Nitrogen load and forest type determine the soil emission of nitrogen oxides (NO and N₂O)

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Emission of NO and N$_2$O from forest soils

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Abstract

Soil emissions of NO and N\textsubscript{2}O were measured continuously at high frequency for more than one year at 15 European forest sites as part of the EU-funded project NOFRETETE. The locations represent different forest types (coniferous/deciduous) and different nitrogen loads. Geographically they range from Finland in the north to Italy in the south and from Hungary in the east to Scotland in the west.

The highest NO emissions were observed from coniferous forests, whereas the lowest NO emissions were observed from deciduous forests. The NO emissions from coniferous forests were highly correlated with N-deposition. The site with the highest average annual emission (82 \( \mu \text{g NO-N m}^{-2} \text{h}^{-1} \)) was a spruce forest in South-Germany (Höglwald) receiving an annual N-deposition of 2.9 g m\(^{-2}\). NO emissions close to the detection limit were observed from a pine forest in Finland where the N-deposition was 0.2 g N m\(^{-2}\) y\(^{-1}\). No significant correlation between N\textsubscript{2}O emission and N-deposition was found. The highest average annual N\textsubscript{2}O emission (20 \( \mu \text{g N}_2\text{O-N m}^{-2} \text{h}^{-1} \)) was found in an oak forest in the Mátra mountains (Hungary) receiving an annual N-deposition of 1.6 g m\(^{-2}\). N\textsubscript{2}O emission was significantly negatively correlated with the C/N ratio.

The difference in N-oxide emissions from soils of coniferous and deciduous forests may partly be explained by differences in N-deposition rates and partly by difference in characteristics of the litter layer and soil. NO was mainly derived from nitrification whereas N\textsubscript{2}O was mainly derived from denitrification. In general, soil moisture is lower at coniferous sites (at least during spring time) and the litter layer of coniferous forests is thick and well aerated favouring nitrification and thus release of NO. Conversely, the higher rates of denitrification in deciduous forests due to a compact and moist litter layer lead to N\textsubscript{2}O production and NO consumption in the soil.

The two factors soil moisture and soil temperature are often explaining most of the temporal variation within a site. When comparing annual emissions on a regional scale, however, factors such as nitrogen deposition and forest and soil type become much
1 Introduction

Increasing emissions of N-oxides from combustion processes and NH$_3$-volatilisation from agriculture have led to an increase of N-deposition in Europe during the last decades. Atmospheric N-deposition is estimated to be at least 0.5 g N m$^{-2}$ y$^{-1}$ in most parts of Europe, in central Europe significantly above 2 g N m$^{-2}$ y$^{-1}$ (Umweltbundesamt, 1997), and in The Netherlands, parts of Northern Germany, and UK up to 5 g N m$^{-2}$ y$^{-1}$ (e.g. van der Eerden et al., 1998). As a result, natural ecosystems, especially forests which have a huge filtering capacity, receive an N-fertilization equivalent to approx. 15% of N-fertilizer input to arable land (Kristensen et al., 2004). Due to this high atmospheric N-deposition the N-status of forest ecosystems is changing from naturally N-limited to N-saturated (Aber et al., 1989; Dise and Wright, 1995; Fenn et al., 1998). Nitrogen saturation of forest ecosystems has serious environmental consequences by changing the soil chemistry, forest composition and productivity, and by altering the fluxes of radiatively active trace gases (e.g. NO, N$_2$O, CO$_2$, CH$_4$) (Aber, 1992; Butterbach-Bahl et al., 1997; Priha and Smolander, 1995). The improved N-availability in forest soils has been shown to reduce C/N-ratios in leaves and litter (Magill et al., 1997) and, at least initially, has stimulated tree growth and forest productivity (Beck, 1996). Increased atmospheric N-deposition is a matter of concern, as it can change the ground vegetation (increasing dominance of nitrophilic species) (e.g. Hofmann, 1995; Pitcairn et al., 2002); decrease forest vitality (induction of nutrient imbalances) (e.g. Schulze, 1989); accelerate soil acidification due to increased nitrification (e.g. Kreutzer and Weiss, 1998); and increase losses of N to the environment in form of N-leaching to the groundwater (e.g. Kreutzer, 1995) and/or in form of N-gas emissions (N$_2$O, NO, N$_2$) into the atmosphere (e.g. Butterbach-Bahl et al., 1997; Pilegaard et al., 1999; van Dijk and Duyzer, 1999; Skiba et al., 1998).

Oxidised nitrogen compounds in the atmosphere such as nitrous oxide (N$_2$O), nitric
oxide (NO) and nitrogen dioxide (NO₂) play an important role by affecting the oxidising capacity of the troposphere (NO and NO₂), by affecting ecosystems through deposition (NO₂ and derivates) or by acting as a greenhouse gas (N₂O).

Forests cover a large part of the European continent (approx. 35%), but the exchange of nitrogen oxides (NO, N₂O and NO₂) has so far only been investigated in a few European forests. These studies in N-affected forests in Central (Butterbach-Bahl et al., 1997; van Dijk and Duyzer, 1999; Brumme and Beese, 1992; Gasche and Papen, 1999) and Northern Europe (Pilegaard et al., 1999; Skiba et al., 1998) have shown that European forests have a much higher NO and N₂O emission than other temperate forests in the world (Williams et al., 1992; Castro et al., 1993). It has been suggested that the high emissions found in European forests are due to the high atmospheric N-input to these forests. The contribution of oxidised and reduced nitrogen species to the total deposition varies according to location, and is dominated by NH₃ in intensively farmed countries (e.g. The Netherlands), but by oxidised species in the remote parts of Europe. Comparing earlier results from forest sites with different N-input and studies of NO and N₂O emission at various distances from poultry and pig farms support this hypothesis (Skiba et al., 1998).

