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## Factors controlling regional differences in forest soil emission of nitrogen oxides (NO and N<sub>2</sub>O)

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**Abstract.** Soil emissions of NO and N<sub>2</sub>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 μg NO-N m<sup>-2</sup> h<sup>-1</sup>) was a spruce forest in South-Germany (Höglwald) receiving an annual N-deposition of 2.9 g m<sup>-2</sup>. 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<sup>-2</sup> a<sup>-1</sup>. No significant correlation between N<sub>2</sub>O emission and N-deposition was found. The highest average annual N<sub>2</sub>O emission (20 μg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>) was found in an oak forest in the Mátra mountains (Hungary) receiving an annual N-deposition of 1.6 g m<sup>-2</sup>. N<sub>2</sub>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 differences in characteristics of the litter layer and soil. NO was mainly

derived from nitrification whereas N<sub>2</sub>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<sub>2</sub>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 more important.

### 1 Introduction

Increasing emissions of N-oxides from combustion processes and NH<sub>3</sub>-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<sup>-2</sup> a<sup>-1</sup> in most parts of Europe, in central Europe significantly above 2 g N m<sup>-2</sup> a<sup>-1</sup> (Umweltbundesamt, 1997), and in The Netherlands, parts of Northern Germany, and UK up to 5 g N m<sup>-2</sup> a<sup>-1</sup> (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

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**Fig. 1.** NOFRETETE field stations.

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<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>) (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. Kreuzer and Weiss, 1998); and increase losses of N to the environment in form of N-leaching to the groundwater (e.g. Kreuzer, 1995) and/or in form of N-gas emissions (N<sub>2</sub>O, NO, N<sub>2</sub>) 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<sub>2</sub>O), nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) play an important role by affecting the oxidising capacity of the troposphere (NO and NO<sub>2</sub>), by affecting ecosystems through deposition (NO<sub>2</sub> and derivatives) or by acting as a greenhouse gas (N<sub>2</sub>O).

Forests cover a large part of the European continent (approx. 35%), but the exchange of nitrogen oxides (NO, N<sub>2</sub>O and NO<sub>2</sub>) 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 N<sub>2</sub>O 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 NH<sub>3</sub> 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 (Butterbach-Bahl et al., 1997) and studies of NO and N<sub>2</sub>O 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 N<sub>2</sub>O and NO still have a high degree of uncertainty.

NO and N<sub>2</sub>O 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 N<sub>2</sub>O. 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 N<sub>2</sub>O 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<sub>2</sub>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<sup>-2</sup> a<sup>-1</sup>) to high deposition (~4 g N m<sup>-2</sup> a<sup>-1</sup>). We relate annual mean emission rates of NO and N<sub>2</sub>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), Höglwald (Germany), and Mátra mountains (Hungary) both coniferous and deciduous forest sites were investigated.

### 2.2 Flux measurements

The soil emissions of NO and N<sub>2</sub>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<sub>3</sub> 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<sub>2</sub>O was measured using manual and/or automatic static chambers. Headspace N<sub>2</sub>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<sub>2</sub>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<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> 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<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> 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<sup>-2</sup> h<sup>-1</sup>. The highest emissions were found in the Höglwald spruce forest followed by the Speulderbos Douglas fir forest (75.2 μg N m<sup>-2</sup> h<sup>-1</sup>) and the lowest in the Hyytiälä Scots pine forest (0.006 μg N m<sup>-2</sup> h<sup>-1</sup>) and the Parco Ticino mixed forest (below detection limit). Emissions of N<sub>2</sub>O ranged from 0.3 to 20.3 μg N m<sup>-2</sup> h<sup>-1</sup> 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<sup>-2</sup> h<sup>-1</sup>) and the lowest values in Hyytiälä, San Rossore (2.1 μg N m<sup>-2</sup> h<sup>-1</sup>) and Speulderbos (2.3 μg N m<sup>-2</sup> h<sup>-1</sup>).

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

The results of the regression analyses of the emissions of NO and N<sub>2</sub>O, the sum of NO and N<sub>2</sub>O and the ratio between NO and N<sub>2</sub>O 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

**Table 1.** Geographical location, and tree species of forest field sites for continuous measurements of NO and N<sub>2</sub>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	Höglwald(B)	beech	48.50° N	11.17° E
Germany	Höglwald(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	Soil moisture	WFPS	Precipitation
		years			°C	% v/v	%	mm a <sup>-1</sup>
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

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 ( $\text{NO} (\mu\text{g N m}^{-2} \text{ h}^{-1}) = -13.9 + 25.5 * [\text{N deposition} (\text{g m}^{-2} \text{ a}^{-1})]$ ,  $r^2 = 0.82$ ). The relationships between NO emission and N deposition are shown in Fig. 2.

