest in Saxony, central eastern Germany. The grassland is part of the campus of TU Bergakademie Freiberg in the Erzgebirge foreland (397 m a.s.l.; coordinates: 50°55'30"N, 13°19'52"E; loamy brown soil; avg. annual temperature 7.7 °C; avg. annual precipitation 764 mm a^{-1}, 1961–1990 DWD). The spruce forest site lies close to Oberbärenburg in the upper Erzgebirge on the atmospheric and forest ecosystem research station of TU Bergakademie Freiberg and TU Dresden (740 m a.s.l.; coordinates: 50°47'16"N, 13°43'22"E; loamy podsol; avg. annual temperature 5.5 °C; avg. annual precipitation 996 mm a^{-1}). This site lies about 30 km southeast from the grassland site. The vegetation is dominated by Norway spruce (*Picea abies*). Due to their dense stand, direct sunlight is limited and undergrowth missing. Soil samples for the laboratory experiments were taken at both sites and additionally at an agricultural site north of Freiberg (369 m a.s.l.; coordinates: 50°56'25"N, 13°19'42"E; loamy brown soil).

Experimental Setup

Field experiments

To sample NO emitted by soil, we use acrylic glass chambers with variable volumes, which are installed on the soil. To measure meteorological parameters and to control the influence of the chamber system onto the soil, the chamber is equipped inside and on the outside with sensors for air temperature, air pressure and air humidity. Additionally, a CO_2-sensor (GMP 343, Vaisala, Finland) and sensors for soil temperature und soil humidity can be found inside the chamber (Figure 1). The chamber systems are connected via tubes to the NOx-analyser (HORIBA, model APNA 360, detection limit 2σ: 0.5 ppb_v, reproducibility: ± 1% F.S).

Accumulation time for the emitted gas was 10–30 minutes and was set to fit the measuring range of the NOx-analyser, the volume of the chamber system and the expected emission values. Air from the chamber was pumped into the NOx-analyser after each accumulation interval. Values were averaged, based on 1-minute intervals, over a total time of 5-minutes. Following each data acquisition series, ambient air was pumped into the chamber for five minutes to restore ambient conditions. Thereafter, a new accumulation phase started. Ambient NO-concentrations were determined during this accumulation phase. The measuring flux was rerouted with a commercial magnetic valve. The average value of this measurement was subtracted from the subsequent soil emission measurement.

Laboratory experiments

Laboratory experiments were performed in a climate chamber (VC 4034, Vötsch Industrietechnik, Germany) with soil temperature and air humidity regulation. Disturbed soil samples from the uppermost 10 cm of the soil profile were used for the analysis. The chamber system was placed inside and the NOx-spectrometer outside of the climate chamber. Gas tubes were run through an opening into the climate chamber to take air samples. Soil temperatures were adjusted in a range from ~ 0 to 60 °C, and temperatures increased in 5 K steps to measure emissions. Following each measurement,

Figure 1 Measuring Setup to Analyse NO-Emissions from Soils.[5]
1) pumps to restore ambient conditions in the chamber; 3) acrylic measuring chamber with 2) GMP 343 CO_2-sensor and 4) sensorbox; 5) sampling tube connected to 7) NOx-analyser; 6) magnetic valve to switch between sampling of ambient and chamber air

conditions in the chamber were restored. The NO-concentration value in the climate chamber was subtracted from the NO-value determined in the chamber system.

Results and Discussion

Field Measurements

Meadow

NO-emission values and air temperature values of the eight-day experimental period are shown in Figure 2(a). This period was characterized by zero precipitation and an average air temperature of 17.2 °C. The average NO-emission was 6.1 µg NO-N m^{-2} h^{-1}, with the highest values in the afternoon (maximum 18.3 µg NO-N m^{-2} h^{-1}). The lowest values occurred after midnight and in the early morning (minimum 2.0 µg NO-N m^{-2} h^{-1}). On the seventh day, air temperatures were low in comparison to previous days, and no NO-peak occurred. The following and last day delivered the highest air temperatures, but not the highest NO-emission values, since soil temperatures react delayed on air temperature changes. The highest daily average value occurred on the fourth day (7.6 µg NO-N m^{-2} h^{-1}), and the lowest average value (1.6 µg NO-N m^{-2} h^{-1}) on the second day.

