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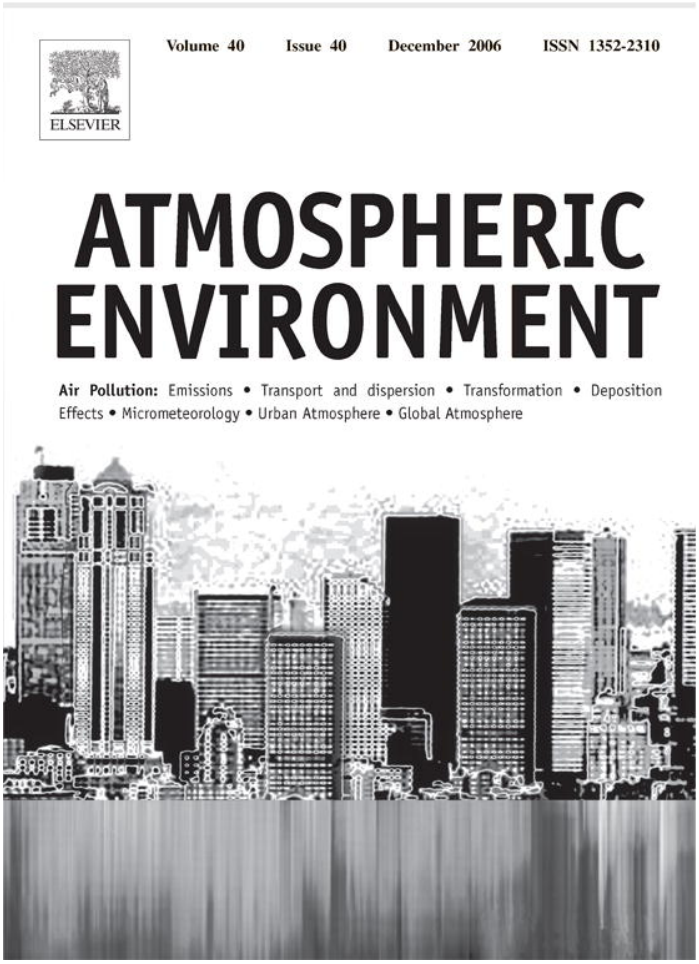

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Nitric oxide and nitrous oxide emission from Hungarian forest soils; linked with atmospheric N-deposition

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Abstract

Studies of forest nitrogen (N) budgets generally measure inputs from the atmosphere in wet and dry deposition and outputs via hydrologic export. Although denitrification has been shown to be important in many wetland ecosystems, emission of N oxides from forest soils is an important, and often overlooked, component of an ecosystem N budget. During 1 year (2002–03), emissions of nitric oxide (NO) and nitrous oxide (N_2O) were measured from Sessile oak and Norway spruce forest soils in northeast Hungary. Accumulation in small static chambers followed by gas chromatography-mass spectrometry detection was used for the estimation of N_2O emission flux. Because there are rapid chemical reactions of NO and ozone, small dynamic chambers were used for in situ NO flux measurements. Average soil emissions of NO were 1.2 and 2.1 $\mu g\,N\,m^{-2}\,h^{-1}$, and for N_2O were 15 and 20 $\mu g\,N\,m^{-2}\,h^{-1}$, for spruce and oak soils, respectively. Due to the relatively high soil water content, and low C/N ratio in soil, denitrification processes dominate, resulting in an order of magnitude greater N_2O emission rate compared to NO. The previously determined N balance between the atmosphere and the forest ecosystem was re-calculated using these soil emission figures. The total (dry + wet) atmospheric N-deposition to the soil was 1.42 and 1.59 $g\,N\,m^{-2}\,yr^{-1}$ for spruce and oak, respectively, while the soil emissions are 0.14 and 0.20 $g\,N\,m^{-2}\,yr^{-1}$. Thus, about 10–13% of N compounds deposited to the soil, mostly as NH_3/NH_4^+ and HNO_3/NO_3^-, were transformed in the soil and emitted back to the atmosphere, mostly as greenhouse gas (N_2O).
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1. Introduction

Forest ecosystem nitrogen (N) budgets have received considerable attention in recent years, in part due to increasing concern over increased N delivery to receiving waters from N-saturated ecosystems (Aber et al., 1998; Dise et al., 1998; Pregitzer et al., 2004). In order to create predictive models of ecosystem and stream response to elevated N deposition, all pathways of N input and loss must be known (Baron et al., 1994). Nitric oxide (NO) and nitrous oxide (N_2O) are known as intermediate products of nitrification and denitrification processes in soils, and forest soil may be an

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important source for these compounds. Recent research has shown that the emission of NO and N_2O depends, among other things, on forest type, soil characteristics, and on atmospheric deposition of N to the forest ecosystem (Groffman and Tiedje, 1989; Henrich and Haselwandter, 1997; Vermes and Myrold, 1992). In a cross-site study of 15 European forests sites (Pilegaard et al., 2004, 2006), the ratio of N-oxide emission to N-deposition ranged from very little up to 50%. Although denitrification has shown to be insignificant in many forest ecosystems (e.g. Gundersen, 1991; Myrold et al., 1989), it is clear that in some forests, soils may contribute to the atmospheric N-budget at both a local and a global scale. As a large part of these N emissions may occur in the form of N_2O, such emissions have significant implications for global warming.

Field-based measurements of nitrogen oxide emissions from forested soils are limited. The aim of this work was to extend the forest soil nitrogen oxide emission network to Eastern Europe and provide data for its special climate, N deposition history, and vegetation. This paper summarises the Hungarian contribution to the NOFRETETE objectives based on a 1-year long field study of nitrogen oxide emission from Sessile oak (*Quercus petraea*) and Norway spruce (*Picea abies* (L.) Karst.) forest soils in Hungary. A second objective was to compare the emission of nitrogen oxides from soils to the atmospheric N deposition fluxes, thus placing emissions into the context of the ecosystem N budget.