The N<sub>2</sub>O 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 N<sub>2</sub>O emission improved the significance of the correlation. Restricting the

analysis to sites with  $\text{C/N} < 20$ , because very little nitrification occurs above this threshold, resulted in a non-significant regression. There was no significant correlation between the N<sub>2</sub>O emission and the nitrogen deposition (Fig. 4).

The sum of NO and N<sub>2</sub>O 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 sum (NO+N<sub>2</sub>O) was not significantly correlated with any other of the investigated parameters.

The NO/N<sub>2</sub>O ratio was positively correlated with nitrogen deposition and negatively correlated with age of the stands.

**Table 3.** Characteristics of chamber systems used in NO flux measurements.

Site	Type	Method	Chambers No.	Frames No.	Frequency	Area m <sup>2</sup>	Volume l	Flow l min <sup>-1</sup>	Analysis	Analyser	Reference
Hyytiälä	dynamic	automatic	3	3	1/h	0.028	5.7	4	field	TEI42S	Pumpanen 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)
Sorø	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	Butterbach-Bahl et al. (1997)
Höglwald(S)	dynamic	automatic	5+1	5+1	1/h	0.25	37.5	50	field	CLD770ALppt+PLC760	Butterbach-Bahl et al. (1997)
Schottenwald	dynamic	automatic	5+1		2/h	0.0314	3.27	1	field	Horiba APNA-360	Holtermann (1996)
Klausen-L.	dynamic	automatic	5+1		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/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	Butterbach-Bahl et al. (1997)

**Table 4.** Characteristics of chamber systems used in N<sub>2</sub>O flux measurements.

Site	Type	Method	Chambers No.	Frames No.	Frequency	Area m <sup>2</sup>	Volume l	Analysis	Analyser	Reference
Hyytiälä	static	manual	2	6	2/month	0.116	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)
Sorø	static	manual	6	6	2/month	0.071	8	laboratory	Shimadzu 14b w/ECD	Ambus et al. (2001)
Sorø	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-9001 GC <sup>63</sup> Ni-ECD	Duyzer (1995)
Höglwald(B)	static	automatic	5	5	2/hour	0.25	37.5	field	Shimadzu 14a w/ECD	Butterbach-Bahl et al. (1997)
Höglwald(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- <sup>63</sup> Ni ECD	Härtel et al. (2002)
Schottenwald	static	semi-automatic	1	1	1/day	0.49	49	laboratory	GC- <sup>63</sup> Ni ECD	Härtel et al. (2002)
Klausen-L.	static	manual	4	4	1/month	1.0	80	laboratory	GC- <sup>63</sup> Ni ECD	Härtel et al. (2002)
Klausen-L.	static	semi-automatic	1	1	1/day	0.49	49	laboratory	GC- <sup>63</sup> Ni ECD	Härtel et al. (2002)
Mátra mtns.(S)	static	manual	8	8	2/month	0.0080	0.4	laboratory	HP-GC 5890 + HP-MS 5972	Christensen et al. (1990)
Mátra 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- <sup>63</sup> Ni ECD	Härtel et al. (2002)
Achenkirch	static	semi-automatic	1	1	1/day	0.49	49	laboratory	GC- <sup>63</sup> Ni 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	manual	4	4	2/month	0.13	28	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	manual	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)

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<sub>2</sub>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<sub>2</sub>O emission between the two sites was substantial (Table 5) with the oak site having the highest emission.

#### 4 Discussion

In this investigation we related annual mean emission rates of NO and N<sub>2</sub>O to the parameters soil temperature, soil moisture, C/N ratio, pH, nitrogen deposition, forest type, and

stand age. The study showed that when comparing annual emission rates over a larger regional area the most important parameters for NO were nitrogen deposition and forest type, and for N<sub>2</sub>O the most important parameters were C/N ratio and stand age. The parameters normally explaining most of the temporal variation within a single site (soil temperature and soil moisture) had less influence on the mean annual emission rates at the regional scale.

