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Emission of gaseous nitrogen oxides from an extensively managed grassland in NE Bavaria, Germany.

I. Annual budgets of N_2O and NO_x emissions

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Abstract. In a one-year field study (June 1998 to April 1999), we quantified N_2O and NO_x emissions from an extensively managed grassland in NE Bavaria (Germany) in unfertilized controls and after application of slurry or mineral N (calcium ammonium nitrate), respectively. Emissions were measured every 2–4 weeks, with additional daily measurements for 10 days after each fertilizer application. The closed chamber method was used for N_2O and the open chamber method for NO_x measurements. Fertilizer applications resulted in significantly increased N_2O emission rates in comparison to the low annual mean of the control plots (1.4 μmol m^{-2} h^{-1}). Episodical emission peaks during the summer were attributed to high microbial activity after rainfall. Mineral N fertilization resulted in the highest emission rates. Cumulative annual N_2O emissions were 11.2 kg N ha^{-1} a^{-1} for the mineral N, 8.8 kg N ha^{-1} a^{-1} for the slurry and 3.4 kg N ha^{-1} a^{-1} for the control plots. This represents 10.5% (mineral N) and 7.2% (slurry) of the applied nitrogen. The fertilizer-induced N_2O emission factors on this extensively managed grassland are high in comparison to emission factors on intensively managed grassland and substantially higher than the 1.5% estimate used by the global emission inventory. NO_x emissions increased after the first fertilizer application in summer, but not after the two following fertilizations in fall and spring. Differences between treatments were not significant. Annual NO_x emissions were 1.9 kg N ha^{-1} a^{-1} for both, mineral N and slurry plots and 1.5 kg N ha^{-1} a^{-1} for the controls, representing 0.5% of the N applied with each fertilizer. The ratio of emitted NO_x to N_2O was 1:4.7 for both fertilized treatments (based on N-atoms).

Introduction

Nitrous oxide (N_2O) is a trace gas, which contributes approximately 5% to the anthropogenically induced greenhouse effect, despite its low atmospheric concentration of about 0.310 ppm (parts per million) (IPCC 1995). Due to its long atmospheric lifetime of ca. 130 years (IPCC 1992), it has a global warming potential of

320 relative to CO_2. N_2O is also the major source of stratospheric nitric oxide (NO) and therefore contributes indirectly to the destruction of the ozone layer (Crutzen 1981; Granli and Bøckman 1994). The atmospheric concentration of N_2O currently increases at a rate of ca. 0.25% per year (IPCC 1995).

Soils are responsible for about 70% of both, the natural and anthropogenically induced global annual N_2O emissions (IPCC 1995). Both, nitrification and denitrification, can produce N_2O as a by-product (Davidson 1991). Most of the N_2O emissions from soils derive from anthropogenic nitrogen (N) inputs (IPCC 1995; Mosier et al. (1998)). 30% worldwide and about 40% of the agriculturally used soils in Europe are grasslands, used either for grazing or for the production of silage or hay (Statistisches Bundesamt 1999). Grassland soils often receive high N inputs in the form of animal excreta or fertilizer and have high N turnover rates. Thus, they must be considered as one of the most important N_2O emitting terrestrial ecosystem types (Granli and Bøckman 1994).

Soils are also a significant source of NO and NO_2, together addressed as NO_x (Davidson and Kingerlee 1997). Tropospheric NO_x is an important part of summer “smog” (Crutzen 1981) and contributes to atmospheric N deposition, either directly or as nitrate. N inputs affect the N status of natural and semi-natural ecosystems considerably (Gebauer et al. 2000; Harrison et al. 2000). NO_x production in the soil is generally ascribed to denitrification and chemodenitrification, the chemical disintegration of HNO_2, which derives from NO_2^- in acidic soils (Scheffer and Schachtschabel 1998). There are, however, indications that nitrification is an important source of NO_x as well (Kester et al. 1997). NO_x emissions increase with decreasing soil water content (Skiba et al. 1992; Yamulki et al. 1995) and N losses as NO_x can be higher than through N_2O emissions in dry soils. For example, Yamulki et al. (1995) observed an NO/N_2O ratio of 271 after a period of 10 days with only 3 mm of cumulative rainfall.

Current trends in agricultural management of European grasslands generally go towards intensification and higher N inputs in regions with favourable climatic and soil conditions and towards more extensive use in less suitable areas (Knauer 1993). These land-use changes will affect the emission rates of gaseous nitrogen oxides on regional scales. So far, N_2O and NO_x emission measurements have focussed mainly on intensively managed agricultural systems (applications of $\geqslant$ 200 kg N ha^{-1} a^{-1}) (Bouwman 1990; Granli and Bøckman 1994; Velthof and Oenema 1995b; Fowler et al. 1997; Velthof et al. 2000) or on non-agricultural systems (e.g. Papen and Butterbach-Bahl (1999)). Information on extensively managed agricultural systems (N inputs $\leqslant$ 100 kg ha^{-1} a^{-1}) is still scarce. However, to improve the estimates of gaseous nitrogen oxides emissions on a regional or global scale this information is essential. Furthermore, N_2O and NO_x emissions have only rarely been monitored simultaneously.

Our aim was to quantify N_2O and NO_x emissions from an extensively managed grassland over a one-year period. Experimental plots received either slurry or mineral N (calcium ammonium nitrate) or no fertilization (control). Soil nitrate and ammonium concentrations were measured periodically. In parallel with the N_2O emission measurements, the stable isotope composition of the emitted N_2O, the fertilizers, and soil mineral N were analysed. The relative abundance of the stable isotopes of N and O is altered by chemical and biological turnover and can be used to gain insight into N_2O generating soil processes. Data of the stable isotope composition of fertilizers and soil nitrate and ammonium are included in this paper. Results of the N_2O isotope studies are published in an accompanying paper (Tilsner et al. 2002).