2. Measurements

2.1. Field sites

Both sites used in this study lie in the forested area of Mátra Mountains, NE Hungary, and are located in Ecology Research Stations of Forest Research Institute. Co-ordinates of the 8 ha Norway spruce stand (Nyirjes) are: 19° 57′ 05″ E, 47° 53′ 38″ N, $h = 560$ m. The age of the stand is 38–40 years, and leaf area index measured in 1993 is 3.3. Co-ordinates of the 20 ha Sessile oak stand (Tetves-rét) are: 19° 58′ 01″ E, 47° 51′ 56″ N, $h = 660$ m. The age of this stand is 71–76 years, and leaf area index was estimated as 4.0. The distance between the two stands is 5 km. Mean annual precipitation at both sites is 780 mm, and mean annual air temperature is 5.7 °C. The main characteristics of the stand and soil can be seen in Table 1.

2.2. N_2O soil flux measurements

N_2O fluxes were determined by small static (closed) chambers following methods of Christensen et al. (1990). A total of 8 parallel chambers were used at both sites. Circular rims for gas analysis chambers were placed approximately 3–4 m apart along a transect. These were left in situ for the duration of the experiment in order to avoid the high emission peaks frequently observed due to installation disturbance effects. The rims were pushed 4 cm into the soil and were covered by the chamber body only during the 30 min of the samplings, allowing normal light and precipitation exposure at all other times. Although there were not visible differences between soil conditions inside and outside the rims, some disturbances in soil moisture cannot be ruled out.

The area and volume of the chambers were 0.008 m^2 and 0.4 L, respectively. After closure, gas samples were taken at $t = 0$, 10, 20 and 30 min with a syringe. A total of 6 ml of sample was injected into a 5.6 ml evacuated tube. Accumulation of N_2O was measured by a gas chromatography–mass spectrometry (GC–MS) system. Emission fluxes were calculated from the accumulation of N_2O gas in the chamber. The calibration standard gas was 313 ppb N_2O in N_2, provided by NOAA, Environmental Monitoring and Diagnostics Laboratory. We sampled weekly except when soils were covered by snow. Pilot measurements for the spruce stand were taken June–August 2002, and regular measurements were taken October 2002–October 2003. We calculated the non-systematic error (coefficient of variation) of sampling and analysis with repeated sampling performed on 1 day at the two sites. The time difference between repeated samplings was 45 min. Assuming that the emission flux from the soil was stable during this time, our bulk (sampling and analysis) error is approximately 10%. Repeated GC–MS analyses from samples of 3 October 2002 from the oak site resulted in 52.1 and 51.4 $\mu g\,N\,m^{-2}\,h^{-1}$ mean calculated flux. During a test run by sampling every minute, the coefficient of variation determined from the detrended line was 11%.

There is evidence for a systematic underestimation of soil gas flux using closed chambers. For carbon dioxide soil efflux, Rayment (2000) pointed out one bias caused by the fact that the effective volume of a chamber is larger than the physical chamber volume since it also includes the volume of air-filled spaces in the soil. This underestimation

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Table 1
Stand and soil characteristics of the Norway spruce and Sessile oak stands used in this study (surveyed in 2000)

	Depth	Unit	Spruce	Oak
Stand density		trees ha^{-1}	1188	776
Stand height		m	20.1	20.5
Mean breast diameter		cm	20.1	22
Rooting depth		m	>1	>1
Soil type			Eutric Leptosol	Mollic Leptosol
Organic layer type			moder/mull	mull
Organic layer C stocks	Humus layer	$g\,C\,kg^{-1}$	236	144
Organic layer N stocks	Humus layer	$g\,N\,kg^{-1}$	12	9.3
Organic layer, C:N ratio	Humus layer		19.7	15.4
Organic layer, pH	Humus layer		4.5	5.7
Mineral soil, clay:silt:sand	0–10 cm	%	15:29:56	17:38:45
Mineral soil, clay:silt:sand	10–20 cm	%	18:31:51	20:42:38
Mineral soil, clay:silt:sand	20–40 cm	%	21:26:53	25:38:37
Mineral soil, C stocks	0–5, 5–10, 10–20, 20–40 cm	$g\,C\,kg^{-1}$	55.2, 29.8, 15.1, 9.6	65.2, 36.5, 27.7, 22.7
Mineral soil, N stocks	0–5, 5–10, 10–20, 20–40 cm	$g\,N\,kg^{-1}$	4.3, 2.5, 1.2, 0.8	4.8, 3.1, 2.2, 2.0
Mineral soil, C:N ratio	0–5, 5–10, 10–20, 20–40 cm		12.9, 11.9, 12.2,12.0	13.5, 11.9, 12.4, 11.5
Mineral soil, pH	0–5, 5–10 cm		3.6, 3.9	4.7, 4.3

increases with a decrease in the height of the chamber. In our case ($h = 5$ cm), using Rayment's estimates for an equivalent depth of air in soil, soil fluxes are underestimated by 24%. Conen and Smith (2000) predicted that N_2O concentration increases in the soil air immediately after closure of the chamber due to high gas concentrations in the upper part of the soil profile. Christensen et al. (1996) compared 10 different closed, dynamic chambers and micro-meteorological methods and found a good agreement between results. However, they also reported that the magnitude of underestimation is 20% using small chambers. In this study, the underestimation was not taken into account; therefore, the reported N_2O fluxes can be taken as a lower limit.

2.3. NO soil flux measurements

For the estimation of soil NO flux, small dynamic chambers were used with the same volume described above. A HORIBA gas monitor was used to detect the concentration of NO leaving the chambers at both the spruce and oak sites. The ozone-mixing ratio was simultaneously monitored. The calibration standard gas was 8 ppm NO/N_2. A Thermo Electron gas calibration system was used for multipoint calibration in the mixing ratio range of 0–10 ppb. The coefficient of variation determined for a calibration gas of 8 ppb was 0.9%. For soil samples with a mixing ratio of 1 and 10 ppb, the measured coefficients of variation were 5.3% and 1.5%, respectively. Since the average mixing ratio found during the flux measurements lies between these two figures, our estimated coefficient of variation ranges between 1% and 5%.