The question of whether predictive understanding of N<sub>2</sub>O 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 N<sub>2</sub>O flux at the ecosystem scale in forest, cropland, and rangeland ecosystems but that ecosystem-scale

**Table 5.** Annual nitrogen deposition (NO<sub>3</sub><sup>-</sup>+NH<sub>4</sub><sup>+</sup>) in throughfall (g N m<sup>-2</sup> a<sup>-1</sup>) and average emission of NO and N<sub>2</sub>O (μg N m<sup>-2</sup> h<sup>-1</sup>) 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 <sup>-2</sup> a <sup>-1</sup>	NO emission μg N m <sup>-2</sup> h <sup>-1</sup>	N <sub>2</sub> O emission μg N m <sup>-2</sup> h <sup>-1</sup>
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 <sup>†</sup>	2.1
Glencorse(B)	0.52	1.5	11.9
Hyytiälä	0.22	0.006	0.3

\* Based on 2 measurements in August and November 2002

<sup>†</sup> Based on continuous measurements during 23 April–4 June 2003 and 28 October–3 December 2003 (Rosenkranz et al., 2006)

controls of N<sub>2</sub>O flux vary within and between regions and only emerge with continuous (at least daily) flux measurements over multiple years. Compared to the analysis of Groffman et al. (2000) the present investigation deals with both NO and N<sub>2</sub>O, measured within the same time-period and with a high frequency.

#### 4.1 Effects of soil moisture and temperature

Production of NO and N<sub>2</sub>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<sub>2</sub>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<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and influences the rate of O<sub>2</sub> supply and thereby controls whether aerobic processes such as nitrification or anaerobic processes such as denitrification dominate within the soil. While N<sub>2</sub>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 (Ormecci et al., 1999; van Dijk and Duyzer, 1999; Gasche and Papen, 1999).

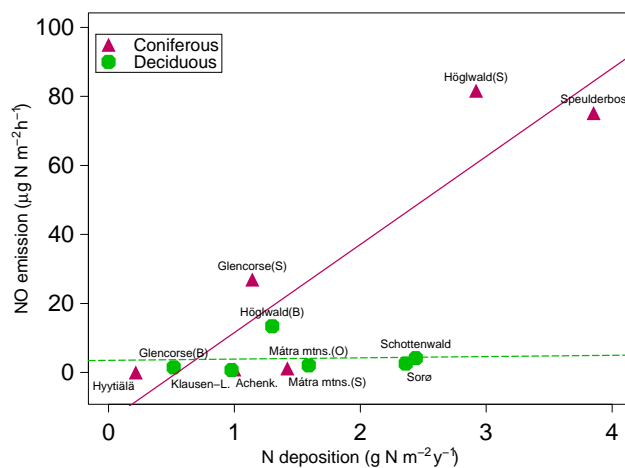
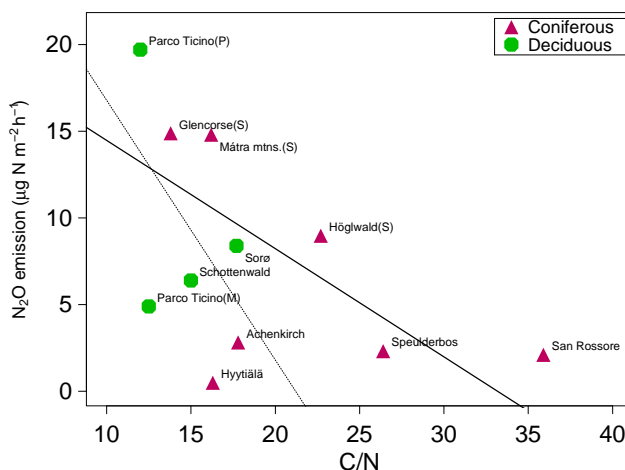
The effects of soil moisture and temperature on NO and N<sub>2</sub>O emission were studied in a laboratory experiment with soil cores from some of the same field sites as in the present study (Parco Ticino(M), Schottenwald, Klausen-Leopoldsdorf, Achenkirch, Höglwald (spruce) and Hyytiälä) (Schindlbacher et al., 2004). Soil moisture and temperature explained most of the variations in NO (up to 74%) and N<sub>2</sub>O (up to 86%) emissions for individual soils. NO and N<sub>2</sub>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<sup>-2</sup> h<sup>-1</sup> and largely exceeded emissions from other soils. Average N<sub>2</sub>O emissions from this soil tended also to be highest (171.7±42.2 μg N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>), but did not differ significantly from other soils. NO and N<sub>2</sub>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<sub>2</sub>O emission.