The limited information on the impact of anthropogenic influences like e.g. atmospheric N-deposition on N-trace gas emissions from forest soils, the limited number of field studies, restricted temporal coverage of field measurements and the lack of information on the effect of forest types on the magnitude of N-oxides emissions from forest ecosystems are the reasons why the contribution of forest ecosystems to regional and global budgets of atmospheric N₂O and NO still have a high degree of uncertainty.

NO and N₂O emissions are known to vary considerably with both soil temperature and soil moisture and are therefore strong functions of climate (Smith et al., 1998; Pilegaard et al., 2001). However, the relationships are not simple and not the same for NO and N₂O. It is therefore important to study these relationships over a range of climates at long time-scales to cover different seasons for each locality.

In this paper we report the results of continuous measurements of NO and N₂O
emissions at 15 different forest sites as part of the EU-funded project NOFRETETE. The measurements were made by chamber methods, either by manual measurements or by fully automated systems at a high frequency (up to hourly) throughout at least an entire year. Emission measurements were carried out using either the dynamic (NO) or the static chamber (N\textsubscript{2}O) technique. The locations chosen include different types of forests (coniferous and deciduous) in different European climates, ranging from boreal to temperate continental forests and from Atlantic to Mediterranean forests. Furthermore the sites differ in atmospheric N-deposition ranging from low deposition (0.2 g N m\textsuperscript{-2} y\textsuperscript{-1}) to high deposition (4 g N m\textsuperscript{-2} y\textsuperscript{-1}). We relate annual emissions of NO and N\textsubscript{2}O to the main parameters soil temperature, soil moisture, C/N ratio, pH, nitrogen deposition, and stand age. Temporal variation throughout the year is not dealt with here, but will be treated in site-specific papers (e.g. Ferré et al., 2005; Horváth et al., 2005; Kitzler et al., 2005a,b; Rosenkranz et al., 2006).

2 Materials and methods

2.1 Sites

An overview of the 15 forest sites is given in Table 1 and Fig. 1 and some characteristics of the sites is given in Table 2. The sites range from Finland in the north to Italy in the south and from Scotland in the west to Hungary in the east. The sites investigated represent different forest types:

Coniferous forests: Scots pine (Pinus silvestris), Finland; Sitka spruce (Picea sitchensis), Scotland; Norway spruce (Picea abies), Germany, Austria, Hungary; Douglas fir (Pseudotsuga menziesii viridis), The Netherlands; Mediterranean pine (Pinus pinaster), Italy.

Deciduous forests: birch (Betula pubescens), Scotland; beech (Fagus sylvatica), Denmark, Germany, Austria; sessile oak (Quercus petraea), Hungary; poplar (Populus sp.), Italy; mixed forest with black poplar (Populus nigra), aspen (Populus tremuloides),
white willow (*Salix alba*), and common alder (*Alnus glutinosa*), Italy.

At three locations, Glencorse (Scotland), Hölwald (Germany), and Mátra mountains (Hungary) both coniferous and deciduous forest sites were investigated.

### 2.2 Flux measurements

The soil emissions of NO and N\textsubscript{2}O were measured with the chamber technique (e.g. Butterbach-Bahl et al., 1997; Pilegaard et al., 1999; van Dijk and Duyzer, 1999). NO was measured with dynamic chambers and the flux was estimated by comparing the steady-state concentration in the chamber with a reference measurement or by using the full mass balance equation (Altimir et al., 2002). In some cases the reference measurement was made in a chamber similar to the measurement chambers but shielded from the soil with a cover of the same material; in other cases the reference measurement was made of the incoming ambient air and corrections for wall losses in chamber and tubes were made. NO was analysed by chemiluminescence technique. Because O\textsubscript{3} interacts with the NO emitted from the soil it was analysed simultaneously and any loss of NO due to this reaction was corrected for (Remde et al., 1993). N\textsubscript{2}O was measured using manual and/or automatic static chambers. Headspace N\textsubscript{2}O concentrations were analysed by gas chromatography (electron capture detector) either in the field or in the laboratory.

Characteristics of the chamber systems applied for flux measurements at the different sites are given for NO in Table 3 and for N\textsubscript{2}O in Table 4. The use of a reference chamber is indicated by “+1” in the column giving the number of chambers simultaneously in use. The chambers were mounted on frames previously inserted into the soil. At some sites chambers were moved among different sets of frames, indicated in Tables 3 and 4 by a larger number of frames than chambers. The tables give references to the specific methods applied at each site.
2.3 Additional measurements

Nitrogen deposition was measured by analysing concentrations of NO$_3^-$ and NH$_4^+$ in throughfall collected with a large number of funnels or with specially designed throughfall collectors. In deciduous forests stem-flow was also collected and analysed for NO$_3^-$ and NH$_4^+$ concentrations and the values were added to the throughfall to give the input to the forest floor. Soil moisture was measured by TDR probes and soil temperature by thermocouples. C/N ratio, pH, and bulk density (for calculation of water filled pore space, WFPS) was measured in the upper 0–5 cm of the mineral soil.

