

Introduction

NO_x is a main precursor for tropospheric O₃ and a key substance determining the oxidative capacity of the atmosphere. Soil NO emissions, contributing 15–20% to the global atmospheric NO_x budget (IPCC, 2007), are the result of biogenic, mostly microbial, biochemical and physicochemical N cycling processes. It is known that NO emissions from soils are the result of simultaneously occurring production and consumption processes (Medinets *et al.*, 2015). Several studies showed that NO emitted from soils mainly originate from the topmost centimetres and that NO produced in deeper soil layers might be consumed during upward diffusion. However, information on NO concentrations and profiles of NO concentrations in soils is extremely scarce and to our knowledge limited to the works of Gut *et al.* (1998, 1999, 2002).

The aim of this study is to elucidate the seasonal dynamics of soil NO concentrations by continuous measurements over a 15 months period along a soil depth profile down to 65 cm.

Materials and Methods

The study was carried out at the Höglwald Forest (HGW) research site (48°30'N 11°11'E, 540 m a.s.l.) exposed to high atmospheric nitrogen (N) deposition (20–30 kg N ha⁻¹ yr⁻¹) (Butterbach-Bahl *et al.*, 1997, 2002). Soil gas concentrations of NO and CO₂ were continuously measured at five soil depths (Fig. 1) using gas permeable hydrophobic polypropylene membrane tubes (Accurel® PP V8/2, Akzo Nobel Faser AG, Germany) with an inner diameter of 5.5 mm, a wall thickness of 1.55 mm and a nominal pore size of 0.2 μm. For the installation of the membrane tubes in the field a central square shape pit and three trenches were dug in the forest soil, leaving three undisturbed soil profiles of 1 m width between the openings (Fig. 2).

Fig. 1 Depth of sampling lines

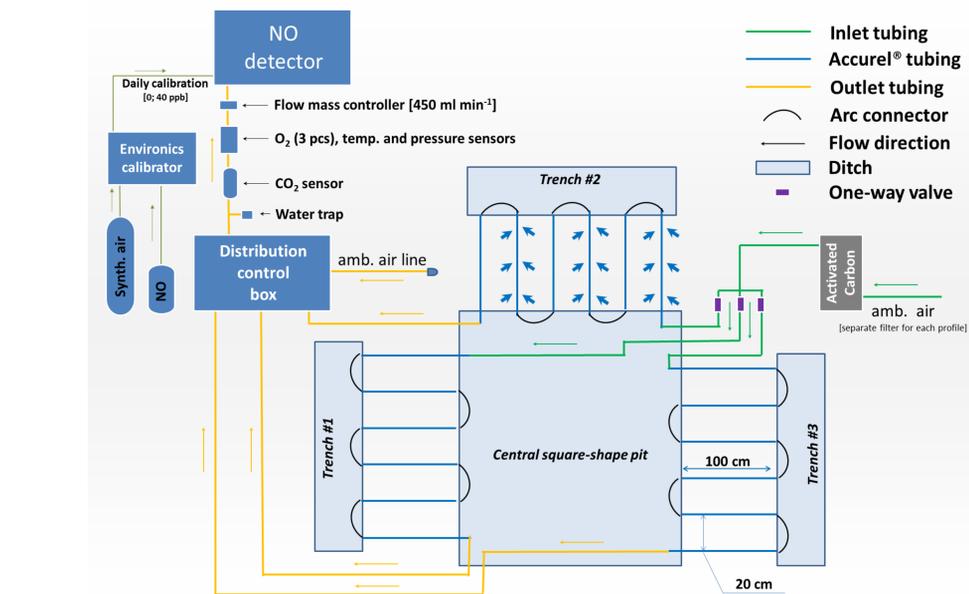


Fig. 2 Schematic diagram of the experimental layout [only 1 depth sampling line per profile is shown]

Our system sucked every two hours sampling air at a constant rate of 450 mL min⁻¹ for 5 min out of the sampling lines, and thus also out of the membranes, thereby replacing the sampling air with conditioned ambient air, as the inlet air was passed through a filter with activated carbon (see Fig. 2). This was in contrast to Gut *et al.* (1998) and Parent *et al.* (2013) who measure soil gas concentrations in circulated sampling air between the analyzers and the membranes in the soil profiles.

Those measurements were accompanied by continuous soil-atmosphere NO flux measurements using a dynamic chamber approach (Butterbach-Bahl *et al.*, 1997; Medinets *et al.*, 2016a,b).