Schindlbacher et al. (2004) also showed that N<sub>2</sub>O emissions increased with increasing WFPS or decreasing water tension, respectively. Maximum N<sub>2</sub>O emissions were

**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.

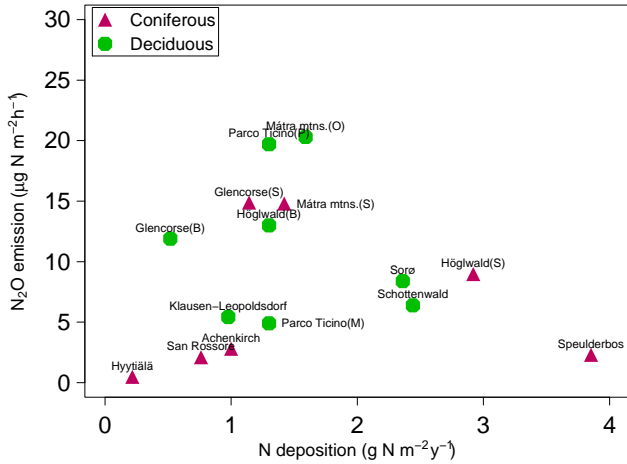
	parameter	coefficient	signif.
NO emission all ( <i>r</i> <sup>2</sup> =0.71)	intercept	-3.29	
	N deposition	19.45	**
	type (dec.)	-22.45	+
NO emission coniferous ( <i>r</i> <sup>2</sup> =0.82)	intercept	-13.93	
	N deposition	25.52	*
NO emission deciduous ( <i>r</i> <sup>2</sup> =0.004)	intercept	3.52	
	N deposition	0.37	
N <sub>2</sub> O emission all ( <i>r</i> <sup>2</sup> =0.67)	intercept	26.49	***
	C/N	-0.69	***
	age	-0.07	*
N <sub>2</sub> O emission C/N < 20 ( <i>r</i> <sup>2</sup> =0.25)	intercept	31.76	
	C/N	-1.50	
ln(N <sub>2</sub> O emission) all ( <i>r</i> <sup>2</sup> =0.87)	intercept	4.82	***
	C/N	-0.14	***
	age	-0.01	*
N <sub>2</sub> O emission all ( <i>r</i> <sup>2</sup> =0.03)	intercept	9.60	*
	N deposition	-0.33	
NO+N <sub>2</sub> O emission all ( <i>r</i> <sup>2</sup> =0.53)	intercept	-6.33	
	N deposition	20.06	**
NO+N <sub>2</sub> O emission coniferous ( <i>r</i> <sup>2</sup> =0.80)	intercept	-6.20	
	N deposition	25.34	*
NO+N <sub>2</sub> O emission deciduous ( <i>r</i> <sup>2</sup> =0.04)	intercept	16.58	
	N deposition	-1.05	
NO/N <sub>2</sub> O emission all ( <i>r</i> <sup>2</sup> =0.73)	intercept	-2.23	
	N deposition	7.82	***
	age	-0.10	+

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<sub>2</sub>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.

**Fig. 2.** NO emission ( $\mu\text{g N m}^{-2} \text{h}^{-1}$ ) as a function of nitrogen deposition ( $\text{g N m}^{-2} \text{a}^{-1}$ ). Regression lines (solid=significant, dashed=non significant) for coniferous and deciduous sites, respectively.**Fig. 3.** N<sub>2</sub>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 of the full data set and the dotted line a linear regression of sites with C/N < 20 (non significant).

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





**Fig. 4.** N<sub>2</sub>O emission ( $\mu\text{g N m}^{-2} \text{h}^{-1}$ ) as a function of nitrogen deposition ( $\text{g N m}^{-2} \text{a}^{-1}$ ).

annual temperature. They hypothesised that differences in soil respiration among forests are likely to depend more on forest productivity rather than on temperature.

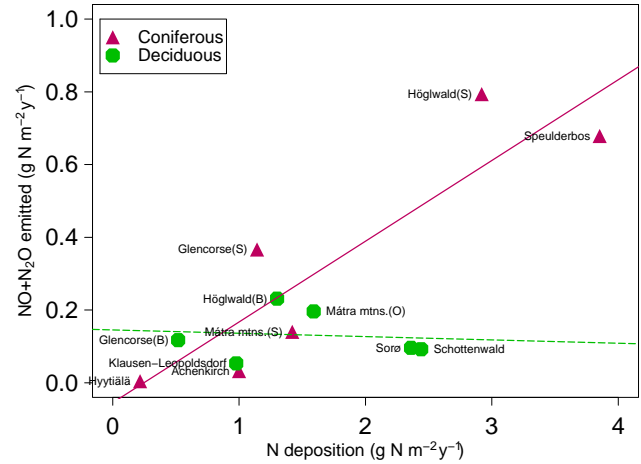
#### 4.2 Effects of C/N ratio and pH

This study showed a significant negative correlation between N<sub>2</sub>O 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, which could be due to the acidifying effect of NH<sub>4</sub><sup>+</sup> 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).