Ten-minute concentration averages were recorded. Flow rate of the air through the dynamic chamber was 0.327 $L\,min^{-1}$. The flux was calculated according to Meixner et al. (1997) as follows, taking into account the rapid chemical reaction of NO and ozone: $NO + O_3 \rightarrow NO_2 + O_2$.

The photolysis rate of NO_2 inside the dark chambers was estimated to be zero. Under steady state conditions the mass balance equation for NO can be written as

$$F_f + F_m + F_{bl} + F_{gp} = 0, \quad (1)$$

where F_f is the soil flux, F_m is the difference between fluxes entering and leaving the chamber, F_{bl} is the term for the wall effect, and F_{gp} is the loss of NO due to the chemical reaction with ozone. According to our measurements F_{bl} is negligible because of the relatively short residence time (~80 s) of the gas mixture in the chamber. The soil flux (in units of $\mu g\,N\,m^{-2}\,h^{-1}$) can be calculated by the following equation where the two terms on the right represent the input and output fluxes from the chamber and the effect of the chemical reaction, respectively:

$$F_f = \{[NO]_{out} - [NO]_{in}\} f_1 f_2 \times Q/A + \{k[NO]_{out}[O_3]_{out}\} f_1 \times V/A, \quad (2)$$

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where Q is the flow rate ($0.327 \times 10^{-3}\,m^3\,min^{-1}$), A is the surface of the soil covered by the chamber [$8 \times 10^{-3}\,m^2$], $[NO]_{out}$ and $[NO]_{in}$ are the NO mixing ratios leaving and entering the chamber [ppb], $f_1 = 14/V_t$, V_t is the molar volume at the given temperature t [°C] ($V_t = 0.0795 \times t + 22.41$), $f_2 = 60$ [$min\,h^{-1}$] is the conversion term from minutes into hours, V is the volume of the chamber, including tubing ($4.44 \times 10^{-4}\,m^3$), k is the reaction rate constant calculated as $k = 1.8 \times 10^2 \exp(-1400/T)$ [$ppb^{-1}\,h^{-1}$] (Seinfeld and Pandis, 1998), where T is the air temperature [K], and $[O_3]_{out}$ is the mixing ratio of ozone (ppb) leaving the chamber. Because the latter term was not recorded, soil flux was calculated first using $[O_3]_{out}$ assuming that: $[O_3]_{in} \approx [O_3]_{out}$. This approximation is valid, if ozone is in excess of NO. In our case, the average mixing ratios of NO and ozone were 1.43 and 47.1 ppb, respectively, showing order of magnitude differences in the mixing ratios. However, in some cases the mixing ratio of NO was high and $[O_3]_{in} > [O_3]_{out}$. For this reason $[O_3]_{out}$ was estimated from the following equation:

$$[O_3]_{out} = [O_3]_{in} - \{[NO]_{out} - [NO]_{in}\} \times F_{gp}/F_m = \{[NO]_{out} - [NO]_{in}\} \times V/Q\, f_2, \quad (3)$$

which takes into account NO loss via reaction with ozone through the ratio of F_{gp}/F_m. From this equation the exact calculation of $[O_3]_{out}$ is impossible, but through iteration we are able to estimate the mixing ratio of ozone in the output air. First, $[O_3]_{out}$ was calculated assuming $[O_3]_{in} \approx [O_3]_{out}$ for the calculation of F_{gp}. Then F_{gp} was re-calculated with the inferred $[O_3]_{out}$. This process was repeated 5 times until there was no further change in the estimate of $[O_3]_{out}$. The use of the correction for $[O_3]_{out}$ gives a lower value for the mean estimated soil fluxes by 10%. The difference is much lower when the mixing ratio of NO is low. The variation in diurnal flux rate was checked by longer (approximately 24 h) measurements. The signal was relatively stable for 20 h, but a small decrease was observed at night.

At the spruce site, NO flux was measured once or twice a month generally by 2 chambers (5 times by 8 chambers). We used the same permanently installed chamber rims as for N_2O, with different chamber covers. Three times per day, 10 min concentration averages were recorded per chamber, with background control measurements taken between each chamber measurement. Background concentrations were determined in open chambers.

The volume of the chamber with tubing was 0.444 L and the measured air flow rate was 0.327 L/min, and thus average transition time of the air in the chamber was 1.4 min. Measurements started after the signal stabilized, which we found to be about 2 min, and 10 min averages were recorded.

Ozone concentrations were measured at 5 different heights, from 3 m above the ground to 10 m above the canopy. This lowest measurement was used as the input concentration to the chamber. We chose a height of 3 m above the soil surface for this input value because ozone measurements closer to the soil can be confounded by materials having a UV absorption similar to that of ozone.

NO flux rates were measured only 4 times at the oak site, so the magnitude of yearly mean flux was estimated using the ratio of fluxes in spruce and oak forest measured during the same period (twice in May, and once in June and September, 2003). The ratio of observed fluxes during these measurements was 1.744. This factor was used to generate monthly values for NO flux in oak. Our NO flux estimate from the oak site therefore has a high degree of uncertainty, but data from both spruce and oak suggest that NO flux is quite low compared to N_2O.

Physical and chemical characteristics of the soil were measured in parallel with soil emission flux measurements. Soil temperature and moisture at three depths (5, 10 and 20 cm) have been recorded in the spruce stand since 1999 and since November 2002 in the oak stand. Soil moisture data are available only at 20 cm at the spruce stand. For the estimation of total atmospheric N-input to the canopy, dry deposition was inferred as $DD = C \times v$, where C is the daily mean concentration measured in 2001–03, v is the mean dry deposition velocity in the different seasons, determined during earlier field trials. This estimate considered the net dry flux of ammonia (NH_3) and nitrogen dioxide (NO_2) gases and nitric acid (HNO_3) vapor as well as the dry flux of ammonium (NH_4^+) and nitrate (NO_3^-) ions in aerosol particles.