Material & methods

Field site

The field experiment was carried out on an extensively managed grassland near Bayreuth (NE Bavaria), Germany (49°55′ N, 11°31′ E). In this area agriculture is gradually extensified (Bayer. Staatsministerium für Ernährung, Landwirtschaft und Forsten 1998). The grassland is situated at an altitude of 355 m. The mean annual temperature in the area is 8.3 °C. Monthly mean temperatures range between −0.4 °C (January) and 17.9 °C (July). The mean annual precipitation is 680 mm with monthly means ranging between 40 mm (May) and 84 mm (July). The soil is a clay loam with a pH_{KCl} of 5.7 ± 0.2 and a pH_{H2O} of 6.3 ± 0.1 in the topmost 10 cm. The meadow is fertilized three times per year with 10–15 m^3 ha^{-1} slurry per application and mown 2–3 times for silage and hay production. Total biomass production during this study was 1.5×10^4 kg_{dw} ha^{-1} a^{-1} (dw: dry weight), of which 20% were contributed by legumes.

Design of the field experiment

Three treatments were set up on 4 × 4 m plots with four replicates each: (1) slurry surface application (75 kg N ha^{-1} a^{-1}, split in three applications), (2) mineral N fertilizer application (74 kg N ha^{-1} a^{-1} as calcium ammonium nitrate, split in three applications) and (3) unfertilized control. Mineral N and control treatments received water to compensate for the amount of liquid applied with the slurry. The fertilizer quantities (Table 1) were in the range of common agricultural practice in the area. Plots were distributed randomly in two parallel lines to limit interference with the farmer's work. Fertilizer applications were carried out in June and September 1998 and in March 1999 (Table 1), in parallel with the farmer's slurry applications on the rest of the meadow. Soil samples for concentration measurements and isotope analysis of soil mineral N were taken on days 4, 10, 31, 47, 257 (controls only), 264, 273 and 353 after the first fertilizer application.

N_2O and NO_x emissions were monitored from June 1998 to April 1999. Each fertilizer application was followed by 10 daily measurements with one to four measurements per plot and per day. Otherwise, emission measurements were carried out every two to four weeks (except for 12 weeks between September and December 1998, when the meadow was completely flooded due to heavy rainfall).

Table 1. Dates and amounts of applied N and δ^{15}N-N_{total}, δ^{15}N-NH_4^+, δ^{15}N-NO_3^- and δ^{18}O-NO_3^- values of the fertilizers as used for the one-year field experiment on an extensively managed grassland in NE Bavaria, Germany, with three different types of treatments: slurry application, mineral N (calcium ammonium nitrate) application and unfertilized control. The N contents of the slurry varied between 85.7 mmol N l^{-1} (March 1999) and 301.2 mmol N l^{-1} (June 1998). For the March 1999 fertilizer application, δ^{15}N means ± SD (n = 3) are given. For the two other fertilizations and δ^{18}O values, n = 1. Total annual δ^{15}N values were calculated as means weighted by the amount of applied N.

date	treatment	kg N ha^{-1}	mmol N m^{-2}	δ^{15}N [‰]	δ^{18}O [‰]
6 June 1998					
(day 0)	**slurry N_{total}**	42	301.2	8.6	
	mineral fertilizer N_{total}	13	89.6	– 0.7	
	mineral fertilizer NH_4^+			– 2.6	
	mineral fertilizer NO_3^-			1.8	*no data*
19 Sept. 1998					
(day 84)	**slurry N_{total}**	15	106.0	7.1	
	mineral fertilizer N_{total}	13	89.6	– 0.7	
	mineral fertilizer NH_4^+			–2.6	
	mineral fertilizer NO_3^-			1.8	*no data*
15 Mar. 1999					
(day 262)	**slurry N_{total}**	18	128.5	8.6 ± 0.4	
	mineral fertilizer N_{total}	48	341.9	–0.7 ± 0.2	
	mineral fertilizer NH_4^+			0.7 ±5.2	
	mineral fertilizer NO_3^-			0.5 ± 1.9	21.3
annual total[1] **or**					
annual mean[2]	**slurry N_{total}**	75	535.7	8.3	
	mineral fertilizer N_{total}	74	521.1	–0.7	
	mineral fertilizer NH_4^+			–1.5	
	mineral fertilizer NO_3^-			1.4	

[1] for amounts of applied N.

[2] for δ values.

Soil sample analyses

Soil samples from three depths (0–5, 5–10 and 10–15 cm) were taken with a corer of 8 cm diameter. Mineral N was extracted from the soil samples with 1 M KCl (200 ml per 100 g_{fw} (fw: fresh weight), shaken for 1 h). The NH_4^+ and NO_3^- concentrations in the KCl extracts were measured by flow injection analysis (QuickChem AE, Lachat Instruments, Milwaukee, USA). For N isotope analysis, NH_4^+-N and NO_3^--N were separated from subsamples of the KCl extracts from the 0–5 cm horizon by fractionary steam distillation according to Bremner and Keeney (1965) using a micro-distillation system similiar to that described by Gerlach (1973). 20

ml of each soil extract were distilled first with 0.4 g MgO and then with 0.2 g Devarda's reagent, for 8 min each. NH_3 developing in both reactions was trapped separately in 5 ml 0.01 M H_2SO_4. The solutes were then freeze-dried on silica.

The relative ^{15}N isotope abundance of NH_4^+-N and NO_3^--N was determined using an elemental analyser-isotope ratio mass spectrometer (EA-IRMS) coupling (EA type 1108 for Dumas combustion, Carlo Erba, Milano, Italy; ConFlo II interface and gas-IRMS delta S, both Finnigan MAT, Bremen, Germany). N_2 (99.9995%, Linde, Munich, Germany) calibrated against the reference substances N1 and N2 from the IAEA (Vienna, Austria) was used as a laboratory standard. The internal reproducibility of the mass spectrometer for N_2 measurements is typically ± 0.15‰ or better. Isotope ratios are presented as δ values, which are defined as:

$$\delta x = \left(\frac{R_{sample}}{R_{standard}} - 1\right) \times 1000 \quad [‰] \tag{1}$$

where δx is the δ value of the heavy isotope x and R is the ratio of heavy isotope (at%, atom percent) to light isotope (at%). The international standard for $\delta^{15}N$ is N_2 in ambient air (Mariotti 1983).