Klemetsson et al. (2005) found a strong negative relationship between N<sub>2</sub>O 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 N<sub>2</sub>O 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 Hyytiälä.

#### 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 N<sub>2</sub>O (Fig. 5), but no significant relationship for N<sub>2</sub>O (Fig. 4). Clear relationships have been reported



**Fig. 5.** Sum of N-oxides emitted as a function of nitrogen deposition ( $\text{g N m}^{-2} \text{a}^{-1}$ ). Regression lines (solid=significant, dashed=non significant) for coniferous and deciduous sites, respectively.

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 N<sub>2</sub>O 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 N<sub>2</sub>O emission were Hyytiälä 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<sub>2</sub>O 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<sup>-1</sup> a<sup>-1</sup> and +150 kg N ha<sup>-1</sup> a<sup>-1</sup>) 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<sub>2</sub>O 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<sub>2</sub><sup>-</sup> (van Cleemput and Baert, 1984). Conversely, higher rates of denitrification are found in deciduous forests leading to N<sub>2</sub>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<sub>2</sub>O emission and on the ratio between NO and N<sub>2</sub>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<sub>2</sub>O emission was slightly higher in deciduous forests compared to coniferous. The correlation between N<sub>2</sub>O emission and N-deposition was not significant, but there was a significant negative correlation between the N<sub>2</sub>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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## References

- Aber, J. D.: Nitrogen cycling and nitrogen saturation in temperate forest ecosystems, *Tree*, 7, 220–224, 1992.
- Aber, J. D., Nadelhofer, K. J., Steudler, P., and Melillo, J. M.: Nitrogen saturation in northern forest ecosystems, *BioScience*, 39, 378–386, 1989.
- Altimir, N., Vesala, T., Keronen, P., Kulmala, M., and Hari, P.: Methodology for direct field measurements of ozone flux to foliage with shoot chambers, *Atmos. Environ.*, 36, 19–29, 2002.
- Ambus, P., Jensen, J., Priemé, A., Pilegaard, K., and Kjølter, A.: Assessment of CH<sub>4</sub> and N<sub>2</sub>O fluxes in a Danish beech (*Fagus sylvatica*) forest and an adjacent N-fertilised barley (*Hordeum vulgare*) field: effects of sewage sludge amendments, *Nutrient Cycling in Agroecosystems*, 60, 15–21, 2001.
- Ambus, P., Zechmeister-Boltenstern, S., and Butterbach-Bahl, K.: Relationship between nitrous oxide production and nitrogen cycling in European forests, *Biogeosciences*, 3, 135–145, 2006, <http://www.biogeosciences.net/3/135/2006/>.
- Beck, W.: Veränderungen im Wachstumsverhalten von Kiefer und Buche im nordostdeutschen Tiefland in Abhängigkeit von Fremdstoffeintrag und Witterung, in 9. Hamburger Forst- und Holtztagung 1996, 73–96, Bundesforschungsanstalt für Forst- und Holtzwirtschaft, Hamburg, 1996.
- Brüggemann, N., Rosenkranz, P., Papen, H., Pilegaard, K., and Butterbach-Bahl, K.: Pure stands of temperate forest tree species