Dry deposition velocity of NO_2 gas was measured for 3 years (1996 and 1998) by the gradient method described in Horváth et al. (1997, 1998). Dry flux was calculated as $F = -K_H\, dC/dz$, where K_H is the turbulent diffusion coefficient for the sensible heat flux, dC/dz is the concentration gradient. Concentration gradient was determined by concentration measurements at different heights (28, 23, 18 m)

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above the 16 m height canopy by a HORIBA APNA-350E NO_x gas monitor. Concentration averages of 5 min were logged at each level. Diffusion coefficients of gases were calculated according to the Monin–Obukhov's semi-empirical similarity theory (Weidinger et al., 2000) for stable and unstable stratification for the layer between 28 and 18 m.

Concentration of ammonia, HNO_3 and ammonium and nitrate particles were determined on the basis of 24-h sampling according to the EMEP (1996) filter pack method. Ammonia gas and ammonium particles were measured as ammonium in the solution of sampling filters by indophenol-blue spectrophotometry. HNO_3 and nitrate particles were analyzed by ion-chromatography. Dry deposition velocity was determined during an intensive campaign in 1998 (Horváth et al., 2001), using the gradient technique. Concentration gradient was determined by two-filter pack samplers settled at the height of 28 and 18 m. Dry flux (DD) was calculated by the Monin–Obukhovs's similarity theory mentioned above. Mean dry deposition velocity was calculated as $v = \mathrm{DD}/C$, where C is the concentration at the upper height.

Wet, through fall (TF) and stem flow (SF) deposition of nitrate and ammonium were also determined during 2001–03. Wet deposition (WD) of nitrogen was determined as $\mathrm{WD} = C \times p$, where C is the concentration of ammonium or nitrate measured in precipitation, p is the precipitation volume. Daily precipitation samples were taken by a wet-only collector out of the forest canopy. Ammonium and nitrate ions were determined by spectrophotometry and ion-chromatography, respectively.

Rain and snow samples were collected for TF by 5 collectors ($0.2\,m^2$ cross-section area) randomly placed under the canopy in each stand, and for SF by flexible tubes attached to the trunk of 10 selected trees in each stand. Details of sampling and measurement are described in Kovács and Horváth (2004) and Horváth (2004). At the spruce site, ozone concentrations were regularly recorded, and daily 24-h concentrations of N and S compounds were measured. There are various meteorological and forestry measurements at the two sites (wind, air temperature, humidity, litter fall, forest growth, etc.).

The relationships between wet (WD), dry (DD), TF, SF depositions can be expressed by the equation:

$$\mathrm{WD} + \mathrm{DD} = \mathrm{TF} + \mathrm{SF} + \mathrm{NCE}, \quad (4)$$

where NCE denotes net canopy uptake, or the amount of deposited N taken up by the plant though stomata (Lovett and Lindberg 1993, Ferm and Hultberg, 1999).

3. Results and discussion

3.1. Measured fluxes

Results of NO and N_2O flux measurements are summarized in Fig. 1 and Table 2. Average soil N_2O flux, measured between October 2002 and 2003 were 15 and $20\,\mu g\,N\,m^{-2}\,h^{-1}$ for spruce and oak, respectively (Fig. 1). Fluxes were not measured from the beginning of January to end of March, 2003 due to snow. Yearly averages were calculated from the monthly means of 4–5 measurements per month assuming zero flux for the winter period with snow cover (Table 2). During this period soil temperature was close to 0 °C.

NO flux was small compared to fluxes of N_2O. Significant soil NO flux was observed only during the summer. Average NO fluxes, measured in the same period as N_2O were 1.2 and $2.1\,\mu g\,N\,m^{-2}\,h^{-1}$ for spruce and oak, respectively.

3.2. Relation with flux controlling parameters

It is well known that NO is produced mainly in well-aerated soils by nitrification processes while both nitrification and denitrification processes are responsible for production of N_2O. Although many factors may control these processes and the subsequent NO and N_2O production and exchange to the atmosphere, most of the research papers agree, there are three major factors that influence the emission of these gases, namely the soil

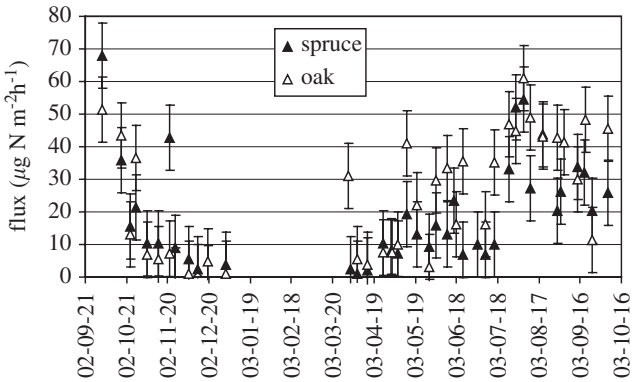

Fig. 1. N_2O soil flux (mean of 8 chambers) error bars represent the 10% bulk error (CV) of sampling and measurement.

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Table 2
Monthly and yearly means of NO and N_2O fluxes, soil temperature and moisture at 20 cm

Period	Spruce				Oak			
	Flux ($\mu g\,N\,m^{-2}\,h^{-1}$)		T (°C)	w_{soil}[a] (V/V)	Flux ($\mu g\,N\,m^{-2}\,h^{-1}$)		T (°C)	w_{soil}[b] (V/V)
	NO	N_2O			NO	N_2O		
October 2002	0.94	35.2	9.3	0.25	n.a.	36.0	n.a.	n.a.
November 2002	1.21	18.1	6.4	0.27	n.a.	4.7	7.3	0.27
December 2002	0.63	2.6	3.0	0.29	n.a.	2.0	3.3	0.29
January 2003	0[c]	3.7	0.9	0.30	n.a.	1.1	1.1	0.31
February 2003	0[c]	0[c]			n.a.	0[c]		
March 2003	0[c]	0[c]			n.a.	30.9	4.3	0.31
April 2003	1.04	4.0	2.8	0.30	n.a.	5.7	4.4	0.30
May 2003	1.17	11.3	8.1	0.27	3.10	16.8	11.0	0.28
June 2003	0.99	14.9	10.4	0.23	2.13	28.6	13.9	0.26
July 2003	5.66	22.5	11.6	0.22	n.a.	35.8	14.8	0.23
August 2003	1.23	36.5	13.4	0.26	n.a.	48.9	16.5	0.18
September 2003	1.59	28.2	11.1	0.15	1.31	32.8	12.8	0.15
Mean ± SE	1.20 ± 0.35	14.8 ± 2.8	5.6	0.26	2.09[d] ± 0.35	20.3 ± 2.9	8.2	0.26

