

Effect of mineral nitrogen fertilizer forms on N₂O emissions from arable soils in winter wheat production

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Abstract

Nitrogen fertilizers are supposed to be a major source of nitrous oxide (N₂O) emissions from arable soils. The objective of this study was to compare the effect of N forms on N₂O emissions from arable fields cropped with winter wheat (*Triticum aestivum* L.). In three field trials in North-West Germany (two trials in 2011/2012, one trial in 2012/2013), direct N₂O emissions during a one-year measurement period, starting after application of either urea, ammonium sulfate (AS) or calcium ammonium nitrate (CAN), were compared at an application rate of 220 kg N ha⁻¹. During the growth season (March to August) of winter wheat, N₂O emission rates were significantly higher in all three field experiments and in all treatments receiving N fertilizer than from the non-fertilized treatments (control). At two of the three sites, cumulative N₂O emissions from N fertilizer decreased in the order of urea > AS > CAN, with emissions ranging from 522–617 g N ha⁻¹ (0.24–0.28% of applied fertilizer) for urea, 368–554 g N ha⁻¹ (0.17–0.25%) for AS, and 242–264 g N ha⁻¹ (0.11–0.12%) for CAN during March to August. These results suggest that mineral nitrogen forms can differ in N₂O emissions during the growth period of winter wheat. Strong variations in the seasonal dynamics of N₂O emissions between sites were observed which could partly be related to weather events (e.g., precipitation). Between harvest and the following spring (post-harvest period) no significant differences in N₂O emissions between fertilized and non-fertilized treatments were detected on two of three fields. Only on one site post-harvest emissions from the AS treatment were significantly higher than all other fertilizer forms as well as compared to the control treatment. The cumulative one-year emissions varied depending on fertilizer form across the three field sites from 0.05% to 0.51% with one exception at one field site (AS: 0.94%). The calculated overall fertilizer induced emission averaged for the three fields was 0.38% which was only about 1/3 of the IPCC default value of 1.0%.

Key words: fertilizer-induced emission factor / nitrification / denitrification / post-harvest emission

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1 Introduction

The increasing demand for agricultural crops to feed the growing world population as well as to supply substitutes for fossil fuels will also enhance the need to use mineral nitrogen (N) fertilizers. The worldwide consumption of total N fertilizer is estimated to increase by about 2.7% from 2000 to 2050 (Tilman et al., 2011). In consequence, greenhouse gas (GHG) emissions are also expected to increase, especially N₂O, as it is quantitatively related to N fertilizer use (Crutzen et al., 2008). The global atmospheric N₂O concentration has been increasing since the middle of the 19th century from about 270 ppb to 319 ppb in 2005 and it is still rising (IPCC, 2007). In addition, N₂O has an average lifetime in the atmosphere of 114 years, a global warming potential of 298 CO₂ equivalents over a 100-year time horizon (Forster et al., 2007) and contributes to the destruction of stratospheric ozone (Crutzen et al., 1981; Ravishankara et al., 2009). N₂O accounts for about 7.9% of the total global GHG emissions (IPCC, 2007). In Europe (EU 27), N₂O emissions amounted

to 7.1% of the annual GHG emissions in 2010 (UNFCCC, 2013). The anthropogenic N₂O emission is the share of the total emission which is directly or indirectly caused by human activity with 38% (6.7 Tg N y⁻¹) of the total global N₂O emission in the 1990s (IPCC, 2007). Agriculture is the major source of N₂O, with agricultural soils representing the single largest source of anthropogenic N₂O emissions (Del Grosso et al., 2006), which account for about 65% of total global N₂O emissions (Prather et al., 1995). In adopting the Kyoto protocol the European Union agreed to reduce emissions of N₂O and other greenhouse gases. In order to achieve this, N₂O mitigation strategies have to be employed to enable more efficient management of N flows in agricultural ecosystems by, e.g., reducing total N input, adapting N input to plant demand, or using different application strategies.

In soils, N₂O is mainly formed during nitrification and denitrification; both processes are stimulated by the input of N fertilizers. During nitrification N₂O can be formed via two biochemical pathways. One possible pathway is a spontaneous



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reaction, in which hydroxylamine is converted to N₂O as a by-product during ammonium oxidation (Stein, 2011). The second possible pathway is the so-called nitrifier denitrification (ND), in which N₂O is an intermediate of the reduction of nitrite to N₂ by specific nitrifying bacteria (Wrage et al., 2004; Kool et al., 2011). During denitrification, N₂O can be emitted through the reduction of nitrate to N₂.