Figure 2(a) shows that NO-emission-values are correlated with air temperature. The Spearman-correlation-coefficient (0.68) delivered a significant positive correlation (slightly exponential) between air temperature and NO-emission. High temperatures lead to high NO-soil emission-values. The relation between both factors was slightly exponential, since NO is produced mainly by nitrification – a temperature-dependent process. Since vegetation had been removed from the measuring plot, obtained NO-emission values are too high. This bias is due to higher warming of the naked soil and decrease of

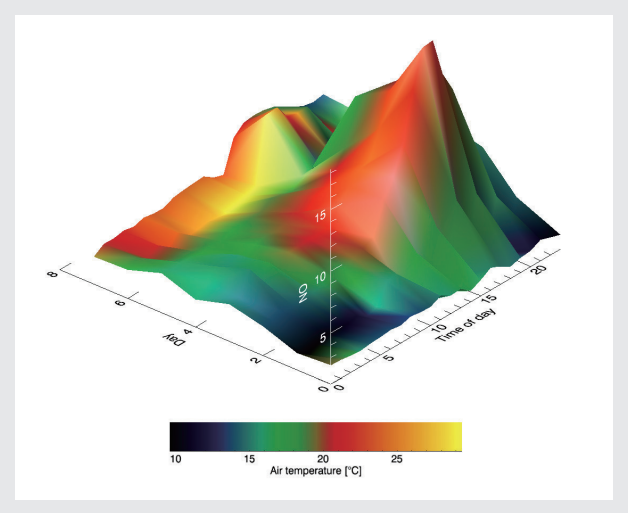

Figure 2(a) Grassland soil NO-degassing in an IDL surface-diagram. X-axis: time of day; Y-axis: measuring day; Z-axis: NO-degassing in µg NO-N m^{-2} h^{-1}. The surface colour of the 3D-object shows air temperature (field experiment)[5]

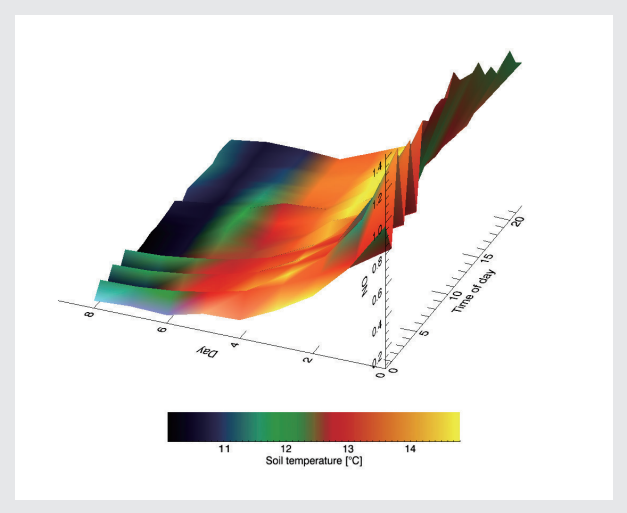

Figure 2(b) Forest soil NO-degassing in an IDL surface-diagram. X-axis: time of day; Y-axis: measuring day; Z-axis: NO-degassing in µg NO-N m^{-2} h^{-1}. The surface colour of the 3D-object shows soil temperature (field experiment)[5]

soil moisture. Both positively influence NO-emission, if soil moisture stays above 10%.[8]

HORIBA's APNA-360 worked very well for these measurements. All values were above the detection limit (~ 0.15 µg NO-N m^{-2} h^{-1}). The noise level of the system (~ 0.3 NO-N m^{-2} h^{-1}) was low enough to clearly distinguish between different emission values.

Forest

Data from the forest site (eight days) are presented in Figure 2(b). The average air temperature was 13.6 °C and the precipitation sum 72.5 mm. The largest precipitation amount (49.5 mm) occurred during the seventh day. No effect of this event onto NO-emissions was observed, since soil moisture already increased up to field capacity after a 28.5 mm precipitation event one day before the NO-measuring period. Soil temperatures decreased (ΔT~ 2 K) as of the first day, and so did NO-values. Minor changes of NO-emissions occurred during the day. These small changes were below the resolution of the detection system. Consequently, the highest NO-values were determined in the first days (maximum 1.5 µg NO-N m^{-2} h^{-1} and maximum average day-time value 1.3 µg NO-N m^{-2} h^{-1}). The minimum values occurred after a continuous decrease during the last days and were below the detection limit of the system, just like the lowest average day-time value. A significant positive correlation between NO-emissions and soil temperature (Spearman correlation 0.47) and a smaller one between NO-emissions and air temperature (Spearman correlation 0.22) were found. No significant correlation between NO-emissions and precipitation can be shown. The low soil temperature changes explain that no exponential correlation between NO-emissions and soil temperature could be found.