- modify soil respiration and N turnover, *Biogeosciences Discuss.*, 2, 303–331, 2005,  
<http://www.biogeosciences-discuss.net/2/303/2005/>.
- Brumme, R. and Beese, F.: Effects of liming and nitrogen fertilization on emissions of CO<sub>2</sub> and N<sub>2</sub>O from a temperate forest, *J. Geophys. Res.*, 96, 9321–9328, 1992.
- Burton, J. L., Pregitzer, K. S., Crawford, J. N., Zogg, G. P., and Zak, D. R.: Simulated chronic NO<sub>3</sub><sup>-</sup> deposition reduces soil respiration in northern hardwood forests, *Global Change Biol.*, 10, 1080–1091, 2004.
- Butterbach-Bahl, K., Gasche, R., Breuer, L., and Papen, H.: Fluxes of NO and N<sub>2</sub>O from temperate forest soils: Impact of forest type, N deposition and of liming on the NO and N<sub>2</sub>O emissions, *Nutrient Cycling in Agroecosystems*, 48, 79–90, 1997.
- Butterbach-Bahl, K., Rothe, A., and Papen, H.: Effect of tree distance on N<sub>2</sub>O and CH<sub>4</sub> – fluxes from soils in temperate forest ecosystems, *Plant and Soil*, 240, 91–103, 2002.
- Castro, M. S., Steudler, P. A., Melillo, J. M., Aber, J. D., and Millhamet, S.: Exchange of N<sub>2</sub>O and CH<sub>4</sub> between the atmosphere and soils in spruce-fir forests in Northeastern United States, *Biogeochemistry*, 18, 119–135, 1993.
- Christensen, S., Simkins, S., and Tiedje, J. M.: Spatial variation in denitrification: Dependency of activity centers on the soil environment, *Soil Sci. Soc. Am. J.*, 54, 1608–1613, 1990.
- Dise, N. B. and Wright, R. F.: Nitrogen leaching from European forests in relation to nitrogen deposition, *Forest Ecol. Manage.*, 71, 153–161, 1995.
- Duyzer, J. H.: Measurements of the atmospheric emission of N<sub>2</sub>O from biogenic sources in general and by grassland ecosystems in particular, Tech. Rep. TNO-MEP R 95/213, TNO Institute of Environmental Sciences, 1995.
- Fenn, M. E., Poth, M. A., Aber, J. D., Baron, J. S., Bormann, B. T., Johnson, D. W., Lemly, A. D., McNulty, S. G., Ryan, D. F., and Stottlemeyer, R.: Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses, and management strategies, *Ecol. Appl.*, 8, 1998.
- Ferré, C., Leip, A., Matteucci, G., Previtali, F., and Seufert, G.: Impact of 40 years poplar cultivation on soil carbon stocks and greenhouse gas fluxes, *Biogeosciences Discuss.*, 2, 897–931, 2005,  
<http://www.biogeosciences-discuss.net/2/897/2005/>.
- Finzi, A., van Breemen, N., and Canham, C. D.: Canopy tree–soil interactions within temperate forests: Species effects on soil carbon and nitrogen, *Ecol. Appl.*, 8, 440–446, 1998.
- Firestone, M. K. and Davidson, E. A.: Microbial basis of NO and N<sub>2</sub>O production and consumption in soil, in: Exchange of trace gases between terrestrial ecosystems and the atmosphere, edited by: Andreae, M. O. and Schimel, D. S., 7–21, John Wiley & Sons Ltd., Chichester, U.K., 1989.
- Gasche, R. and Papen, H.: A 3-year continuous record of nitrogen trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany 2. NO and NO<sub>2</sub> fluxes, *J. Geophys. Res.*, 104, 18 505–18 520, 1999.
- Groffman, P., Brumme, R., Butterbach-Bahl, K., Dobbie, K. E., Mosier, A. R., Ojima, D., Papen, H., Parton, W. J., Smith, K. A., and Wagner-Riddle, C.: Evaluating annual nitrous oxide fluxes at the ecosystem scale, *Global Biogeochem. Cycles*, 14, 1061–1070, 2000.
- Härtel, C., Zechmeister, S., and Gerzabek, M.: Gaseous nitrogen losses from a forest site in the north Tyrolean limestone Alps, *Environ. Sci. Pollut. Res.*, Special Issue, 2, 23–30, 2002.