The mineral N fertilizers commonly used in agriculture can be classified as amide-based N fertilizers (urea), ammonium-based N fertilizers (e.g., ammonium sulfate) and nitrate-based N fertilizers (e.g., calcium nitrate). Depending on the N form applied, N₂O losses can occur due to nitrification and/or denitrification. The IPCC (Intergovernmental Panel on Climate Change) default emission factor for direct N₂O emissions from soils after fertilizer application is 1.0% of N applied for all mineral N forms. In contrast, a review by Eichner (1990) indicated differences in N₂O emissions depending on N fertilizer forms applied. In addition, other work by Clayton et al. (1997) and McTaggart et al. (1997) in the UK as well as work by Henault et al. (1998) in France suggested that there may be differences in N₂O emissions depending on N fertilizer forms under some conditions. From a meta-analysis of about 846 N₂O emission measurements from agricultural fields, differences in N₂O emissions between N fertilizer forms were found (Bouwman et al., 2002). The statistical evaluation of the analyzed experiments showed N₂O emissions in the order of urea > ammonium sulfate (AS) > calcium ammonium nitrate (CAN) > calcium nitrate (CN). However, this data set contained only very few experiments that focused mainly on N form comparisons considering the effect on N₂O emission from soil. Stehfest and Bouwman (2006) extended the 2002 data set, which resulted in less difference in N₂O emissions between N-fertilizer forms compared to earlier results. This might be due to the fact that data sets of different measurement periods, different application rates, countries and environments, and data quality were pooled, which might hide differences between N forms in N₂O emissions.

The objective of this field study was to evaluate in more detail the influence of different mineral N fertilizer sources on N₂O emissions from different types of agricultural soils. This can contribute to a more robust evaluation of the climate change mitigation potential of using different forms of fertilizer N in different cropping environments.

2 Material and Methods

2.1 Field trials with winter wheat

The field experiments were conducted on a one-year measurement basis at three sites in North-West Germany Lavesum (LAV; 51°46'31 N, 7°9'46 E), Billerbeck (BIL; 51°57'5 N, 7°16'58 E) and Münster (MUE; 52°0'47 N, 7°35'57 E) with a maximal distance of 30 km. Two field trials (LAV and BIL) were conducted in 2011/2012 and one field trial (MUE) in 2012/2013. Relevant soil chemical and physical characteristics are summarized in Table 1.

Winter wheat was sown at a density of 350 plants m⁻², with weed control and crop protection (including growth regulators) according to common regional farming practice. Three mineral N forms were evaluated: (1) urea [CO(NH₂)₂; 46% N], (2) ammonium sulfate [AS: (NH₄)₂SO₄; 21% N], and (3) calcium ammonium nitrate [CAN: NH₄NO₃; 27% N], each at an application rate of 220 kg N ha⁻¹. In addition to the fertilizer treatments a non-fertilized control treatment was included. The different N forms were broadcast-applied as solid N fertilizer on plots of 3.5 m × 10 m in a completely randomized design. Mineral N fertilizer (220 kg N ha⁻¹) was split-applied at three phenological stages at field sites LAV and BIL, where 80 kg N ha⁻¹ were applied at tillering, 70 kg N ha⁻¹ at stem elongation and 70 kg N ha⁻¹ at the booting stage. Field site MUE received the same total amount of N fertilizer with split applications of 100 kg N ha⁻¹ at tillering, 80 kg N ha⁻¹ at stem elongation and 40 kg N ha⁻¹ at the booting stage.

Each field site was equipped with a weather monitoring station (iMetos, Pessl Instruments, Weiz, Austria) to record air temperature at 1.2 m height, soil temperature at 10 cm soil depth and rainfall. Volumetric soil water content at 0.15 m soil depth was measured at two field sites (LAV, BIL) with time domain reflectometry (TDR; Mini Trace Kit; Soil Moisture Equipment Corp., Santa Barbara, CA, USA) during the growth period. Bulk density for each field site was determined from core samples (three replications), which were taken by drilling metal cylinders into the undisturbed soil to a soil depth of 0.15 m. The fresh matter of the samples was determined; afterwards the samples were oven-dried (105°C) and weighed again. The bulk density was then calculated as the mass of soil divided by the volume as a whole. Water-filled pore space

Table 1: Site-characteristics, pre-crop, soil texture, N_{min} (NO₃⁻-N + NH₄⁺-N), total N and C, and soil pH of three field trials.