Results

The highest soil NO concentrations, as well as soil surface NO fluxes, were observed during summer times, specifically following rainfall events, which were re-wetting at least the surface soil (Fig. 3). Mean NO concentrations (in ppbv) from background air via soil surface down to -65 cm differed significantly and ranked as follows:



The annual mean emission observed within April 1, 2015 – March 31, 2016 was 63.0±0.6 μg NO-N m⁻² h⁻¹.

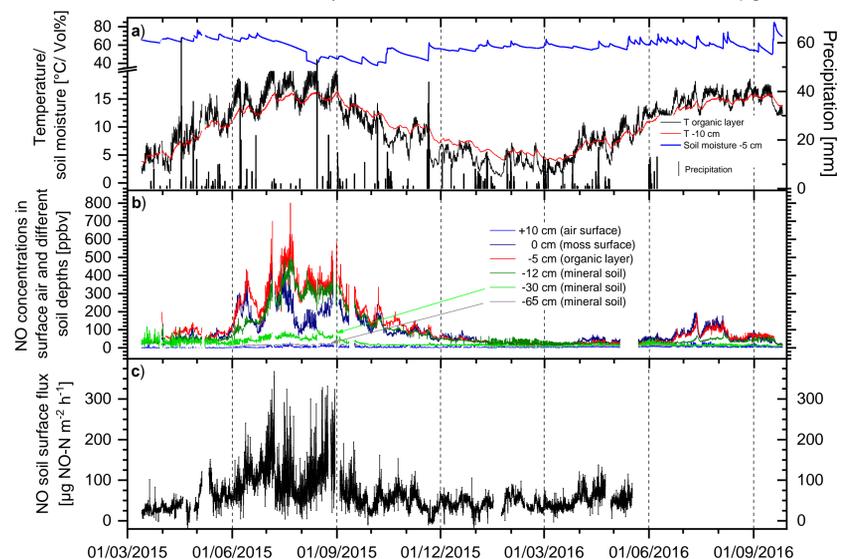


Fig. 3 Temporal variability (bi-hourly data) of air and soil temperatures, soil moisture (-5 cm) and rainfall (a), NO concentrations in surface air and different soil depths (b), and soil surface NO (c)

Stratifying observational data in three temperature classes using the organic layer temperature as parameter (as that layer showed highest NO concentrations) shows that at temperatures <5°C mean NO concentrations in different soil layers (surface down to -65 cm) range from 6.4 to 33.4 ppbv, while for temperatures >15°C mean NO concentrations varied within a range of 16.3 – 370.5 ppbv (Fig. 4a).

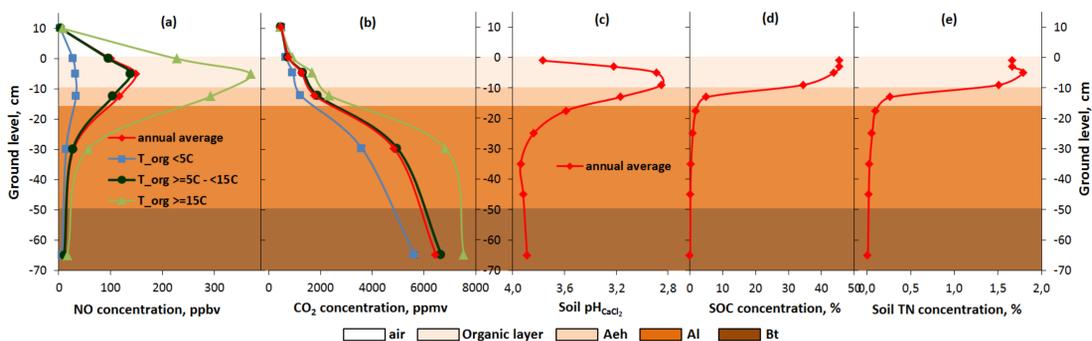


Fig. 4 Mean NO (a), CO₂ (b), soil organic carbon (d) and soil total N (e) concentrations and pH (c) in various soil depths for annual period and periods with organic layer temperature <5°C, 5–15°C or >15°C (April 1, 2015 – March 31, 2016) [(c), (d) and (e) data taken from Kreuzer and Weiss (1998)]