Different behaviour of NO-soil emissions at Oberbärenburg, as compared with the grassland measurements in Freiberg were caused by the dense vegetation cover at this site. Solar radiation is inhibited to penetrate to the soil and only small diurnal variations of the soil temperatures (1–2 K) could occur, leading to small daily variations in soil NO-emissions. The lower average temperatures accompanied with continuous small rain events in Oberbärenburg, explainable with the different orography, lead to the clearly lower daily average values of NO-emissions in comparison to the grassland in Freiberg. Very low NO-emissions at this spruce forest site could not be detected. This problem can be solved with longer accumulation times. However, the use of HORIBA's APNA-generation is suitable for spruce forest sites too, since German spruce forests deliver an average value of 1.3–608.9 µg NO-N m^{-2} h^{-1}.[9] This range can be easily detected with APNA measurement system.

Laboratory experiments

Disturbed soil samples from an agricultural site, a grassland and a forest were analysed in a climate chamber (Figure 3(a)-(c)). Strong exponential correlations with highly significant correlation R-squares (agricultural soil: 0.99; grassland: 0.93; forest: 0.95) were observed for all three soil types between NO-emissions and temperature and were much higher than for field measurements. In the agricultural soil, a temperature increase from 10 to 50 °C led to 15 times higher NO-emissions. A strong NO-emission increase started at a soil temperature of about 30

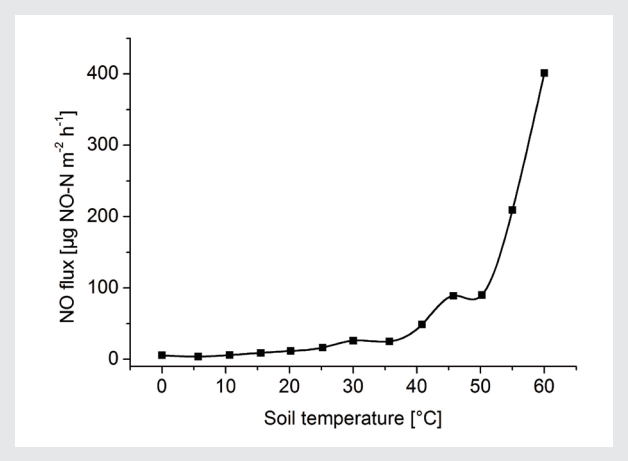

Figure 3(a) Agricultural soil NO-Eissions (climate chamber experiment)[5]

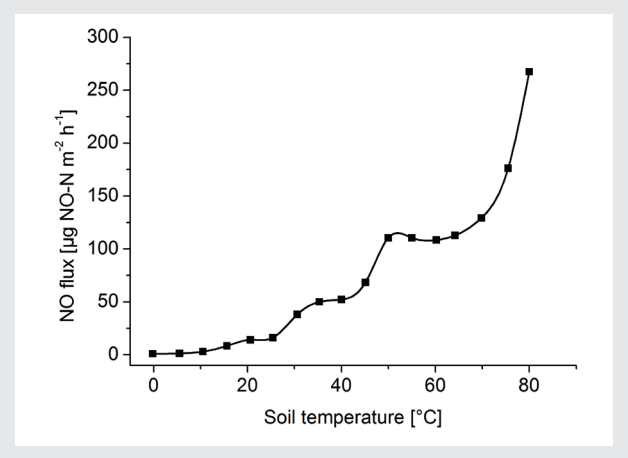

Figure 3(b) Grassland soil NO-Eissions (climate chamber experiment)[5]

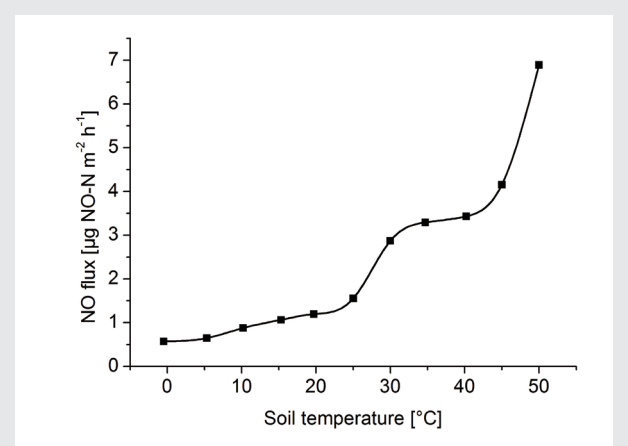

Figure 3(c) Forest soil NO-Eissions (climate chamber experiment)[5]