Samples for $\delta^{18}O$-NO_3^- measurements were prepared according to Durka (1994) and Voerkelius (1990). H_2O extracts from the 0–5 cm horizon (2 l H_2O_{dest} per 500 g_{fw}, shaken for 1 h) were filtered with active charcoal, followed by cation exchange (Kationenaustauscher I, Merck, Germany), and then neutralized with KOH. After elimination of sulphate and phosphate by precipitation with $BaCl_2$, samples were evaporated to dryness. Aliquots were heated with $Hg(CN)_2$ in an evacuated sealed tube to 550 °C for 6 h. The CO formed was converted to CO_2 by slow cooling of the tube. $\delta^{18}O$ of the CO_2 was analysed on a Finnigan MAT delta E IRMS by Hydroisotop GmbH, Schweitenkirchen, Germany. $\delta^{18}O$ values are based on standard mean ocean water (Vienna-SMOW) as international standard. The isotope composition of the fertilizers applied in the field experiment is included in Table 1.

Measurement of N_2O and NO_x emissions

N_2O emissions were measured with the vented closed flux chamber method, using a photoacoustic trace gas analyzer (Multigas Monitor 1302, Bruel & Kjaer, Ballerup, Denmark) in a setup similiar to that described by Velthof and Oenema (1995a). N_2O accumulation in the chambers (diameter 20 cm, height 17 cm) was measured at 0, 10, 20, 30 and 40 min. Emission rates were calculated from the slope of the N_2O accumulation (Velthof and Oenema 1995a).

An open flow-through chamber method was employed for NO_x measurements. We used the setup described by Ryden and Dawson (1982) and Yamulki et al. (1995), with Teflon clad PVC chambers (diameter 20 cm, height 17 cm, with an opening of 1 cm diameter in the topside to compensate for pressure fluctuations). O_3 and NO_x were removed from the air flow by active charcoal and $KMnO_4/Al_2O_3$

traps (Purafil, Headline Filters, INFILTEC, Speyer, Germany) before entering the chamber (Shepherd et al. 1991). The flux rate of the fresh air supply was 230 ± 5 $l\ h^{-1}$. Sample air was pumped to a chemiluminescent nitrogen oxides analyzer (Thermo Environmental Instruments, model 42, Franklin, MA, USA) through a Teflon tube. Emission rates were calculated from the NO_x concentration in sample air at steady state equilibrium between NO_x emission from the soil and removal in the air flow, i.e. when the NO_x concentration was constant (Ryden and Dawson 1982).

To estimate cumulative N_2O and NO_x emissions after each fertilizer application and for the entire year, time weighted means of emission rates ($\bar{j}$) were calculated for every plot. The time-weighting factor Δt_i was:

$$\Delta t_i = 0.5(t_{i+1} - t_{i-1}) \tag{2}$$

where t_i represents days since the first fertilizer application for the i^{th} measurement.

$$\bar{j} = \frac{\Sigma(j_i \times \Delta t_i)}{n\Sigma\Delta t_i} \tag{3}$$

with j_i being the emission rate corresponding to t_i and n being the number of measurements. Cumulative emissions were calculated by multiplying weighted mean emission rates with the corresponding time period and averaging for each treatment (n = 4). Fractions of applied N emitted as N_2O or NO_x, respectively, were calculated based on N atoms as:

$$\text{emission factor} = \frac{\text{total } N \text{ emission}_{\text{fertilized treatment}} - \text{total } N \text{ emission}_{\text{control}}}{\text{applied } N} \tag{4}$$

Statistical methods

The following statistical analyses were performed: (1) Comparison of cumulative emissions from the three treatments (n = 4) for each fertilizer application and the entire year and for both, N_2O and NO_x emissions. (2) Comparison of emission rates in the first 10 days after fertilizer applications (days 1–10, 84–94 and 262–272) with periods between fertilizations (days 11–83, 95–261 and 273–292) for each treatment and both, N_2O and NO_x emissions. (3) Comparison of winter emissions (days 174–252, 4 measurements) with a control data set of four zeros for each treatment for N_2O emissions. (4) Comparison of fertilized treatments with controls for each measurement day (n = 4) for N_2O emissions.

For all these analyses, data sets were first tested for normal distribution and homogeneity of variances. If more than 75% of the tested data groups fulfilled these requirements, comparisons were done by one-way ANOVA. When effects were significant at the 0.05 level, multiple comparisons of means by the *post hoc* LSD test were executed. If less than 75% of the tested data met the requirements for ANOVA analysis, comparisons were done by a non-parametric Kruskal-Wallis test. In case of significant effects ($\alpha = 0.05$), Schaich-Hamerle analysis was used for multiple comparisons of means. ANOVA analysis was possible for the comparison of fertilization and between-fertilization emissions of both, N_2O and NO_x and for treatment effects on cumulative NO_x emissions. For all other statistical analyses, the non-parametric test was employed. All results are given as means ± standard deviations (SD).

Results

Soil nitrogen

Due to the highly variable N concentration of the slurries, the amounts of N applied with the slurry and mineral fertilizers differed at each application (Table 1). The amount of mineral fertilizer chosen for the third application was selected so as to have the same total annual amounts applied to both treatments. $\delta^{15}N$ values ranged from −0.7‰ for the mineral fertilizer (N_{total}) to 7.1 − 8.6‰ for the slurry. $\delta^{18}O$ of NO_3^- contained in the mineral fertilizer was 21.3‰ (Table 1).