[a]Saturation (i.e. water-filled pore space = 1.0) at $w_{soil} = 0.32$.
[b]Saturation (i.e. water-filled pore space = 1.0) at $w_{soil} = 0.34$.
[c]Estimated (snow cover on soil).
[d]Estimated from the ratio of spruce/oak fluxes from 3 months where data were available for both stations (mean of 2 May, June, September measurements for spruce: 1.25, for oak: 2.18, ratio = 1.744).

Table 3
Correlation (r) of N_2O and NO flux with soil temperature and moisture

	t_{soil}			w_{soil}		
	5 cm	10 cm	20 cm	5 cm	10 cm	20 cm
N_2O emission						
Spruce	0.45	0.67	0.67			NS
Oak	0.66	0.64	0.72	−0.63	−0.68	−0.67
NO emission						
Spruce	0.38	0.26	0.25			−0.29
Oak	0.53	0.49	0.48	NS	NS	NS

All relationships are significant at $P = 0.05$. NS = not significant.

moisture, the soil temperature, and the nitrogen availability (e.g. Meixner and Yang, 2004).

In our study, all gas flux rates were positively correlated with soil temperature, in both stands for all depths where soil temperature was recorded (Table 3), which was not surprising as many indices of soil microbial activity, such as respiration, are positively related to temperature (Chen et al., 2000; Curiel Yuste et al., 2004; Franzluebbers et al., 2002; Sulzman et al., 2005) and N-gas fluxes commonly increase with increasing soil temperature (e.g. Ludwig et al., 2001; Meixner and Yang, 2004; Schindlbacher et al., 2004). From the figures of Table 2 the higher yearly mean N-flux ($NO + N_2O$) for oak compared with spruce (22.4 against 16.0 $\mu g\,N\,m^{-2}\,h^{-1}$) may be attributed to the higher annual mean soil temperature in the oak stand (8.2 against 5.6 °C), but the difference in N-availability may also be responsible for this phenomenon. Though correlations are week, it can be followed from Table 3 that N_2O emission correlates better with soil temperature in deeper (20 cm) layer, while NO correlations are stronger with the upper layer temperature (5 cm) of the soil. This suggest that production of the two gases are effective at different depths, in accordance with other measurements (e.g. in Meixner and Yang, 2004). NO is mainly derived from aerobic nitrification and N_2O is mainly derived from denitrification, well-aerated soils in upper layers, should favor the production of NO whereas the presence of anaerobic microsites, due to thick litter layers or compaction, should favor N_2O production.

Correlation between emission rates of the two gases was calculated for the two sites when emission data were available ($r = 0.4$, $n = 20$). The week correlation is not surprising if we take into account the different mechanisms for NO and N_2O

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production. The correlation between the two fluxes are probably due to the temperature dependence of the NO and N_2O producing soil microbial processes.

Both NO and N_2O fluxes are negatively correlated with soil moisture (Table 3). Strongest correlation was observed between the N_2O flux and soil moisture in oak stand. In some cases the relation is not significant. Although the optimum soil moisture for NO and N_2O production varies with the type and characteristics of the soil, the optimum water content for NO production is well below that of for N_2O. Davidson and Schimel (1995) suggest a 60% of water-filled pore space (WFPS) as a border line over which denitrification exceeds nitrification and N_2O flux exceeds NO flux. According to Schindlbacher et al. (2004), optimum WFPS for NO production lies generally between 15% and 65% for German soils with an average of 45%. Davidson (1991) reported an optimum WFPS for NO production of about 30% in contrast to an optimum value for N_2O production of around 70%. In our cases the WFPS calculated from measured soil water content (SWC) and from measured bulk density is 53% for spruce and 59% for oak (Pilegaard et al., 2006). Thus, moisture of our soils was closer to the optimum denitrification range, where the NO production is suppressed, water content promotes the production of N_2O in contrast of NO. The one-order of magnitude higher ratio for N_2O/NO fluxes can thus perhaps partly be explained by the relatively high SWC in both our soils.

Although the water content effect the production of NO and N_2O in different ways a quasi-linear relationship was found between the log(N_2O/NO) flux and the WFPS in the HIP (whole in the pipe) model of Davidson et al. (2000). In the range of WFPS in our study (ranged between 53% for spruce and 59% for oak) Davidson's model predicts a ratio of $N_2O/NO \approx 10$ which perfectly agrees with our measurements. The lack of significant differences in flux rates from our sites in this study might suggest that our soils are quite similar with respect to moisture regime (mean WFPS 53–59% and mean $w_{soil} = 0.26$ V/V, Table 2, at both sites).

N availability is also important factor influencing the N_2O and NO productivity. Amount of available nitrogen depends on the N input to the soil. The most important N source for the soil is the litter fall (4.77 and 9.12 $g\,N\,m^{-2}\,yr^{-1}$, for spruce and oak, respectively). The bulk input, i.e., the total deposition is 6.19 and 10.7 $g\,N\,m^{-2}\,yr^{-1}$. In this interval HIP model of Davidson et al. (2000) predicts 0.05–0.23 $g\,N\,m^{-2}\,yr^{-1}$ $N_2O + NO$ emission that fits well again to our measurements: 0.14–0.20 $g\,N\,m^{-2}\,yr^{-1}$, for spruce and oak, respectively.