°C. Temperature changes below 30 °C had little influence on soil emission, in full agreement with the field experiments at Oberbärenburg. The exponential growth is interrupted at two points for each curve. There, NO-emissions do not follow the soil temperature increase. This can be explained by the nitrification driven by different groups of bacteria, which all have different temperature optima. The temperature optimum of five bacterial groups ends at a temperature of 30 °C.[10] A first plateau of NO-emission occurred at about 30 °C for all three samples. The remaining bacterial groups cannot increase soil emissions. Above soil temperatures of 40 °C, NO-emissions were strongly increasing again. This strong increase could be a result of chemo-denitrification. Urease activity is also supposed to be responsible for high NO-emission values at high soil temperatures. Urease decomposes urea to ammonium. Since ammonium is a precursor of nitrification, high urease activity can lead to higher NO-emissions. The temperature optimum of urease is about 70 °C. Accordingly more ammonium is formed at high soil temperatures.

The highest NO-emission was found at soil temperatures above 60 °C; an unrealistic value even for dark soils of this climate zone. The highest values occurred with the agricultural soil (maximum values above 400 µg NO-N m^{-2} h^{-1}), followed by the grassland. The lowest values were found for the forest soil. For a soil temperature of 40 °C, an average sequence emerged: agricultural soil 49 µg NO-N m^{-2} h^{-1}; grassland soil 14 µg NO-N m^{-2} h^{-1}, and forest soil 3 µg NO-N m^{-2} h^{-1}. Measured NO-values seem to overestimate the true soil response due to disturbed soil samples and low soil humidity in the climate chamber. In consequence, higher NO-emissions result from better aeration. NO-emission values for the agricultural soil should be most realistic, since plant cover is low and the management practices can lead to similarly disturbed soil. In general, measurements of NO-emissions under laboratory conditions seem to be more comparable with natural conditions in comparison with laboratory experiments for soil emissions of CO_2 or N_2O, since NO is mainly produced in the uppermost centimetres of the soil cover.[11] (Figure 3(d))

All NO-emission values, even for low soil temperatures, of the climate chamber measurements were above the detection limit of the APNA-measurement system. Since NO-values were generally higher than values for field experiments, the APNA-analyser is well suitable for these measurements. It has to be mentioned, that air samples have to be dried for the climate chamber measurements, since high temperature gradients can occur between climate chamber and outside, where the NOx-analyser is

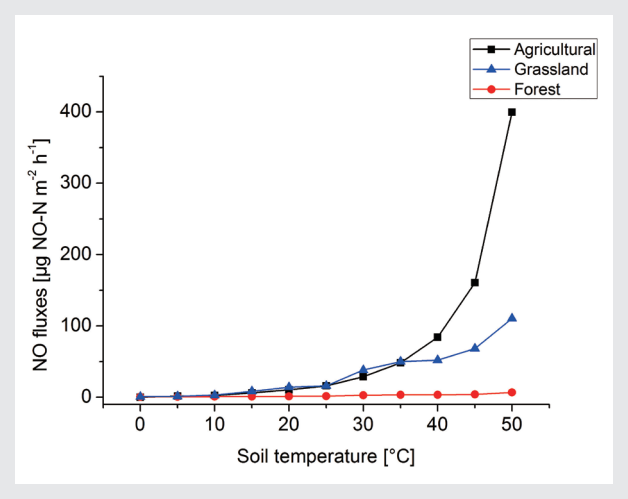

Figure 3(d) Comparison of the degassing responses from agricultural, forest and grassland soils from Figure 2(a)-(c) (climate chamber experiments) measured with APNA-360[5]

placed. Without drying, water may form through condensation and get into the NOx-analyser.

Conclusions

In combination with chamber systems HORIBA APNA-analysers are a sensitive tool to measure NO-emissions from soils. Excluding very low NO concentrations, which are not relevant for global budgets, the system could detect the soil emissions very well and has showed a fine cost-performance ratio. Further development of our automatic chamber systems will improve detection of NO-emissions from soils. Accordingly the quality of global and regional estimations of NO-emissions from soils could be further improved.

Acknowledgments

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