Location	Experimental year	Pre-crop	Soil texture	Sand / %	Silt	Clay	N _{min} * / kg N ha ⁻¹	Total N / %	Total C	pH _{CaCl2}
Billerbeck (BIL)	2011/2012	oil seed rape	clay loam	35.5	31.1	33.4	24	0.16	1.48	6.5
Lavesum (LAV)	2011/2012	maize	silt loam	21.2	71.2	7.5	13	0.15	1.82	5.3
Münster (MUE)	2012/2013	winter wheat	clay	17.9	25.9	56.2	41	0.18	1.9	7.4

* N_{min}: top soil (0–30 cm) before first N fertilizer application.

Table 2: Mean monthly precipitation for three experimental sites (LAV, BIL, MUE) and 50-year long-term average of precipitation during the growth period (Mar–July) and post-harvest season (Aug–Feb).

Parameter	Year	Site	Mar	April	May	June	July	Aug	Sept	Oct	Nov	Dec	Jan	Feb	Sum		
															Growth period	Post-harvest	Total
Precipitation / mm	2011	BIL	10	27	25	72	94	119	53	6	0	151	144	23	228	496	724
	2011	LAV	17	22	27	88	94	117	61	104	11	185	169	27	248	674	922
	2012	MUE	14	60	38	96	112	66	54	64	35	114	59	32	320	424	744
50-y avg.			68	56	70	80	86	80	73	70	80	85	81	58	360	527	887

(WFPS) was calculated from gravimetric soil water content assuming a standard particle density of 2.65 g m^{-3} for mineral soils. Prior to each fertilizer application and at harvest, soil samples were taken at two depths (0–15 cm and 15–30 cm) from all pots and analyzed for $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$ contents. Above-ground biomass and grain yield were determined at maturity. Cumulative rainfall during the growing season (mid of March to end of July) ranged from 228 mm to 320 mm in the three field experiments and corresponded to 63–89% of the 50-year average amount of rainfall (Table 2).

2.2 Incubation experiment

Parallel to the field experiments, an incubation experiment with soil from the experimental field Lavesum (LAV) was conducted in the greenhouse to measure the rate of nitrification of applied urea and AS during a period of 20 d. During the experiment, temperatures ranged between 20°C during daytime and $16\text{--}18^\circ\text{C}$ during the night. The sieved soil (0.7 kg) was filled into PVC pots of 0.77 L volume (diameter: 7 cm ; height: 20 cm). Urea and AS were applied in granular form to the soil surface with an amount of $55 \text{ mg N kg soil}^{-1}$ (equivalent to 100 kg N ha^{-1} based on surface area). After urea and AS application, the soil was irrigated to a water-holding capacity of 70% and covered with parafilm to avoid water loss via evaporation. Soil samples were taken 0, 1, 2, 3, 6, 9, 13, and 20 d after N application to determine the mineral N status of the soil as well as the soil pH.

2.3 Nitrous oxide sampling and measurements

In the field experiments, emissions of N_2O were measured using the closed-chamber method (Hutchinson and Mosier, 1981). Gas chambers were constructed from PVC cylinders (60 cm diameter), adjustable in height to adapt the chamber to plant growth by installing an elongation part which fits between soil rings and chamber. Prior to the first N fertilizer application, soil rings (60 cm diameter, 10 cm height) were permanently installed in each plot by pushing them about 5 cm into the soil. At each sampling date, the chambers were fitted to the soil rings and sealed with a rubber band on the outside to make them gas-tight. Changes in headspace gas concentrations were measured at a time interval of 0–30–60 min after chamber closure. For each sampling, 30 mL of gas from the headspace in the chamber were sampled with a syringe

equipped with a three-way cock (Braun Melsungen AG, Melsungen, Germany) and injected into pre-evacuated glass vials (12 mL ; Labco Limited, Ceredigion, UK). Nitrous oxide concentrations were analyzed using gas chromatography GC (Agilent Technologies, Santa Clara, CA, USA) equipped with ECD (Electron Capture Detector; detector temperature 330°C) and TCD (Thermal Conductivity Detector; detector temperature 200°C) in combination with an auto-sampler (Gilson Inc., Middleton, TN, USA). The three different concentrations were then used to calculate the emission per chamber area and minute with linear regression and finally extrapolated to emissions per hectare and day. After each N application, gas samples were taken daily for a period of 1 week and every 2–3 d thereafter until the end of the growth period. Post-harvest emissions were determined once or twice per week. After harvest, the soil rings were removed for soil tillage and shortly afterwards installed again in the same treatment plots, but not in exactly the same position as during crop growth.