3.3. Comparison with other European measurements

Our results can be compared to those collected at 15 European forest sites surveyed by Pilegaard et al. (2006) as part of the EU-funded project NOFRETETE. The NOFRETETE locations represent different forest types (coniferous vs. deciduous) and span the typical nitrogen deposition rates found across Europe. In that survey, NO emissions varied between 0.006 and 81.7 $\mu g\,N\,m^{-2}\,yr^{-1}$ with an average of 15.8 $\mu g\,N\,m^{-2}\,yr^{-1}$ (including Hungarian sites) an order of magnitude higher than NO emission rate in our study. The N_2O emission rates were between 0.3 and 20.3 $\mu g\,N\,m^{-2}\,yr^{-1}$ with an average of 8.2 $\mu g\,N\,m^{-2}\,yr^{-1}$ 2–3 times lower than our measurements. While the total ($NO + N_2O$) emissions are about two times higher for European coniferous vs. deciduous forests (33.9 vs. 15.5 $\mu g\,N\,m^{-2}\,yr^{-1}$), in the current study there were no significant differences between the spruce and oak sites for flux rates of either NO or N_2O, although the oak site had slightly higher mean flux rates. At our Hungarian coniferous site the total ($NO + N_2O$) mean soil emission was half of the European average (16.0 vs. 33.9 $\mu g\,N\,m^{-2}\,yr^{-1}$), and was a little higher at our deciduous site compared to other European sites (22.4 vs. 15.5 $\mu g\,N\,m^{-2}\,yr^{-1}$). Our measured N_2O emissions were one-order of magnitude higher than NO emissions, which is a surprising result that was not observed at other NOFREETE sites. NO emissions were generally lower and N_2O emissions higher compared to other NOFREETE stations, but the total ($NO + N_2O$) emission (19.2 $\mu g\,N\,m^{-2}\,yr^{-1}$) is close to the European average (24.0 $\mu g\,N\,m^{-2}\,yr^{-1}$) taking into account both deciduous and coniferous forests.

The total ($NO + N_2O$) emission and N deposition gives a significant positive correlation in European sites. The mean TF + SF N deposition in Europe was 1.5 $g\,N\,m^{-2}\,yr^{-1}$ that is practically the same as our data in Table 4.

Although our total ($NO + N_2O$) emission fits well to the European flux rates the large differences in the emission of NO and N_2O can be explained by the dominance of denitrification processes in soils in Hungarian sites. Because NO is mainly derived from nitrification and N_2O is mainly derived from

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Table 4
Atmospheric deposition and emission of nitrogen compounds at the spruce and oak stands (flux [$g\,N\,m^{-2}\,yr^{-1}$])

Site	Spruce	Oak	Spruce	Oak	Spruce	Oak
Deposition (2001–2003)	Nitrate (NO_3^-)		Ammonium (NH_4^+)		Total N	
Atmospheric wet deposition to the canopy (WD)	0.25	0.25	0.29	0.29	0.54	0.54
Atmospheric dry deposition to the canopy (DD)[a]	0.56	0.56	0.60	0.60	1.16	1.16
Through fall deposition[b] (TF)	0.49	0.31	0.85	1.01	1.34	1.32
Stem flow deposition[b] (SF)	0.02	0.08	0.06	0.19	0.08	0.27
Atmospheric deposition to the soil (TF + SF)	0.51	0.39	0.91	1.20	1.42	1.59
Atmospheric dry deposition to the soil (TF + SF − WD = DD − NCE)	0.26	0.14	0.62	0.91	0.88	1.05
Net canopy exchange (NCE = WD + DD − TF − SF)					0.28	0.11
Total atmospheric deposition to the canopy (WD + DD = TF + SF + NCE)					1.70	1.70
NCE as % of total N deposition					16%	6.5%
Litter fall deposition[b] (LF)					4.77	9.12
Total deposition to the soil (TF + SF + LF)					6.19	10.7
Emission	Nitrous oxide (N_2O)		Nitric oxide (NO)		Total N	
Soil emission (SE)	0.13	0.18	0.011	0.018	0.14	0.20
Soil emission/atmospheric deposition to the soil (%) [100 × SE/(TF + SF)]					10%	13%

[a]Estimated from Horváth (2004) following measurements between 1996–98 in spruce, assuming the same dry deposition rate for oak and spruce sites.
[b]Courtesy of Miklós Manninger and Judit Sitkey, Forest Research Institute, Hungary.

denitrification, the ratio of N_2O and NO emission is increasing with the denitrification. There are two factors that are responsible for enhanced denitrification in Hungarian sites, the high WFPS and the low C/N ratio in the soil. The WFPS in the study of Pilegaard et al. (2006) varied between 21% and 60% with an average of 44%. Our values are 53% and 59% for spruce and oak, respectively, showing that our soils are among the most saturated ones, resulting in higher N_2O production. On the other hand, there is a strong significant negative correlation between the N_2O emission and C/N ratio (Pilegaard et al., 2006). The latter parameter varies between 12.9 and 37.7 in European soils, while our value are 12.9 and 13.5, being among the lowest in Europe. In the study of Pilegaard et al. (2006) it was found that net nitrification could be detected when ratio of C/N is higher than 28. These two factors, namely the high WFPS and low soil C/N ratio favor the N_2O production with parallel suppression of nitrification processes and NO production. The suppressed nitrification rate for our soil is quantified by the work of Ambus et al. (2006) where gross nitrification rates were measured in the samples collected at European NOFRETETE sites. According to this study negative ($-3\,\mu g\,N\,cm^{-3}\,d^{-1}$) net nitrification was measured in our spruce soil samples collected in late autumn that is the one of the lowest negative rate among the examined European soils.