- Hofmann, G.: Kiefernökosysteme im Wandel, *Der Wald*, 45, 262–267, 1995.
- Holtermann, C.: A transportable system for the on-line measurements of NO<sub>x</sub> (NO, NO<sub>2</sub>) -emission from soils, *Die Bodenkultur*, 47, 235–244, 1996.
- Horváth, L., Führer, E., and Lajtha, K.: Nitric oxide and nitrous oxide emission from Hungarian forest soils; link with atmospheric N-deposition, *Biogeosciences Discuss.*, 2, 703–722, 2005,  
<http://www.biogeosciences-discuss.net/2/703/2005/>.
- Janssens, I. A., Lankreijer, H., Matteucci, G., Kowalski, A., Buchmann, N., Epron, D., Pilegaard, K., Kutsch, W., Longdoz, B., Grünwald, T., Montagnani, L., Dore, S., Rebmann, C., Moors, E., Grelle, A., Rannik, Ü., Morgenstern, K., Clement, R., Gudmundsson, J., Minerbi, S., Berbigier, P., Ibrom, A., Moncrieff, J., Aubinet, M., Berhofer, C., Jensen, N., Vesala, T., Granier, A., Schulze, E.-D., Lindroth, A., Dolman, A., Jarvis, P., Ceulemans, R., and Valentini, R.: Productivity and disturbance overshadow temperature in determining soil and ecosystem respiration across European forests, *Global Change Biol.*, 7, 269–278, 2001.
- Kitzler, B., Zechmeister-Boltenstern, S., Holtermann, C., Skiba, U., and Butterbach-Bahl, K.: Nitrogen oxides emission from two beech forests subjected to different nitrogen loads, *Biogeosciences*, 3, 293–310, 2006,  
<http://www.biogeosciences.net/3/293/2006/>.
- Kitzler, B., Zechmeister-Boltenstern, S., Holtermann, C., Skiba, U., and Butterbach-Bahl, K.: Controls over N<sub>2</sub>O, NO<sub>x</sub> and CO<sub>2</sub> fluxes in a calcareous mountain forest soil, *Biogeosciences*, 3, 383–395, 2006,  
<http://www.biogeosciences.net/3/383/2006/>.
- Klemetsson, L., von Arnold, K., Weslien, P., and Gundersen, P.: Soil CN ratio as a scalar parameter to predict nitrous oxide emissions, *Global Change Biol.*, 11, 1142–1147, 2005.
- Kreutzer, K.: Effects of liming on soil processes, *Plant and Soil*, 168–169, 447–470, 1995.
- Kreutzer, K. and Weiss, T.: The Höglwald field experiments – aims, concepts and basic data, *Plant and Soil*, 199, 1–10, 1998.
- Kristensen, H. L., Gundersen, P., Callesen, I., and Reinds, G. J.: Throughfall nitrogen deposition has different impacts on soil solution nitrate concentration in European coniferous and deciduous Forests, *Ecosystems*, 7, 180–192, 2004.
- Leip, A.: Nitrous oxide (N<sub>2</sub>O) emissions from a coastal catchment in the Delta of the Po river. Measurement and modeling of fluxes from a Mediterranean lagoon and agricultural soil, Tech. Rep. EUR 19052, Office for Official Publications of the European Communities, Luxembourg, 2000.
- Ludwig, J., Meixner, F. X., Vogel, B., and Förstner, J.: Soil–air exchange of nitric oxide: An overview of processes, environmental factors, and modeling studies, *Biogeochemistry*, 52, 225–257, 2001.
- MacDonald, J. A., Skiba, U. M., Sheppard, L. J., Ball, B., Roberts, J. D., Smith, K. A., and Fowler, D.: The effect of nitrogen deposition and seasonal variability on methane oxidation and nitrous oxide emission rates in an upland spruce plantation and moorland, *Atmos. Environ.*, 31, 3693–3706, 1998.
- Magill, A. H., Aber, J. D., Hendricks, J. J., Bowden, R. D., Melillo, J. M., and Steudler, P. A.: Biogeochemical response of forest ecosystems to simulated chronic nitrogen deposition, *Ecol.*