Soil mineral N concentration in the 0–5 cm horizon depended largely on the fertilizer applications (Figure 1). Without fertilization both, NO_3^- and NH_4^+ concentrations, were typically $\leqslant 0.5\ \mu mol\ g_{dw}^{-1}$. Both concentrations increased up to 1–10 $\mu mol\ g_{dw}^{-1}$ after applications, depending on the type of fertilizer and the applied amounts. Concentrations dropped to pre-fertilization levels within approximately 1 month. Similiar trends were observed in the 5–10 and 10–15 cm soil horizons, with lower amplitudes (data not shown). A significant increase in soil mineral N concentrations was also observed on the unfertilized control plots immediately after fertilizer applications. After the third fertilization, for which data immediately prior to the fertilizer application were available (for the control plots only), this increase could be shown to coincide with a brief decrease in $\delta^{15}N$-NH_4^+. $\delta^{15}N$-NH_4^+ increased in all treatments (including controls after the initial decrease) in the first ten days after fertilizations (Figure 1). Then, $\delta^{15}N$-NH_4^+ values dropped and pre-fertilization levels of −0.4 ± 5.0‰ were reached again within ca. 1 month. $\delta^{15}N$-NO_3^- remained constant at 1.4 ± 5.4‰ in all treatments. $\delta^{18}O$-NO_3^- values were 30.3 ± 2.6‰ for mineral N fertilization and 33.2 ± 2.3‰ for the controls (annual means).

N_2O emissions

N_2O emission rates from the fertilized treatments increased significantly after each fertilizer application (Figure 2): N_2O emission rates in the first ten days after each fertilizer application and in the subsequent periods until the next fertilizer applica-

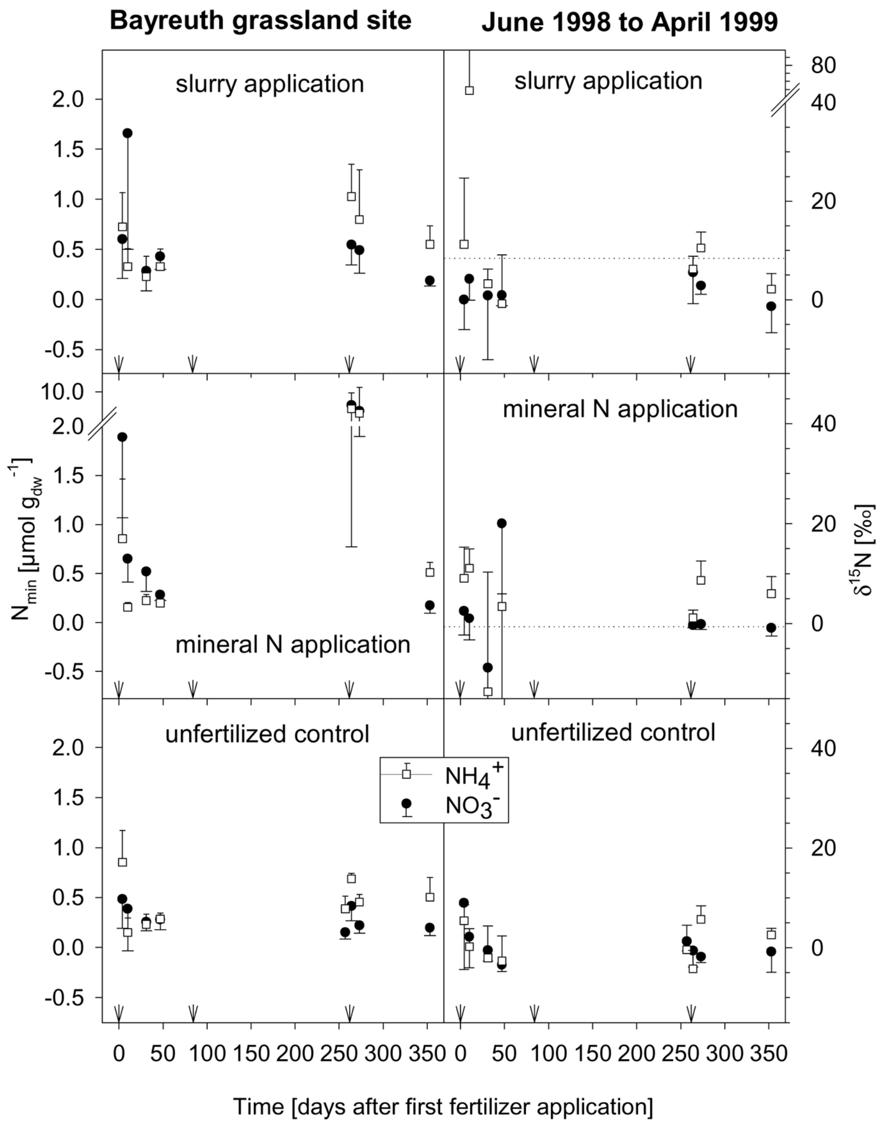

Figure 1. : Mean soil mineral N concentrations (left column) and mean $\delta^{15}N$ values (right column) in the uppermost 5 cm during the one-year field experiment on an extensively managed grassland in NE Bavaria, Germany, with three different treatments: slurry application, mineral N application and unfertilized control. Error bars represent standard deviations (n = 4). Fertilizer applications on 6 June 1998, 19 September 1998 and 15 March 1999 are indicated by arrows. Dotted lines indicate annual mean $\delta^{15}N$-N_{total} values of the fertilizers (slurry or calcium ammonium nitrate, respectively).

tion differed significantly for slurry plots ($p = 0.005$) and mineral N plots ($p < 0.001$), but not for the controls. When N_2O emissions from fertilized treatments were compared to emissions from the unfertilized control plots for each individual measurement day by non-parametric tests, N_2O emissions from slurry plots were significantly different on only 3 out of 36 days, 2 of which belonged to the first 10 days after the June 1998 slurry application. N_2O emissions from mineral N plots were significantly different from control plots on 8 of 36 days, 6 of which were during the first 10 days after the third (March 1999) fertilizer application. Between N applications, when soil mineral N had dropped to approximately pre-fertilization levels, N_2O emissions remained below 1 μmol m^{-2} h^{-1}, with occasional emission peaks in the summer, all occurring 0–1 days after rainfall events. N_2O emissions in winter (December 1998 – March 1999) were not significantly different from a test group of zero values for any of the three treatments.