2.4 Data analysis

The relationships between fluxes and the main parameters were investigated by stepwise multiple regression analysis using the S-PLUS statistical software (Insightful Corp.).

3 Results

The annual average emissions of NO (Table 5) ranged from below detection limit to 81.7 µg N m$^{-2}$ h$^{-1}$. The highest emissions were found in the Högwald spruce forest followed by the Speulderbos Douglas fir forest (75.2 µg N m$^{-2}$ h$^{-1}$) and the lowest in the Hyytiälä Scots pine forest (0.006 µg N m$^{-2}$ h$^{-1}$) and the Parco Ticino mixed forest (below detection limit). Emissions of N$_2$O ranged from 0.3 to 20.3 µg N m$^{-2}$ h$^{-1}$ with the highest values found in the oak forest in the Mátra mountains followed by the Parco Ticino poplar forest (19.7 µg N m$^{-2}$ h$^{-1}$) and the lowest values in Hyytiälä, San Rossore (2.1 µg N m$^{-2}$ h$^{-1}$) and Speulderbos (2.3 µg N m$^{-2}$ h$^{-1}$).

Atmospheric nitrogen deposition at the 15 field sites investigated ranged between 0.22 g m$^{-2}$ y$^{-1}$ and 3.85 g m$^{-2}$ y$^{-1}$ with the highest value for the Speulderbos forest in The Netherlands and the lowest value for the Hyytiälä forest in Finland (Ta-
ble 5). The average nitrogen deposition to coniferous forests (1.6±0.5 g N m⁻² y⁻¹) was similar to deciduous forests (1.5±0.2 g N m⁻² y⁻¹). On average coniferous forests showed much higher emission of NO (31.0±15.6 µg N m⁻² h⁻¹) than deciduous forests (4.1±1.9 µg N m⁻² h⁻¹). For N₂O it was found that the deciduous forests had higher emission (11.3±2.2 µg N m⁻² h⁻¹) than the coniferous forests (6.6±2.3 µg N m⁻² h⁻¹).

The results of the regression analyses of the emissions of NO and N₂O, the sum of NO and N₂O and the ratio between NO and N₂O with the parameters nitrogen deposition, forest type, age, C/N, pH, soil temperature and WFPS are given in Table 6. In analyses of NO emission, values from the Italian sites were excluded, because of the very few measurements from these sites. NO emission was dependent on forest type and positively correlated with nitrogen deposition. The parameter WFPS was tested for curvature by including a quadratic term, but this was not significant. Separately performed regression analyses for deciduous and coniferous forests showed, however, that the relationship between nitrogen deposition and NO emission was only significant for the coniferous forests (NO (µg N m⁻² h⁻¹)=−13.9+25.5° [N deposition (g m⁻² y⁻¹)], r²=0.82). The relationships between NO emission and N deposition are shown in Fig. 2.

The N₂O emission was significantly negatively correlated with both the C/N ratio and the age of the stands (Table 6 and Fig. 3); a logarithmic transformation of N₂O emission improved the significance of the correlation. There was no significant correlation between the N₂O emission and the nitrogen deposition (Fig. 4).

The sum of NO and N₂O was positively correlated with nitrogen deposition (Fig. 5) although when split into forest types only for the coniferous stands (Table 6). The amount of N-oxides emitted relative to total N deposition ranged from 2% (Hyytiälä) to 32% (Glencorse spruce). The ratio was not significantly correlated with any of the investigated parameters.

The NO/N₂O ratio was positively correlated with nitrogen deposition and C/N ratio and negatively correlated with age of the stands.

The relationship between pH and nitrogen deposition (Fig. 6) shows that in general
a low pH was associated with high nitrogen deposition, but pH was not found to be a significant parameter for N oxides emission.

At three locations (Glencorse, Höglwald and Mátra mountains) both deciduous and coniferous forests were investigated. At Glencorse and Höglwald the coniferous sites had higher N deposition as compared to the deciduous sites. In addition, NO emission was highest at coniferous sites at both locations, whereas N$_2$O emission was highest at the spruce site in Glencorse, but lowest at the spruce site in Höglwald. The differences in both deposition and NO emission between the two forests in the Mátra mountains were much smaller whereas the difference in the magnitude of N$_2$O emission between the two sites was substantial (Table 5) with the oak site having the highest emission.

4 Discussion

4.1 Effects of soil moisture and temperature

Production of NO and N$_2$O in soils is primarily driven by microbial processes such as nitrification and denitrification (Firestone and Davidson, 1989), therefore soil temperature is a key variable affecting the emission rates of both gases. Emissions of both NO (Slemr and Seiler, 1984) and N$_2$O (Skiba et al., 1998; Smith et al., 1998) increase with increasing soil temperature due to the fact that rates of enzymatic processes generally increase with temperature as long as other factors (e.g. substrate or moisture) are not limiting. Soil water acts as a transport medium for NO$_3^-$ and NH$_4^+$ and influences the rate of O$_2$ supply and thereby controls whether aerobic processes such as nitrification or anaerobic processes such as denitrification dominate within the soil. While N$_2$O emissions are known to increase at higher water contents through larger losses from denitrification (Wolf and Russow, 2000; Papen and Butterbach-Bahl, 1999) the relationship between the NO flux and the soil water is more complex. Due to limited substrate diffusion at very low water content and limited gas diffusion at high water content, nitric oxide emissions are suspected to have a maximum at low to medium
soil water content. Ludwig et al. (2001) suggested an optimum of NO emissions at approximately 20% WFPS and a strong decrease towards extreme moisture conditions. However, other studies reported maximum NO fluxes between 43% and 85% WFPS (Ormeci et al., 1999; van Dijk and Duyzer, 1999; Gasche and Papen, 1999).