3.4. Relation to the atmospheric N-deposition

The total atmospheric N-deposition to the canopy, calculated as the sum of wet + dry deposition, was estimated as $1.7\,g\,N\,m^{-2}\,yr^{-1}$ (Horváth, 2004). Deposition to the soil was estimated from TF and SF measurements, and should equal N deposition to the canopy minus net canopy exchange (NCE). NCE was calculated to be 16% of total N deposition to the spruce forest canopy, and 6.5% for the oak forest. Though litter fall deposition is much higher than other deposition forms, it represents the internal circulation of N-compounds inside the canopy (Table 4). Emission of NO and N_2O together returns 10–13% of the atmospheric deposition to the soil (TF + SF).

The estimate of canopy uptake by foliage in these two stands was 16% and 6.5% of total inorganic N deposition for the spruce and oak sites, respectively. This is quite low compared to results found for a variety of forests in the USA measured as part of the Integrated Forest Study (Lovett and Lindberg, 1993), where NCE was estimated to be about 40% of inorganic N deposition. These authors

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found a good correlation between NCE and total deposition, indicating that as deposition increases, N consumption in the canopy increases. There are many possible explanations for this discrepancy, including variations in methodology for measuring total N inputs. Alternatively, climatic differences and histories of N deposition to the sites may cause real differences in NCE among sites. The Hungarian forests in the current study have received chronic elevated N deposition for a longer period of time than have the US forests, and thus might be experiencing greater N saturation. Similarly, it is quite likely that chemical species of N in deposition, particularly in dry deposition, may be significantly different, and react differently on leaf surfaces. It is also possible that NCE is variable from year-to-year. An earlier (1996–98) study of atmospheric fluxes in these same forests (Horváth, 2004) measured higher N in wet deposition but lower N in TF and produced a higher estimate of NCE, more similar to estimates in the Lovett and Lindberg (1993) survey. TF deposition has been shown to be quite variable both spatially and temporally, and only long-term studies can address the variability of true NCE.

Comparing N deposition numbers and gas efflux values, we found that factoring in NO and N_2O emissions reduces the estimate of net N deposition to the canopy from 1.7 to 1.5–1.6 $g\,N\,m^{-2}\,yr^{-1}$, and thus does not affect this estimate significantly. We did not measure N_2 emission from the soil, which can be significant especially at high moisture levels, and thus our estimates of N flux from the soil is an underestimate. Nevertheless, fluxes of NO and N_2O were found to be a measurable portion of N deposition to soil, which was estimated as 1.42 and 1.59 $g\,N\,m^{-2}\,yr^{-1}$ for spruce and oak, respectively, and accounting for 10–13% of the total atmospheric N deposition to the soil. It is also important to note that while deposition to the soil is mostly as NH_3/NH_4^+ and HNO_3/NO_3^-, these compounds are transformed in the soil and can be emitted as a greenhouse gas (N_2O) back into the atmosphere. Thus, forest soils play a role in the transformation of deposited N compounds from regional or continental pollution sources into a greenhouse gas that acts at a global scale.

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References

Aber, J., McDowell, W., Nadelhoffer, K., Magill, A., Berntson, G., Kamakea, M., McNulty, S., Currie, W., Rustad, L., Fernandez, I., 1998. Nitrogen saturation in temperate forest ecosystems. BioScience 48, 921–934.

Ambus, P., Zechmeister-Boltenstern, S., Butterbach-Bahl, K., 2006. Sources of nitrous oxide emitted from European forest soils. Biogeosciences 3, 135–145.

Baron, J.S., Ojima, D.S., Holland, E.A., Parton, W.J., 1994. Analysis of nitrogen saturation potential in rocky mountain tundra and forest: implications for aquatic systems. Biogeochemistry 27, 61–82.

Chen, H., Harmon, M.E., Griffiths, R.P., Hicks, W., 2000. Effects of temperature and moisture on carbon respired from decomposing woody roots. Forest Ecology and Management 138, 51–64.

Christensen, S., Simkins, S., Tiedje, J.M., 1990. Spatial variation in denitrification: dependency of activity centers on the soil environment. Soil Science Society of America Journal 54, 1608–1613.

Christensen, S., Ambus, P., Arah, J.R.M., Clayton, H., Galle, B., Griffith, D.W.T., Hargreaves, K.J., Klemedtsson, L., Lind, A.-M., Maag, M., Scot, A., Skiba, U., Smith, K.A., Welling, M., Wienhold, F.G., 1996. Nitrous oxide emission from an agricultural field: comparison between measurements by flux chamber and micro-meteorological techniques. Atmospheric Environment 30, 4183–4190.

Conen, F., Smith, A., 2000. An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere. European Journal of Soil Science 51, 111–117.

Curiel Yuste, J., Janssens, I.A., Carrara, A., Ceulemans, R., 2004. Annual Q_{10} of soil respiration reflects plant phenological patterns as well as temperature sensitivity. Global Change Biology 10, 161–169.

Davidson, E.A., 1991. Fluxes of nitrous oxide and nitric oxide from terrestrial ecosystems. In: Rogers, J.E., Whitman, W.B. (Eds.), Microbial Production and Consumption of Greenhouse Gases: Methane, Nitrogen Oxides, and Halomethanes. American Society for Microbiology, Washington, DC, pp. 219–235.

Davidson, E.A., Schimel, J.P., 1995. Microbial processes of production and consumption of nitric oxide, nitrous oxide and methane. In: Matson, P.A., Harriss, R.C. (Eds.), Biogenic Trace Gases: Measuring Emissions from Soil and Water. Blackwell Scientific Publications Ltd, Oxford, pp. 327–357.

Davidson, E.A., Keller, M., Erickson, H.E., Verchot, L.V., Veldkamp, E., 2000. Testing a conceptual model of soil

emissions of nitrous and nitric oxides. BioScience 50, 667–680.

Dise, N.B., Matzner, E., Gundersen, P., 1998. Synthesis of nitrogen pools and fluxes from European forest ecosystems. Water, Air and Soil Pollution 105, 143–154.

EMEP, 1996. EMEP co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe. EMEP Manual for sampling and chemical analysis. EMEP/CCC-Report 1/95, NILU, Kjeller, Norway.