Annual time-weighted mean N_2O emission rates were 3.6 ± 1.9, 4.6 ± 2.6 and 1.4 ± 0.8 μmol m^{-2} h^{-1} for the slurry, mineral N and control treatments, respectively (Table 2). Mineral N fertilization resulted in the highest total annual emissions (11.2 ± 6.5 kg N ha^{-1} a^{-1} for mineral N, 8.8 ± 4.6 kg N ha^{-1} a^{-1} for slurry, 3.4 ± 2.0 kg N ha^{-1} a^{-1} for control plots) and also showed the highest emission rates after the September 1998 and March 1999 fertilizations. After the June 1998 fertilization, the slurry plots had the highest emission rates. The mineral N plots emitted 10.5% of the total applied N, compared to 7.2% for the slurry treatment (Table 2). Total N_2O emissions from the mineral fertilizer plots differed significantly from the unfertilized control after the third fertilizer application and for the entire one-year experiment, but not after the first and second fertilizer applications. No significant differences in total N_2O emissions between either slurry and control plots or slurry and mineral N plots were found. By calculating total N_2O emissions from time-weighted mean emission rates, the temporal variability of the emissions caused by fertilizer applications has already been integrated. Thus, the high standard deviations encountered for some emission budgets represent the high spatial heterogeneity of the soil processes, which is well known from the literature (Granli and Bøckman 1994).

NO_x *emissions*

Mean NO_x emissions were low compared to the N_2O emissions throughout the one-year measurement period (Figure 3). No significant increases of emission rates were detectable after fertilizer applications by comparing the first ten days after each fertilizer application to the periods between fertilizations.

No significant differences between treatments could be detected for the annual budgets and for the first and second fertilizer applications, but both fertilized treatments emitted significantly more NO_x than the controls after the third application. Total NO_x emissions (Table 3) ranged from 1.5 ± 0.1 kg N ha^{-1} a^{-1} (control) to 1.9 ± 0.5 (mineral N) and 1.9 ± 0.6 kg N ha^{-1} a^{-1} (slurry), which represents 0.5% of the applied N for both fertilized treatments. The NO_x/N_2O emission ratio based on N-atoms was 1:4.7.

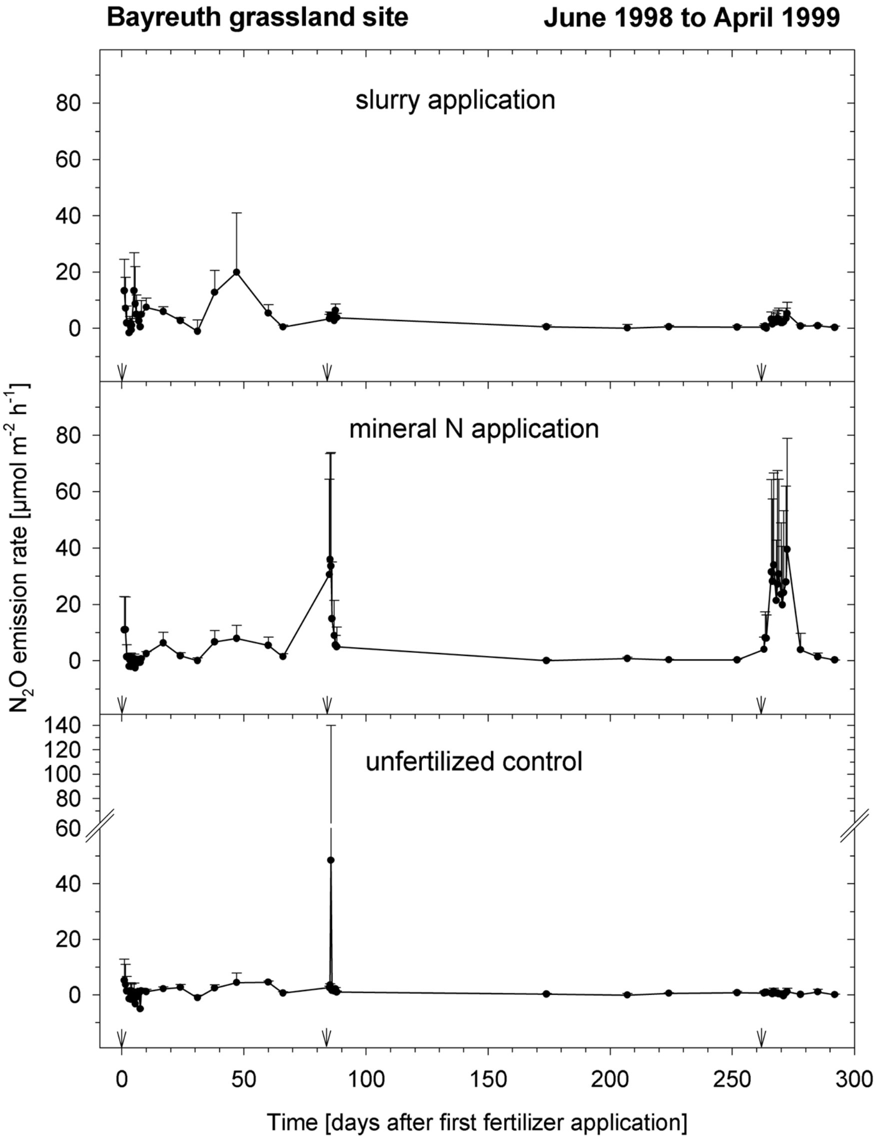

Figure 2. : Mean N_2O emission rates during the one-year field experiment on an extensively managed grassland in NE Bavaria, Germany, with three different treatments: slurry application, mineral N application and unfertilized control. Error bars represent standard deviations (n = 4). Fertilizer applications on 6 June 1998, 19 September 1998 and 15 March 1999 are indicated by arrows.