The effects of soil moisture and temperature on NO and N\textsubscript{2}O emission were studied in a laboratory experiment with soil cores from some of the same field sites as in the present study (Parco Ticino(M), Schottenwald, Klausen-Leopoldsdorf, Achenkirch, H"ogwald (spruce) and Hyyti"al"a) (Schindlbacher et al., 2004). Soil moisture and temperature explained most of the variations in NO (up to 74%) and N\textsubscript{2}O (up to 86%) emissions for individual soils. NO and N\textsubscript{2}O were emitted from all soils except from the boreal pine forest soil in Finland, where the laboratory experiment showed that NO was consumed. NO emissions from the German spruce forest ranged from 1.3 to 608.9 µg NO-N m\textsuperscript{-2} h\textsuperscript{-1} and largely exceeded emissions from other soils. Average N\textsubscript{2}O emissions from this soil tended also to be highest (171.7±42.2 µg N\textsubscript{2}O-N m\textsuperscript{-2} h\textsuperscript{-1}), but did not differ significantly from other soils. NO and N\textsubscript{2}O emissions showed a positive exponential relationship to soil temperature. The results from the annual averages of field data did not show any significant relationship to soil temperature for neither for NO nor for N\textsubscript{2}O emission.

Schindlbacher et al. (2004) also showed that N\textsubscript{2}O emissions increased with increasing WFPS or decreasing water tension, respectively. Maximum N\textsubscript{2}O emissions were measured between 80 and 95% WFPS or 0 kPa water tension. The optimal moisture for NO emission differed significantly between the soils, and ranged between 15% WFPS in sandy Italian floodplain soil and 65% in loamy Austrian beech forest soils. For the field data WFPS was not a significant parameter for N\textsubscript{2}O emission, but had a positive significant effect on NO emission. The annual average WFPS in the field was higher than the optima found for NO in the laboratory experiment, but since not all field sites were studied in the laboratory it is difficult to provide a general conclusion.

In general, rather clear relationships between nitrogen oxides emission and soil moisture and soil temperature can be found within a single locality when studying short-
term variations. However, using the same parameters when comparing annual values from different localities within a large region as in this study does not necessarily reveal comparable relationships since other factors such as soil properties, stand age, and site hydrological conditions interfere. Equally, in a study of 18 European forests Janssens et al. (2001) found large differences in observed annual soil respiration and total ecosystem respiration, but despite good correlations with temperature within the single forests, the differences between the forests were not correlated with mean annual temperature. They hypothesised that differences in soil respiration among forests are likely to depend more on forest productivity rather than on temperature.

The question of whether predictive understanding of N₂O fluxes can be increased by examining relationships between fluxes and environmental parameters at larger spatial and temporal scales was also addressed by Groffman et al. (2000). They compared relationships between annual rather than hourly or daily fluxes and ecosystem-scale variables such as plant community and soil type and annual climate rather than field-scale variables such as soil moisture and temperature. They found that there were coherent patterns in annual N₂O flux at the ecosystem scale in forest, cropland, and rangeland ecosystems but that ecosystem-scale controls of N₂O flux vary within and between regions and only emerge with continuous (at least daily) flux measurements over multiple years.

4.2 Effects of C/N ratio and pH

This study showed a significant negative correlation between N₂O emission and the C/N ratio (Fig. 3). This is in accordance with the laboratory studies by Ambus et al. (2006). No significant effects of pH could be found, but there was a (non significant) negative correlation between pH and nitrogen input (Fig. 6), which could be due to the acidifying effect of NH₄⁺ in soil. Consistently, the sites with high NO emission also had a low pH (Speulderbos, Höglwald), but a low pH in itself did not seem to lead to high emission (Hyytiälä).
Klemedtsson et al. (2005) found a strong negative relationship between N₂O emissions and soil C/N ratios in forested histosols in Sweden. A decaying exponential equation could describe the relationship and was validated with published data from similar sites in Finland and Germany. They found that at low C/N ratios below 15–20 other parameters such as climate, pH and groundwater tables increase in importance as predictors for N₂O emission. A similar negative relationship was found between net nitrification and C/N ratio in spruce and beech forests throughout Europe (Persson et al., 2000). In the study it was also found that no net nitrification could be detected when the C/N ratio exceeded 28 which is consistent with the low emissions found from the soils in San Rossore and Hyytiäälä.

4.3 Effects of increased N-input

This study showed significant positive correlations between input of nitrogen to forests and NO emission (Fig. 2) and the sum of NO and N₂O (Fig. 5), but no significant relationship for N₂O (Fig. 4). Clear relationships have been reported previously when comparing the temporal variation in nitrogen deposition at a single site by e.g. Butterbach-Bahl et al. (1997). However, increased nitrogen input does not always lead to enhanced microbial activity. In an experiment with chronic N additions to forest ecosystems (Burton et al., 2004) it was found that soil N availability was enhanced, but after an initial increase soil respiration was reduced probably due to reduced decomposition activity of the microbial community.