Nitrous oxide flux rates were calculated using the slope of the temporal change in gas concentration within the closed chamber considering chamber volume and surface area of the chamber. Cumulative N_2O emissions were calculated by linear interpolation between calculated daily fluxes. Emission rates are expressed as arithmetic means of the three replicates. To derive the mineral N fertilizer-induced N_2O emission (EF) in % of N applied, the cumulative N_2O emissions from the non-fertilized (control) plots were subtracted from total cumulative N_2O emissions during the experimental time (IPCC, 2006). The non-fertilized control plot represents the natural N_2O background emission for the respective experimental site during the experimental period. Nitrous oxide emissions per ton of product (yield-scaled N_2O emission) were calculated by dividing the cumulative one-year N_2O emission [$\text{g N (ha} \cdot \text{a)}^{-1}$] with the obtained grain yield (t ha^{-1}).

2.4 Soil analysis

For the analysis of soil N_{min} ($\text{NO}_3^-\text{-N}$ and $\text{NH}_4^+\text{-N}$) in the incubation experiment and field experiments, samples of 2 mm sieved moist soil were extracted with 0.01 M CaCl_2 solution for 60 min. The extracts were filtered and analyzed for $\text{NO}_3^-\text{-N}$ and $\text{NH}_4^+\text{-N}$ colorimetrically using a continuous-flow analyzer (CFA, Continuous Flow Analyzer, SPX Flow Technology Nor-

derstedt GmbH, Norderstedt, Germany) equipped with an autosampler (Technicon Corporation, Terrytown, NY, USA).

the span for which a local cubic function is fitted. The package was also used to plot the data.

2.5 Statistical analysis

Statistical analyses were conducted using the statistical software package SPSS Statistics version 20.0 (SPSS Inc., Chicago, IL, USA). Tukey's HSD post-hoc tests with $P = 5\%$ were used to reveal significant differences in cumulative N₂O emissions between treatments for each of the three field trials independently. Additionally, statistical analysis of cumulative N₂O emissions for field sites BIL and LAV during growth period and post-harvest was carried out using pair-wise comparison of treatments for growth period and post-harvest emissions separately. Family-wise error rate of 0.05 was controlled by the method of Holm (1979). Statistical differences are referred to in the text as significant at the $P = 5\%$ level.

Field data for sites LAV, BIL and MUE are displayed as smoothed curves to show important patterns within the time series. For each N form, a curve was computed based on measured data by a local regression method called "loess splines", as implemented in the free software R (*R Core Team*, 2013) in the package "ggplot2" (Wickham, 2009). The function used is named "geom_smooth()". The degree of smoothing of a time series is controlled by the relative size of

3 Results

3.1 Cumulative N₂O emissions

Cumulative fertilizer-induced N₂O emissions from the three experimental sites were significantly higher than from the non-fertilized control treatments during the growth period of winter wheat (Fig. 1A, B, C), except for the CAN treatment at site BIL (Fig. 1B). In two (LAV, BIL) of three field sites urea caused significantly higher N₂O emissions compared to the CAN treatment, with more than two times higher N₂O emissions than from CAN at sites LAV and BIL (Fig. 1), respectively; while in 2012 at site MUE no significant difference in N₂O emissions between N fertilizer forms was detected.

During the growth period the cumulative N₂O emission from the AS treatment at sites BIL and LAV were 11% and 29% lower compared to the N₂O emission from urea, although this difference proved not statistically significant. At site BIL, the percentage of N₂O loss during the growth period in relation to the total N applied (EF, emission factor) ranged between 0.12% (CAN) and 0.28% (urea). At site LAV the EFs were 0.11% (CAN) and 0.24% (urea), whereas at site MUE the EFs