Ferm, M., Hultberg, H., 1999. Dry deposition and internal circulation of nitrogen, sulphur and base cations into a coniferous forest. Atmospheric Environment 33, 4421–4430.

Franzluebbers, K., Franzluebbers, A.J., Jawson, M.D., 2002. Environmental controls on soil and whole-ecosystem respiration from a tallgrass prairie. Soil Science Society of America Journal 66, 254–262.

Groffman, P.M., Tiedje, J.M., 1989. Denitrification in north temperate forest soils: relationships between denitrification and environmental factors at the landscape scale. Soil Biology and Biochemistry 21, 621–626.

Gundersen, P., 1991. Nitrogen deposition and the forest nitrogen cycle: role of denitrification. Forest Ecology and Management 44, 15–28.

Henrich, M., Haselwandter, K., 1997. Denitrification and gaseous nitrogen losses from an acid spruce forest soil. Soil Biology and Biochemistry 29, 1529–1537.

Horváth, L., 2004. Determination of the nitrogen compound balance between the atmosphere and a Norway spruce forest ecosystem. Nutrient Cycling in Agroecosystems 70, 143–146.

Horváth, L., Weidinger, T., Nagy, Z., Führer, E., 1997. Measurement of dry deposition velocity of ozone, sulfur dioxide and nitrogen oxides above Pine forest and low vegetation in different seasons by the gradient method. In: Borrell, P.M., Borrell, P., Cvitas, T., Kelly, K., Seiler, W. (Eds.), Proceedings of EUROTRAC Symposium '96 Garmisch-Partenkirchen, Germany 25–29 March 1996. Computational Mechanics Publications, Southampton, pp. 315–318.

Horváth, L., Nagy, Z., Weidinger, T., 1998. Determination of the dry flux of ozone and sulfur dioxide during the TRACT campaign. Atmospheric Environment 32, 1317–1322.

Horváth, L., Mészáros, R., Pinto, J.P., Weidinger, T., 2001. Estimate of the dry deposition of atmospheric nitrogen and sulfur species to spruce forest. In: Midgley, P.M., Reuther, M., Williams, M. (Eds.), Proceedings of EUROTRAC Symposium 2000 Garmisch-Partenkirchen, Germany 27–31 March 2000. Springer, Berlin, Heidelberg.

Kovács, E.A., Horváth, L., 2004. Determination of sulfur balance between the atmosphere and a Norway spruce forest ecosystem: comparison of gradient dry + wet and throughfall deposition measurements. Journal of Atmospheric Chemistry 48, 235–240.

Lovett, G.M., Lindberg, S.E., 1993. Atmospheric deposition and canopy interactions of nitrogen in forests. Canadian Journal of Forest Research 23, 1603–1616.

Ludwig, J., Meixner, F.X., Vogel, B., Förstner, J., 2001. Soil–air exchange of nitric oxide: an overview of processes, environmental factors, and modeling studies. Biogeochemistry 52, 225–257.

Meixner, F.X., Yang, W.X., 2004. Biogenic emissions of nitric oxide and nitrous oxide from arid and semi-arid land. In: D'Odorico, P., Porporato, A. (Eds.), Dryland Ecohydrology. Kluwer Academic Publishers B.V., Dordrecht, The Netherlands.

Meixner, F.X., Fickinger, T., Marufu, L., Serca, D., Nathaus, F.J., Makina, E., Mukurumbira, L., Andreae, M.O., 1997. Preliminary results on nitric oxide emission from a southern African savanna ecosystem. Nutrient Cycling in Agroecosystems 48, 123–138.

Myrold, D.D., Matson, P.A., Peterson, D.L., 1989. Relationships between soil microbial properties and aboveground stand characteristics of conifer forests in Oregon. Biogeochemistry 8, 265–281.

Pilegaard, K., and the NOFRETETE team, 2004. Nitrogen load and forest type determine soil emission of nitrogen oxides (NO and N_2O). Geophysical Research Abstracts 6, 05693, 2004.

Pilegaard, K., Skiba, U., Ambus, P., Beier, C., Brüggemann, N., Butterbach-Bahl, K., Dick, J., Dorsey, J., Duyzer, J., Gallagher, M., Gasche, R., Horvath, L., Kitzler, B., Leip, A., Pihlatie, M.K., Rosenkranz, P., Seufert, G., Vesala, T., Westrate, H., Zechmeister-Boltenstern, S., 2006. Nitrogen load and forest type determine the soil emission of nitrogen oxides (NO and N_2O). Biogeosciences Discuss 3, 837–869.

Pregitzer, K.S., Zak, D.R., Burton, A.J., Ashby, J., MacDonald, N.W., 2004. Chronic nitrate additions dramatically increase the export of carbon and nitrogen from northern hardwood ecosystems. Biogeochemistry 68, 179–197.

Rayment, M.B., 2000. Closed chamber systems underestimate soil CO_2 efflux. European Journal of Soil Science 51, 107–110.

Schindlbacher, A., Zechmeister-Boltenstern, S., Butterbach-Bahl, K., 2004. Effect of soil moisture and temperature on NO, NO_2, and N_2O emissions from European soils. Journal of Geophysical Research 109, D17302.

Seinfeld, J.H., Pandis, S.N., 1998. Atmospheric chemistry and physics: from air pollution to climatic change. Wiley, New York, Chichester, Weinheim, Brisbane, Singapore, Toronto.

Sulzman, E.W., Brant, J.B., Bowden, R.D., Lajtha, K., 2005. Contribution of aboveground litter, belowground litter, and rhizosphere respiration to total soil CO_2 efflux in an old growth coniferous forest. Biogeochemistry 73, 231–256.

Vermes, J.-F., Myrold, D.D., 1992. Denitrification in forest soils of Oregon. Canadian Journal of Forest Research 22, 504–512.

Weidinger, T., Pinto, J., Horváth, L., 2000. Effects of uncertainties in universal functions, roughness length, and displacement height on the calculation of surface layer fluxes. Meteorologische Zeitschrift 9, 139–154.

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