The N₂O emission from Speulderbos was very low considering the high nitrogen input (Fig. 4). This can, however, be explained by the very low N-mineralisation and nitrification rate of this soil (Ambus et al., 2006), which is probably due to the rather poor sandy soil. Furthermore, the dense canopy at this site reduced soil moisture, so that conditions favourable for denitrification do not often prevail. The other sites showing very low N₂O emission were Hyytiäälä and San Rossore, which also had a soil with low biological activity, but also a much lower N input.
4.4 Effects of forest type and tree species

The difference between the nitrogen oxides emissions from deciduous and coniferous forest soils found in the present study can most likely be explained by differences in soil and litter properties in the two main types of forests. Laboratory studies on $N_2O$ emission from soils collected in several of the current study sites also confirmed higher emissions from deciduous sites compared with coniferous sites (Ambus et al., 2006). A number of other studies have shown similar differences between forest types and tree species (e.g. Butterbach-Bahl et al., 1997, 2002; Gasche and Papen, 1999; Papen and Butterbach-Bahl, 1999).

In a northwestern Connecticut forest, Finzi et al. (1998) quantified the C and N content of the forest floor and the top mineral soil and the rate of net N mineralisation beneath six different tree species. Large differences among species in the size of the forest floor C and N pools and in net N mineralisation rates were found and explained by interspecific differences in litter production and quality. The effects of five different tree species on soil respiration, gross N mineralisation and gross nitrification rates were investigated in pure tree stands in a species trial in Jutland, Denmark (Brüggemann et al., 2005). The highest rates of soil respiration, gross N mineralisation and gross nitrification were found in the organic layer under spruce, followed by beech >larch>oak>pine.

Consistently elevated fluxes of NO from coniferous forest soil were found in an experiment with addition of N (+50 kg N ha$^{-1}$ y$^{-1}$ and +150 kg N ha$^{-1}$ y$^{-1}$) to coniferous and deciduous forest soils (Venterea et al., 2003). Only the application of the higher amount of N-fertilizer had an effect on NO flux from the deciduous forest soil. Treatment effects on $N_2O$ flux were much smaller and no difference between forest types could be seen. From this experiment it was concluded that atmospheric deposition may result in increased NO emission from forest soils by promoting nitrification, and that the response may vary significantly between forest types under similar climatic regimes. These results confirm the relationship between nitrogen deposition and the difference
of forest types found in the present study.

There are several possible reasons for the difference in N-oxide emission between coniferous and deciduous forests. N-deposition (in throughfall) is often substantially (2–3 times) higher in coniferous forests than in deciduous forest due to their better filtering capacity of the air (higher leaf area index, evergreen) (Rothe et al., 2002). Some factors of the coniferous forest floor favour nitrification and thus NO emission; i.e. soil moisture is generally lower at coniferous forests (at least during spring time), they produce a thick well aerated litter layer, and the lower pH might lead to NO production from chemical decomposition of NO$_2^-$ (van Cleemput and Baert, 1984). Conversely, higher rates of denitrification are found in deciduous forests leading to N$_2$O production and NO consumption in the soil. However, the rather crude partition into deciduous and coniferous forests might not be sustained since, as documented above, different tree species provide different conditions for nitrogen oxides emission and the effects can not always be clearly split into the groups coniferous/deciduous.

The age of the forest had a significant negative effect on the N$_2$O emission and on the ratio between NO and N$_2$O emission. Although age is not a real indicator of successional state when comparing different types of forests, this indicates that nitrogen oxides emission is not suppressed by a higher growth rate in younger forests.

5 Conclusions

From a detailed study throughout a year of nitrogen oxides emission from the soil at 15 forest sites across Europe, it was found that coniferous forest soils had much higher NO emissions than deciduous forest soils. It was also found that NO emission from coniferous forest soils was highly correlated with the N-input to the soil as measured in throughfall and stem-flow. The NO emission from deciduous forest soils was generally low. The N$_2$O emission was slightly higher in deciduous forests compared to coniferous. The correlation between N$_2$O emission and N-deposition was not significant, but there was a significant negative correlation between the N$_2$O emission and the C/N
ratio. The emission of N in N-oxides was 2–32 % of the amount of N in atmospheric input to the soil. The differences between coniferous and deciduous forests are probably partly due to higher N-input to coniferous forest soils and partly due to differences in litter layer properties.

Many studies have shown that the temporal variation of nitrogen oxides emission on a specific site is clearly related to soil moisture and soil temperature. This study shows that when comparing annual emissions on a regional scale, however, factors such as nitrogen deposition and forest and soil type become much more important.