- Appl., 7, 402–415, 1997.
- Meixner, F. X., Fickinger, T., Marufu, L., Serca, D., Nathaus, F. J., Makina, E., Mukurumbira, L., and Andreae, M. O.: Preliminary results of nitric oxide emission from a southern African savanna ecosystem, *Nutrient Cycling in Agroecosystems*, 48, 123–138, 1997.
- Ormeçi, B., Sanin, S. L., and Peirce, J. J.: Laboratory study of NO flux from agricultural soil: Effects of soil moisture, pH, and temperature, *J. Geophys. Res.*, 104, 1621–1629, 1999.
- Papen, H. and Butterbach-Bahl, K.: A 3-year continuous record of nitrogen trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany – I. N<sub>2</sub>O emissions, *J. Geophys. Res.*, D104, 18487–18503, 1999.
- Persson, T., Rudebeck, A., Jussy, J. H., Colin-Belgrand, M., Priemé, A., Dambrine, E., Karlsson, P. S., and Sjöberg, R. M.: Carbon and nitrogen cycling in European forest ecosystems, vol. 142 of *Ecological Studies*, chap. Soil nitrogen turnover – Mineralisation, nitrification and denitrification in European forest soils, 297–340, Springer Verlag, 2000.
- Pilegaard, K.: Air–soil exchange of NO, NO<sub>2</sub>, and O<sub>3</sub> in forests, *Water, Air and Soil Pollution: Focus*, 1, 79–88, 2001.
- Pilegaard, K., Hummelshøj, P., and Jensen, N. O.: Nitric oxide emission from a Norway spruce forest floor, *J. Geophys. Res.*, D(104), 3433–3445, 1999.
- Pilegaard, K., Hummelshøj, P., Jensen, N. O., and Chen, Z.: Two years of continuous CO<sub>2</sub> eddy-flux measurements over a Danish beech forest, *Agric. Forest Meteorol.*, 107, 29–41, 2001.
- Pitcairn, C. E. R., Skiba, U. M., Sutton, M., Fowler, D., Munro, R., and Kennedy, V.: Defining the spatial impacts of poultry farm ammonia emissions on species composition of adjacent woodland groundflora using Ellenberg Nitrogen Index, nitrous oxide and nitric oxide emissions and foliar nitrogen as marker variables, *Environ. Pollut.*, 199, 9–21, 2002.
- Priha, O. and Smolander, A.: Nitrification, denitrification and microbial biomass in soil from two N-fertilized and limed Norway spruce forests, *Soil Biol. Biochem.*, 27, 305–310, 1995.
- Pumpanen, J., Ilvesniemi, H., Keronen, P., Nissinen, A., Pohja, T., Vesala, T., and Hari, P.: An open chamber system for measuring soil surface CO<sub>2</sub> efflux: Analysis of error sources related to the chamber system, *J. Geophys. Res.*, 106, 7985–7992, 2001.
- Remde, A., Ludwig, J., Meixner, F., and Conrad, R.: A study to explain the emission of nitric oxide from a marsh soil, *J. Atmos. Chem.*, 17, 249–275, 1993.
- Rosenkranz, P., Brüggemann, N., Papen, H., Xu, Z., Seufert, G., and Butterbach-Bahl, K.: N<sub>2</sub>O, NO and CH<sub>4</sub> exchange and microbial N turnover over a Mediterranean pine forest soil, *Biogeosciences*, 3, 121–133, 2006, <http://www.biogeosciences.net/3/121/2006/>.
- Rothe, A., Huber, C., Kreutzer, K., and Weis, W.: Deposition and soil leaching in stands of Norway spruce and European Beech: Results from the Höglwald research in comparison with other European case studies, *Plant and Soil*, 240, 33–45, 2002.
- Schindlbacher, A., Zechmeister-Boltenstern, S., and Butterbach-Bahl, K.: Effects of soil moisture and temperature on NO, NO<sub>2</sub>, and N<sub>2</sub>O emissions from European forest soils, *J. Geophys. Res.*, 109, D17302, 1–12, 2004.
- Schulze, E. D.: Air pollution and forest decline in spruce *Picea abies* forest, *Science*, 244, 776–783, 1989.
- Skiba, U., Sheppard, L., Pitcairn, C. E. R., Leith, I., Crossley, A., van Dijk, S., Kennedy, V. H., and Fowler, D.: Soil nitrous oxide and nitric oxide emissions as indicators of elevated atmospheric N deposition rates in seminatural ecosystems, *Environ. Pollut.*, 102, 457–461, 1998.
- Slemr, F. and Seiler, W.: Field measurements of NO and NO<sub>2</sub> emissions from fertilized and unfertilized soils, *J. Atmos. Chem.*, 2, 1–24, 1984.
- Smith, K. A., Thomson, P. E., Clayton, H., McTaggart, I. P., and Conen, F.: Effects of temperature, water content and nitrogen fertilisation on emissions of nitrous oxide by soils, *Atmos. Environ.*, 32, 3301–3309, 1998.
- Syväsalo, E., Regina, K., Pihlatie, M., and Esala, M.: Emissions of nitrous oxide from boreal agricultural clay and loamy sand soil, *Nutrient Cycling in Agroecosystems*, 69, 155–165, 2004.
- Umweltbundesamt: Daten zur Umwelt, Tech. rep., Umweltbundesamt, Berlin; Germany, 1997.
- van Cleemput, O. and Baert, L.: Nitrite – A key compound in N-loss processes under acid conditions, *Plant and Soil*, 76, 233–242, 1984.
- van der Eerden, L. J. M., de Visser, P. H. B., and van Dijk, C. J.: Risk of damage to crops in the direct neighborhood of ammonia sources, *Environ. Pollut.*, 102, 49–52, 1998.
- van Dijk, S. M. and Duyzer, J. H.: Nitric oxide emissions from forest soils, *J. Geophys. Res.*, 104, 15955–15961, 1999.
- Venterea, R. T., Groffman, P. M., Verchot, L. V., Magill, A. H., Aber, J. D., and Steudler, P. A.: Nitrogen oxide gas emissions from temperate forest soils receiving long-term nitrogen inputs, *Global Change Biol.*, 9, 346–357, 2003.
- Williams, E. J., Guenther, A., and Fehsenfeld, F. C.: An inventory of nitric oxide emissions from soils in the United States, *J. Geophys. Res.*, 97, 7511–7519, 1992.
- Wolf, I. and Russow, R.: Different pathways of formation of N<sub>2</sub>O, N<sub>2</sub> and NO in black earth soil, *Soil Biol. Biochem.*, 32, 229–239, 2000.