Table 2. Mean (± SD, n = 4) N_2O emission rate and total N_2O emission and emitted fractions of fertilizer N after each fertilization and during the entire one-year measurement period on an extensively managed grassland in NE Bavaria, Germany, with three different types of treatments: slurry application, mineral N application and unfertilized control. See material and methods for details of calculations. Indices a, b indicate groups of treatments without significant differences (Kruskal-Wallis test and Schaich-Hamerle multiple comparison of means, $\alpha = 0.05$).

period	treatment	emission rate[1]	total emission		emitted fraction of fertilizer N
		[μmol N_2O m^{-2} h^{-1}]	[mmol N_2O m^{-2}]	[kg N ha^{-1}]	[%]
June 1998 fertilization	**slurry**	8.9 ± 5.7	17.7 ± 11.3 ^{a}	5.0 ± 3.2	7.9
	mineral N	6.2 ± 3.8	12.3 ± 7.5 ^{a}	3.5 ± 2.1	13.8
	control	3.1 ± 2.5	6.1 ± 4.9 ^{a}	1.7 ± 1.4	
Sept. 1998 fertilization	**slurry**	1.4 ± 0.3	6.1 ± 1.3 ^{a}	1.7 ± 0.4	5.3
	mineral N	3.2 ± 3.9	13.7 ± 16.6 ^{a}	3.8 ± 4.7	22.3
	control	0.7 ± 0.3	3.2 ± 1.3 ^{a}	0.9 ± 0.4	
March 1999 fertilization	**slurry**	0.8 ± 0.7	2.0 ± 1.8 ^{ab}	0.6 ± 0.5	2.2
	mineral N	5.6 ± 3.6	13.9 ± 9.0 ^{a}	3.9 ± 2.5	7.7
	control	0.3 ± 0.1	0.7 ± 0.3 ^{b}	0.2 ± 0.1	
1 year	**slurry**	3.6 ± 1.9	31.4 ± 16.6 ^{ab}	8.8 ± 4.6	7.2
	mineral N	4.6 ± 2.6	40.1 ± 23.2 ^{a}	11.2 ± 6.5	10.5
	control	1.4 ± 0.8	12.0 ± 7.2 ^{b}	3.4 ± 2.0	

[1] time-weighted mean.

Discussion

Soil nitrogen

The observed increase in soil mineral N concentration and decrease in $\delta^{15}N\text{-}NH_4^+$ on the control plots immediately after slurry applications on the surrounding meadow by the farmer can be due to a deposition of volatilised ammonia, with the slightly acidic soil acting as an NH_3 trap. Considerable fractions of slurry N are known to be volatilised after surface application (Stevens and Laughlin 1997). Mineral N and $\delta^{15}N$ data immediately prior to the fertilizer application (day 257) are only available for the March 1999 application (day 264). At the sampling time, the soil water content was ~30% w/w. With approximate densities of 1 g cm^{-3} for the soil solution and 2.5 g cm^{-3} for the solid fraction, this corresponds to 28 cm^3 solid matter in 58 cm^3 fresh soil or ~48% v/v. Considering only the 0–5 cm horizon, where possible NH_3 inputs would arrive first, 1 m^2 of soil corresponds to 50,000 cm^3 soil, containing ca. 24,150 cm^3 solid fraction or 60,375 g_{dw}. The ob-

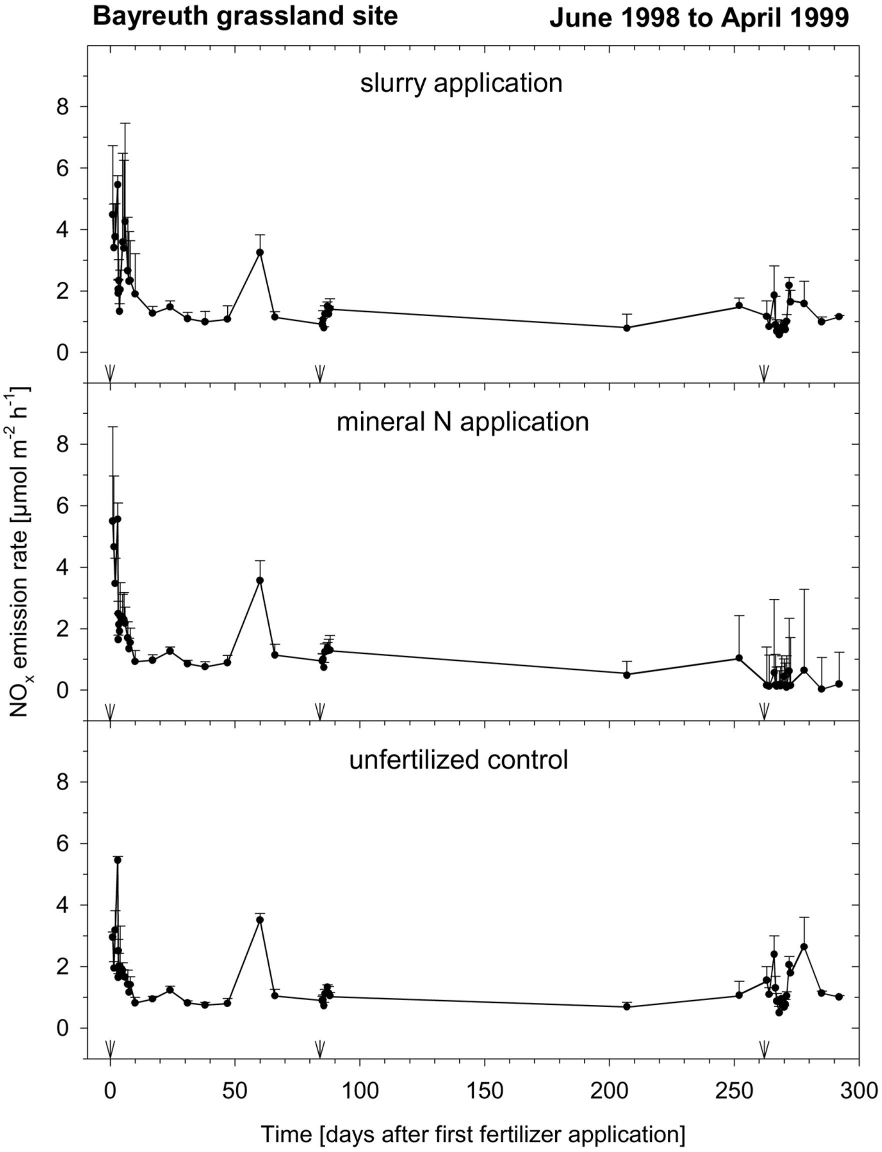

Figure 3. : Mean NO_x emission rates during the one-year field experiment on an extensively managed grassland in NE Bavaria, Germany, with three different types of treatments: slurry application, mineral N application and unfertilized control. Error bars represent standard deviations (n = 4). Fertilizer applications on 6 June 1998, 19 September 1998 and 15 March 1999 are indicated by arrows.