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Table 1. Geographical location, and tree species of forest field sites for continuous measurements of NO and $\text{N}_2\text{O}$ fluxes.

| Country     | Site             | Species     | Latitude   | Longitude  |
|-------------|------------------|-------------|------------|------------|
| Finland     | Hyytiälä        | Scots pine  | 61.85° N   | 24.28° E   |
| Scotland    | Glencorse(B)    | birch       | 55.85° N   | 2.17° E    |
| Scotland    | Glencorse(S)    | Sitka spruce| 55.85° N   | 3.17° W    |
| Denmark     | Sorø             | beech       | 55.48° N   | 11.63° E   |
| The Netherlands | Speulderbos  | Douglas fir | 52.22° N   | 5.65° E    |
| Germany     | Högwald(B)      | beech       | 48.50° N   | 11.17° E   |
| Germany     | Högwald(S)      | spruce      | 48.50° N   | 11.17° E   |
| Austria     | Schottenwald    | beech       | 48.23° N   | 15.25° E   |
| Austria     | Klausen-L.      | beech       | 48.12° N   | 16.05° E   |
| Hungary     | Mátra mtns.(S)  | spruce      | 47.89° N   | 19.95° E   |
| Hungary     | Mátra mtns.(O)  | oak         | 47.87° N   | 19.97° E   |
| Austria     | Achenkirch      | spruce      | 47.58° N   | 11.65° E   |
| Italy       | Parco Ticino(M) | mixed       | 45.20° N   | 9.07° E    |
| Italy       | Parco Ticino(P) | poplar      | 45.20° N   | 9.07° E    |
| Italy       | San Rossore     | pine        | 43.73° N   | 10.28° E   |
Table 2. Characteristics of forest field sites.

| Site              | Type     | Age  | C/N  | pH  | Soil temperature °C | Soil moisture %v/v | WFPS % | Precipitation mm y⁻¹ |
|-------------------|----------|------|------|-----|---------------------|-------------------|--------|----------------------|
| Hyytiälä         | coniferous | 41   | 37.7 | 3.3 | 4.6                 | 26.3              | 38     | 500                  |
| Glencorse(B)     | deciduous | 19   | 13.8 | 5.1 | 6.6                 | 31.4              | 44     | 1047                 |
| Glencorse(S)     | coniferous | 19   | 13.8 | 5.1 | 6.3                 | 25.9              | 36     | 1047                 |
| Sorø             | deciduous | 84   | 17.7 | 4.5 | 7.6                 | 24.6              | 36     | 845                  |
| Speulderbos      | coniferous | 43   | 24.5 | 3.7 | 9.4                 | 17.9              | 31     | 721                  |
| Höglwald(B)      | deciduous | 87   | 15.8 | 3.4 | 8.3                 |                   |        | 937                  |
| Höglwald(S)      | coniferous | 96   | 18.8 | 3.2 | 8.6                 | 31.5              | 56     | 937                  |
| Schottenwald     | deciduous | 141  | 13.4 | 4.3 | 8.1                 | 27.0              | 60     | 509                  |
| Klausen-L.       | deciduous | 60   | 16.0 | 5.0 | 8.4                 | 41.0              | 59     | 612                  |
| Mátra mtns.(S)   | coniferous | 39   | 12.9 | 3.6 | 5.6                 | 26.0              | 53     | 817                  |
| Mátra mtns.(O)   | deciduous | 74   | 13.5 | 4.7 | 8.2                 | 26.0              | 59     | 817                  |
| Achenkirch       | coniferous | 126  | 18.0 | 7.0 | 6.2                 | 50.2              | 60     | 1355                 |
| Parco Ticino(M)  | deciduous | 150  | 17.9 | 4.6 | 12.2                | 30.7              | 44     | 825                  |
| Parco Ticino(P)  | deciduous | 13   | 15.3 | 6.4 | 13.9                | 29.3              | 51     | 825                  |
| San Rossore      | coniferous | 38   | 29.9 | 6.5 | 14.0                | 11.1              | 21     | 959                  |
Table 3. Characteristics of chamber systems used in NO flux measurements.

| Site            | Type   | Method | Chambers No. | Frames No. | Frequency | Area m² | Volume l | Flow l min⁻¹ | Analysis | Analyser | Reference                  |
|-----------------|--------|--------|--------------|------------|-----------|---------|----------|--------------|----------|----------|------------------------------|
| Hyytiälä        | dynamic| automatic | 3            | 3          | 1/h       | 0.028   | 5.7      | 4            | field    | TEI42S   | Pumpinen et al. (2001)      |
| Glencorse(B)    | dynamic| automatic | 4+1          | 4+1        | 1/h       | 0.08    | 17       | 11.5         | field    | TEI42C   | Pilegaard (2001)            |
| Glencorse(S)    | dynamic| automatic | 4+1          | 4+1        | 1/h       | 0.08    | 17       | 11.5         | field    | TEI42C   | Pilegaard (2001)            |
| Sørø            | dynamic| automatic | 4+1          | 10+1       | 4/h       | 0.078   | 12       | 10           | field    | TEI42CTL | Pilegaard (2001)            |
| Speulderbos     | dynamic| automatic | 4            | 4          | 1/h       | 0.48    | 75       | 125          | field    | TEI42S   | van Dijk and Duyzer (1999)  |
| Höglwald(B)     | dynamic| automatic | 5+1          | 5+1        | 1/h       | 0.25    | 37.5     | 50           | field    | CLD770ALppt+PLC760          | Butterfly-Bahl et al. (1997) |
| Höglwald(S)     | dynamic| automatic | 5+1          | 5+1        | 1/h       | 0.25    | 37.5     | 50           | field    | CLD770ALppt+PLC760          | Butterfly-Bahl et al. (1997) |
| Schottenwald    | dynamic| automatic | 5+1          | 2          | 2/h       | 0.0314  | 3.27     | 1            | field    | Horiba APNA-360             | Holtermann (1996)             |
| Klausen-L.      | dynamic| automatic | 5+1          | 2          | 2/h       | 0.0314  | 3.27     | 1            | field    | Horiba APNA-360             | Holtermann (1996)             |
| Mátra mtns.(S)  | dynamic| manual   | 2            | 2          | 1/month   | 0.080   | 0.444    | 0.327        | field    | Horiba   | Meixner et al. (1997)       |
| Mátra mtns.(O)  | dynamic| manual   | 2            | 2          | 4/year    | 0.080   | 0.444    | 0.327        | field    | Horiba   | Meixner et al. (1997)       |
| Achenkirch      | dynamic| automatic | 5+1          | 2          | 2/h       | 0.0314  | 3.27     | 1            | field    | Horiba APNA-360             | Holtermann (1996)             |
| San Rossore     | dynamic| automatic | 5+1          | 5+1        | 1/h       | 0.25    | 37.5     | 50           | field    | CLD770ALppt+PLC760          | Butterfly-Bahl et al. (1997) |
Table 4. Characteristics of chamber systems used in \( N_2O \) flux measurements.