Discussion

The observed vertical profile of NO concentrations in our study, with maximum concentrations (up to 800 ppbv) in -5 cm soil depth (Fig. 3b, Fig. 4a) agree very well with measured rates of NO production under aerobic or anaerobic conditions (data not shown). Those rates were much higher (up to 1500±98 ng NO-N g⁻¹ SDW under anaerobic and 371±19 ng NO-N g⁻¹ SDW under aerobic incubation) in the acidic organic layer (Fig. 4c) with high content of TN and SOC (Fig. 4d,e). Our findings are also in agreement with Gut *et al.* (1998) who showed similar pattern of concentration declining with the depth (from 2 to 25 cm). Concentration values that we found in this study are comparable to observations by Gut *et al.* (2002) who reported that over a one month measuring period at a tropical forest site in Brazil soil NO concentrations varied in a range of 20–460 ppbv (3 cm soil depth), and Dong *et al.* (2016), who measured NO concentration of 127–145 ppbv (0–10 cm soil depths) during summer months for 10 forest stands

planted with spruce/ beech in SW Germany. In our study soil NO concentrations were closely correlated to soil surface NO fluxes (Fig. 5b,c) and soil surface NO fluxes were closely correlated to the organic layer temperature (Fig. 5a). Also, soil NO fluxes were closely linearly correlated to soil CO₂ concentrations in upper soil layers (e.g. in organic layer; Fig. 5d), indicating a close coupling of organic mineralisation activity and NO production, with both being stimulated by increasing temperature (Schindlbacher *et al.*, 2004; Medinets *et al.*, 2016b). Soil moisture was a weak predictor of soil NO concentrations ($r^2 = 0.032$, $p < 0.001$; data not shown) as well as for NO fluxes (excepting short-term rewetting events in summertime), which is in agreement with previous studies (Kim *et al.*, 2012; Medinets *et al.*, 2015, 2016a; Leitner *et al.*, 2017).

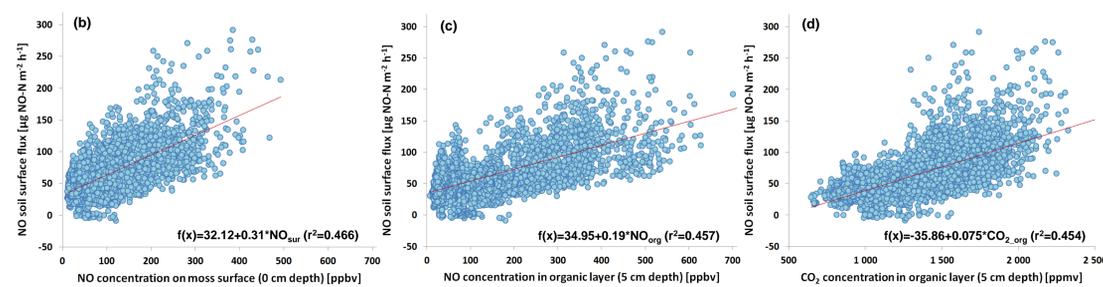


Fig. 5 Correlation between soil temperature in organic layer (a), soil NO concentrations on moss surface (b) and in -5 cm organic layer (c), soil CO₂ concentration in -5 cm organic layer (d) and soil surface NO fluxes

High annual cumulative emission of 5.5 kg NO-N ha⁻¹ yr⁻¹ observed in this study (during April 1, 2015 to March 31, 2016) was a result of excessive NO production in moss, organic and mineral topsoil layers (Fig. 3b,c). These high NO fluxes are mainly owing to the high rates of atmospheric N deposition (>20 kg N ha⁻¹ yr⁻¹), which by far exceed the N demand of the spruce stand (Kreutzer *et al.*, 2009), and the acidic soil conditions, specifically of the organic layer (Fig. 4c), which favours the release of NO during nitrification and chemodenitrification (Kesik *et al.*, 2006).

Conclusion

- This study is the first reporting on high temporal measurements of soil NO concentrations profiles in a temperate spruce forest over 15 months period showing distinctive seasonal variability
- Soil NO concentrations are closely linked to soil surface fluxes, and that NO production is highest in the organic layer
- Temperature was determined as the main driver triggering NO production within the soil and NO emission from the soil
- Annual NO concentration level across the soil profile was strongly depending on soil pH
- The importance of such high NO concentrations for soil microbial and plant physiological processes remains unclear, but should be addressed in future research in order to improve our understanding of microbe-microbe and plant-microbe interactions and the role(s) NO is playing for ecosystem functioning and C and N cycling