served NH_4^+ increase from 0.388 to 0.687 μmol g_{dw}^{-1} then corresponds to an approximal N input of 18.1 mmol NH_4^+ m^{-2}. With a maximum ^{15}N depletion of 40‰ through ammonia volatilisation (Högberg 1997), NH_3 volatilized from slurry of

Table 3. Mean (± SD, n = 4) NO_x emission rate and total NO_x emission and emitted fractions of fertilizer N after each fertilization and during the entire one-year measurement period on an extensively managed grassland in NE Bavaria, Germany, with three different types of treatments: slurry application, mineral N application and unfertilized control. See material and methods for details of calculations. Indices a, b indicate groups of treatments without significant differences (one-way ANOVA and *post hoc* LSD test, $\alpha = 0.05$).

period	treatment	emission rate[1]	total emission		emitted fraction of fertilizer N
		[μmol NO_x m^{-2} h^{-1}]	[mmol NO_x m^{-2}]	[kg N ha^{-1}]	[%]
June 1998 fertilization	**slurry**	2.6 ± 1.0	5.2 ± 1.9 ^{a}	0.7 ± 0.3	0.5
	mineral N	2.8 ± 1.2	5.6 ± 2.3 ^{a}	0.8 ± 0.3	2.3
	control	1.9 ± 0.1	3.8 ± 0.3 ^{a}	0.5 ± 0.04	
Sept. 1998 fertilization	**slurry**	1.1 ± 0.4	4.8 ± 1.8 ^{a}	0.7 ± 0.3	1.3
	mineral N	1.0 ± 0.3	4.1 ± 1.4 ^{a}	0.6 ± 0.2	0.8
	control	0.8 ± 0.1	3.5 ± 0.5 ^{a}	0.5 ± 0.1	
March 1999 fertilization	**slurry**	1.2 ± 0.1	3.0 ± 0.2 ^{a}	0.4 ± 0.03	1.7
	mineral N	1.3 ± 0.1	3.2 ± 0.2 ^{a}	0.4 ± 0.03	0.6
	control	0.3 ± 0.03	0.7 ± 0.1 ^{b}	0.1 ± 0.01	
1 year	**slurry**	1.6 ± 0.5	13.9 ± 4.4 ^{a}	1.9 ± 0.6	0.5
	mineral N	1.6 ± 0.4	13.9 ± 3.5 ^{a}	1.9 ± 0.5	0.5
	control	1.2 ± 0.1	10.8 ± 0.9 ^{a}	1.5 ± 0.1	

[1] time-weighted mean.

$\delta^{15}N = 7.1$ to 8.6‰ can reach a $\delta^{15}N$ value of ca. −32‰. Mixing of the pre-fertilization NH_4^+ pool of ~7.3 mmol m^{-2} ($\delta^{15}N = -0.4$‰) with 18.1 mmol NH_3 ($\delta^{15}N = -32$‰) would result in a $\delta^{15}N$-NH_4^+ of ca. −22.9‰. Deposition of ammonia volatilised from the slurry applied to the surrounding meadow therefore can easily account for the observed decrease in $\delta^{15}N$-NH_4^+ on the control plots. On the fertilized plots, soil mineral N $\delta^{15}N$ values will be much less affected because of the overriding effects of large N inputs with differing $\delta^{15}N$ values.

Increasing $\delta^{15}N$-NH_4^+ values in all treatments in the first week after fertilizer applications indicate nitrification of applied or deposited NH_4^+. Nitrification is accompanied by a discrimination against ^{15}N, resulting in an increase in $\delta^{15}N$ of the remaining NH_4^+ (Högberg 1997). The following slow decrease of $\delta^{15}N$-NH_4^+ was probably caused by dilution with ^{15}N-depleted NH_4^+ from mineralisation, which also discriminates against ^{15}N (Nadelhoffer and Fry 1988). $\delta^{15}N$-NO_3^- remained stable although the NO_3^- concentration increased after fertilizer applications, followed by a slow return to pre-fertilization levels. This can be explained with simultaneous formation of ^{15}N-depleted NO_3^- in nitrification and ^{15}N-enrichment of the soil nitrate pool by denitrification and biological nitrate uptake, resulting in a steady-state of the relative $^{15}NO_3^-$ abundance. All these processes discriminate against ^{15}N (Högberg 1997). The oxygen atoms in nitrate from nitrification originate from O_2 in air ($\delta^{18}O = 23.5‰$) and soil water ($\delta^{18}O \approx -10.0‰$ in the area of this investigation) with a ratio of 1: 2, resulting in very constant $\delta^{18}O$ values of 0.8–5.8‰ (Durka et al. 1994). $\delta^{18}O$ values of NO_3^- from both, nitrification and mineral N fertilizer (21.3‰, Table 1), are lower than those found in soil nitrate. This points towards N losses through denitrification, because denitrification also discriminates against ^{18}O, resulting in an ^{18}O enrichment in the remaining soil NO_3^- (Amberger and Schmidt 1987). For a complete mass balance, however, atmospheric N depositions, which can have $\delta^{18}O$ values of $\approx 60‰$ (Durka et al. 1994) also have to be considered. N deposition sampling was not included in this study.