| Site          | Type       | Method        | Chambers No. | Frames No. | Frequency | Area \( m^2 \) | Volume \( l \) | Analysis   | Analyser               | Reference                  |
|--------------|------------|---------------|--------------|------------|------------|---------------|--------------|-------------|-------------------------|----------------------------|
| Hyytilä      | static     | manual        | 2            | 6          | 2/month    | 0.16          | 32.48        | laboratory  | HP-GC 6890          | Syväsalo et al. (2004)     |
| Glencorse(B) | static     | manual        | 4            | 4          | 4 campaigns| 0.14          | 25           | laboratory  | HP-GC 5890          | MacDonald et al. (1998)   |
| Glencorse(B) | static     | semi-automatic| 1            | 1          | 1/day      | 1             | 72           | laboratory  | HP-GC 5890          | MacDonald et al. (1998)   |
| Glencorse(S) | static     | manual        | 4            | 4          | 4 campaigns| 0.14          | 25           | laboratory  | HP-GC 5890          | MacDonald et al. (1998)   |
| Glencorse(S) | static     | semi-automatic| 1            | 1          | 1/day      | 1             | 72           | laboratory  | HP-GC 5890          | MacDonald et al. (1998)   |
| Søre         | static     | manual        | 6            | 6          | 2/month    | 0.071         | 8            | laboratory  | Shimadzu 14b w/ECD | Ambus et al. (2001)       |
| Søre         | static     | semi-automatic| 1            | 1          | 1/day      | 0.49          | 60           | laboratory  | Shimadzu 14b w/ECD | Ambus et al. (2001)       |
| Speulderbos  | static     | automatic     | 4            | 4          | 1/hour     | 0.48          | 75           | field       | Chompack cp-9011 GC-63Ni-ECD | Duyzer (1995)             |
| Høgliwald(B) | static     | automatic     | 5            | 5          | 2/hour     | 0.25          | 37.5         | field       | Shimadzu 14a w/ECD | Butterbach-Bahl et al. (1997) |
| Høgliwald(S) | static     | automatic     | 5            | 5          | 2/hour     | 0.25          | 37.5         | field       | Shimadzu 14a w/ECD | Butterbach-Bahl et al. (1997) |
| Schottenwald | static     | manual        | 4            | 4          | 2/month    | 1.0           | 80           | laboratory  | GC-63Ni ECD        | Härtel et al. (2002)      |
| Schottenwald | static     | semi-automatic| 1            | 1          | 1/day      | 0.49          | 49           | laboratory  | GC-63Ni ECD        | Härtel et al. (2002)      |
| Klausen-L.   | static     | semi-automatic| 1            | 1          | 1/day      | 0.49          | 49           | laboratory  | GC-63Ni ECD        | Härtel et al. (2002)      |
| Måtra mtns.(S) static | manual    | 8            | 8            | 2/month    | 0.0080      | 0.4          | laboratory  | HP-GC 5890 + HP-MS 5972 | Christensen et al. (1990) |
| Måtra mtns.(O) static | manual    | 8            | 8            | 2/month    | 0.0080      | 0.4          | laboratory  | HP-GC 5890 + HP-MS 5972 | Christensen et al. (1990) |
| Achenkirch   | static     | manual        | 4            | 4          | 2/month    | 1.0           | 80           | laboratory  | GC-63Ni ECD        | Härtel et al. (2002)      |
| Achenkirch   | static     | semi-automatic| 1            | 1          | 1/day      | 0.49          | 49           | laboratory  | GC-63Ni ECD        | Härtel et al. (2002)      |
| Parco Ticino(M) static | manual    | 4            | 4            | 2/month    | 0.13         | 28           | laboratory  | Shimadzu GC14B | Leip (2000)          |
| Parco Ticino(M) static | semi-automatic | 1           | 1            | 1/day      | 0.46         | 60           | laboratory  | Shimadzu GC14B | Leip (2000)          |
| Parco Ticino(P) static | semi-automatic | 1           | 1            | 1/day      | 0.46         | 60           | laboratory  | Shimadzu GC14B | Leip (2000)          |
| San Rossore  | static     | semi-automatic| 4            | 8          | 2/month    | 0.13         | 28           | laboratory  | Shimadzu GC14B | Leip (2000)          |
| San Rossore  | static     | semi-automatic| 1            | 1          | 1/day      | 0.46         | 60           | laboratory  | Shimadzu GC14B | Leip (2000)          |
Table 5. Annual nitrogen deposition ($\text{NO}_3^- + \text{NH}_4^+$) in throughfall (g N m$^{-2}$ y$^{-1}$) and average emission of NO and $\text{N}_2\text{O}$ ($\mu$g N m$^{-2}$ h$^{-1}$) from forests in Europe listed in the order of deposition. Data from July 2002–June 2003, except Speulderbos September 2002–August 2003, and NO in Sorø May 2003–April 2004. nd=below detection limit.

| Site               | Nitrogen deposition g N m$^{-2}$ y$^{-1}$ | NO emission $\mu$g N m$^{-2}$ h$^{-1}$ | $\text{N}_2\text{O}$ emission $\mu$g N m$^{-2}$ h$^{-1}$ |
|--------------------|------------------------------------------|----------------------------------------|----------------------------------------------------------|
| Speulderbos        | 3.85                                     | 75.2                                   | 2.3                                                      |
| Höglwald(S)        | 2.91                                     | 81.7                                   | 9.0                                                      |
| Schottenwald       | 2.44                                     | 4.2                                    | 6.4                                                      |
| Sorø               | 2.36                                     | 2.6                                    | 8.4                                                      |
| Mátra mtns.(O)     | 1.59                                     | 2.1                                    | 20.3                                                     |
| Mátra mtns.(S)     | 1.42                                     | 1.2                                    | 14.8                                                     |
| Höglwald(B)        | 1.30                                     | 13.4                                   | 13.0                                                     |
| Parco Ticino(M)    | 1.3                                      | nd                                     | 4.9                                                      |
| Parco Ticino(P)    | 1.3                                      | 5.0*                                   | 19.7                                                     |
| Glencorse(S)       | 1.14                                     | 27.0                                   | 14.9                                                     |
| Achenkirch         | 1.00                                     | 0.9                                    | 2.8                                                      |
| Klausen-L.         | 0.98                                     | 0.7                                    | 5.4                                                      |
| San Rossore        | 0.76                                     | 5.4†                                   | 2.1                                                      |
| Glencorse(B)       | 0.52                                     | 1.5                                    | 11.9                                                     |
| Hyytiäälä          | 0.22                                     | 0.006                                  | 0.3                                                      |

* Based on 2 measurements in August and November 2002
† Based on continuous measurements during 23 April–4 June 2003 and 28 October–3 December 2003
(Rosenkranz et al., 2006)
Table 6. Regression coefficients. Units as given in Tables 2 and 5. Significance: ***p<0.001; **p< 0.01; *p<0.05; +p<0.1.

| Parameter                        | Coefficient | Signif. |
|----------------------------------|-------------|---------|
| NO emission intercept            | −3.29       |         |
| NO emission type (dec.)          | −22.45      |         |
| NO emission intercept coniferous | −13.93      | *       |
| NO emission intercept deciduous  | 3.52        |         |
| NO emission intercept all        | 0.37        |         |
| N₂O emission intercept           | 26.49       | ***     |
| N₂O emission intercept C/N       | −0.69       | ***     |
| N₂O emission intercept age       | −0.07       | *       |
| ln(N₂O emission) intercept       | 4.82        | ***     |
| ln(N₂O emission) intercept C/N   | −0.14       | ***     |
| ln(N₂O emission) intercept age   | −0.01       | *       |
| N₂O emission intercept all       | 9.60        | *       |
| N₂O emission intercept all       | −0.33       |         |
| NO+N₂O emission intercept all    | −6.33       | **      |
| NO+N₂O emission intercept N deposition | 20.06 | **  |
| NO+N₂O emission intercept coniferous | 25.34 | *    |
| NO+N₂O emission intercept deciduous | −1.05 | *    |
| NO+N₂O emission intercept all    | 16.58       | **      |
| NO/N₂O emission intercept all    | −2.23       | **      |
| NO/N₂O emission intercept age    | −0.10       | +       |
Fig. 1. NOFRETETE field stations.
Fig. 2. NO emission ($\mu$g N m$^{-2}$ h$^{-1}$) as a function of nitrogen deposition (g N m$^{-2}$ y$^{-1}$). Regression lines (solid=significant, dashed=non significant) for coniferous and deciduous sites, respectively.
Fig. 3. \( \text{N}_2\text{O} \) emission (\( \mu \text{g N m}^{-2} \text{ h}^{-1} \)) as a function of C/N ratio. The full line represents a linear regression and the dotted line a regression after logarithmic transformation of \( \text{N}_2\text{O} \) emission.
Fig. 4. $\text{N}_2\text{O}$ emission ($\mu$g N m$^{-2}$ h$^{-1}$) as a function of nitrogen deposition (g N m$^{-2}$ y$^{-1}$).
Fig. 5. Sum of N-oxides emitted as a function of nitrogen deposition (g N m$^{-2}$ y$^{-1}$). Regression lines (solid=significant, dashed=non significant) for coniferous and deciduous sites, respectively.
**Fig. 6.** pH as a function of nitrogen deposition (g N m$^{-2}$ y$^{-1}$).