N_2O emissions

According to Velthof et al. (1996), representative annual N_2O emission budgets can be achieved with weekly measurements in spite of the high temporal and spatial variability of emissions. Although we measured on 50 occasions in 10 months, our data are not evenly temporally distributed and the emission budgets (Table 2) have to be interpreted with some caution. Several authors have reported strong episodical N_2O emissions during freeze-thaw cycles in winter and spring (Christensen and Tiedje 1990; Röver et al. 1998; Papen and Butterbach-Bahl 1999), which can contribute up to 70% of the total annual emissions on an intensively used arable soil (220 kg N ha^{-1} a^{-1}) (Röver et al. 1998). We did not observe any freeze-thaw cycle related emission peaks in winter or spring, but cannot exclude them with any certainty, due to our non-continuous measurement scheme. However, even without such possibly unrecorded emission peaks, the percentages of fertilizer N lost as N_2O (mineral N fertilizer: 10.5%, slurry: 7.2%) are high in comparison to literature data. These are usually in a range of 0.001–4% (Bouwman 1990; Fowler et al. 1997) and the IPCC suggests 1.25% as a reference value (Salway 1995), although higher fractions have been reported as well (5%: Shepherd et al. (1991) and Clayton et al. (1994); 37%: Christensen (1983)). This indicates that N_2O emissions from extensively managed agricultural soils are not negligible and a broader data basis is necessary for evaluation and possibly revision of the IPCC reference value.

Considering the causes of the high emission factors, emissions from intensively managed agricultural soils with constantly high mineral N concentrations interestingly seem to depend mostly on climatic and soil conditions, such as rain events, soil water content and availability of organic carbon, rather than representing direct effects of N inputs (Flessa et al. 1998). On the other hand, N_2O emissions from generally N limited systems tend to react immediately to nitrogen applications (Bergstrom et al. 1994; Harrison et al. 1995; Velthof and Oenema 1995b). In grasslands, with their typically high organic matter content in the densely rooted top soil and a generally fast N turnover (Ellenberg 1977), this effect could be even more pronounced. The high emission factors found in this investigation point towards a fast and strong reaction to N inputs in a nitrogen-limited grassland soil.

For comparison of N_2O emissions from the different treatments, it has to be considered that although total annual N applications as slurry and mineral N were equal, applied amounts differed considerably at individual fertilizations, due to the variability of slurry N concentration. The rapid responses after fertilizer applications indicate a direct relationship between N input and N_2O emissions. Therefore, the emitted fraction of the applied N appears to be a better estimate of the treatment effect than total emissions or emission rates. After each fertilization and in the annual budget, the mineral N plots had the highest **relative** N losses, although cumulative annual emissions did not differ significantly between the fertilized treatments. Total emissions were also highest from the mineral N plots except after the June 1998 application, when the slurry plots emitted more N_2O (Table 2), but had also received a higher N input (Table 1). High relative N_2O losses from mineral fertilizer applications seem to be typical for grassland soils (Eggington and Smith 1986; Hansen et al. 1993) and are probably due to the combination of immediate availability of mineral N (particularly denitrifiable NO_3^-) with the inherently high organic carbon content of the top soil. After the application of slurry, which contains mostly organic N and NH_4^+, the soil nitrate pool does not build up to a size similar to that after ammonium nitrate application. Thus, the rapid N turnover of grassland soils results in a smaller denitrification potential. This pattern explains why total annual emissions were highest from the mineral N plots despite nearly identical total N inputs. However, NH_3 volatilisation, which may reduce the total N input by up to 50% (Stevens and Laughlin 1997), has to be taken into account for the slurry treatment. In sum, our results suggest that N_2O emissions will be lower if mineral N is more slowly released into the soil solution. The differences between fertilizer types indicate that N_2O emissions in extensively managed grasslands are directly related to soil mineral N content, although effects of other nutrients contained in the fertilizers and of fertilizer induced soil pH changes can not be excluded.

NO_x emissions

Annual NO_x emissions, the fractions of applied N lost as NO_x and the NO_x/N_2O emission ratio of 1: 4.7 found in this study all agree well with the literature (Yamulki et al. (1995, 1997)). Since no significant differences between slurry and mineral N treatments were found, climatic factors such as temperature and soil water content seem to have more influence on NO_x emissions than the nitrogen form available in the soil (Yamulki et al. 1995). According to Davidson (1991), there are more possible reactions for the consumption of NO_x in the soil than for N_2O. Thus, strongly hindered diffusion in a wet soil would affect NO_x emissions more than N_2O emissions, and it is generally observed that the ratio of NO_x/N_2O emission shifts towards NO_x in dry and towards N_2O in moist soils (Skiba et al. (1992, 1993)). Under dry conditions, NO_x/N_2O emission ratios can reach values of more than 100: 1 (Skiba et al. 1992). Yamulki et al. (1995) found that 82% of the annual NO emissions occurred in spring. The soil of this field study was very wet (groundwater 0–2.5 cm below the soil surface) from September 1998 until April 1999. Still, the only significant differences between fertilized treatments and unfertilized controls were found in spring 1999, when conditions were most unfavourable for NO_x production. It is possible that NO_x emissions from our field site would be much higher in spring, and thus in the annual budget, for a drier year. Further long-term studies are necessary to test whether our results are typical for extensively used grassland systems or represent unusual soil conditions.

Conclusions

The results of this long-term study of N_2O and NO_x emissions from an extensively managed grassland system, along with other emission measurements on a variety of grassland types during the EU project "COGANOG" (Controlling Gaseous Nitrogen Oxide Emissions from Grassland Farming Systems in Europe), will contribute to improve the database available for predictions of N_2O and NO_x emissions on medium to large scales. The IPCC default value of 1.25% fertilizer-induced emission for N_2O needs further evaluation and possibly correction on the basis of a greater set of emission data, which should include a broader variety of soil types and climate conditions than available so far. For smaller-scale predictions, e.g. for particular areas of Europe, regionally specific emission factors need to be available as well (Fowler et al. 1997). Knowledge on NO_x emissions is even more fragmentary still than for N_2O and more investigations are necessary to elucidate the source processes producing both gases and how they are related.

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