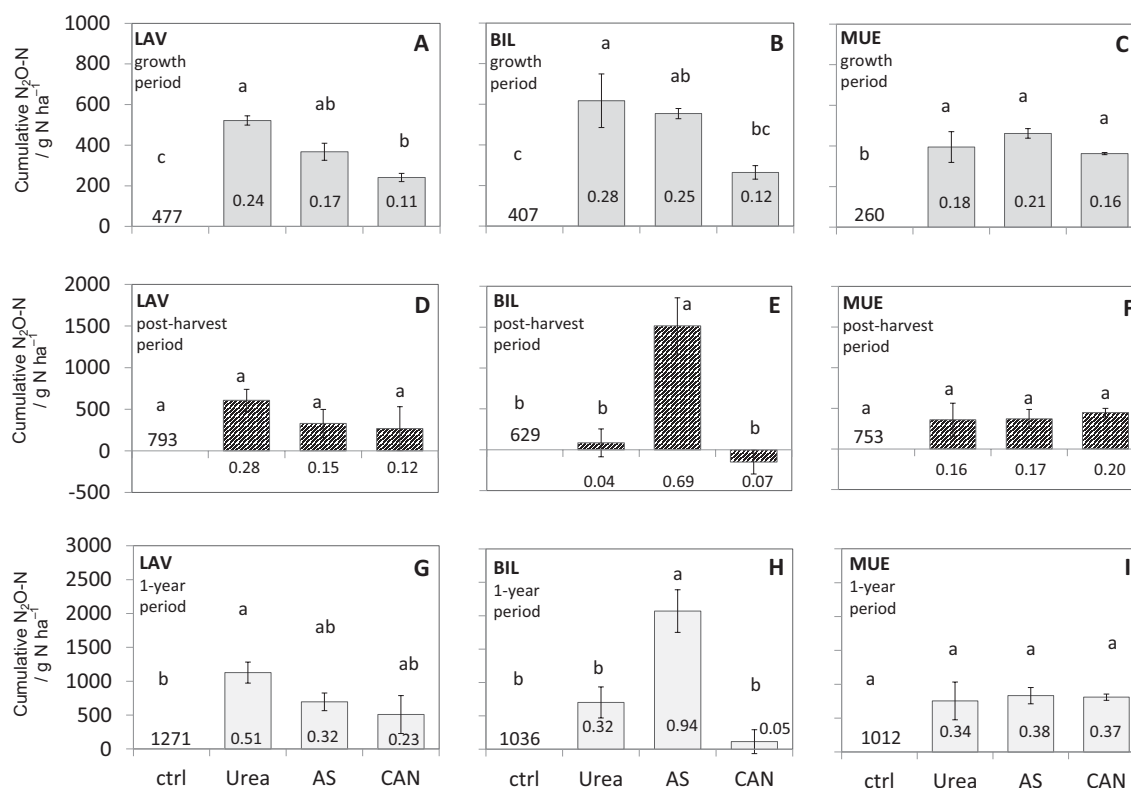


Figure 1: Cumulative fertilizer-induced N₂O emissions from soil after application of different mineral N fertilizer forms during the growth period (A, B, C; March–August; ≈ 140 d), during the post-harvest season (D, E, F; August–March; ≈ 220 d), and for the entire one-year period (G, H, I) at three different sites (total N rate 220 kg N ha⁻¹). Numbers in or next to the bars represent the emission factor (EF in %). The figure shown for the control represents the amount of N₂O-N emitted from the control (non-fertilized) treatment. The bars represent the net N₂O emission; total emission minus the background emission (control). Different letters indicate statistically significant differences between N-form treatments; $n = 3$, mean ± SE.

varied between 0.16% and 0.21% without any significant differences between mineral N-fertilizer forms (Fig. 1).

Cumulative post-harvest fertilizer-induced N_2O emissions accounted for about 50% of total one-year emissions, irrespective of fertilizer form, at sites LAV and MUE. In contrast, at site BIL the share of one-year N_2O emission strongly differed between the N-fertilizer forms with zero emissions from CAN during the post-harvest period, followed by urea with 12% and AS with 73%. During the post-harvest period the fertilizer-induced N_2O emissions ranged between 0.12% and 0.28% for site LAV, at site BIL between –0.07% and 0.69%, and at site MUE between 0.16% and 0.20% (Fig. 1).

The negative value occurred due to the calculations as the background N_2O emission was higher than the emission from the fertilized plots. During the post-harvest period no significant difference in N_2O emissions either between N fertilizer forms or between the fertilized and non-fertilized control could be detected in two of three fields, LAV and MUE (Fig. 1D, F), although at site LAV a trend in cumulative N_2O emissions in the order urea > AS = CAN was observed. At site BIL the highest emissions were detected from AS (Fig. 1E). Nitrous oxide emissions obtained for a one-year period were generally low and the emission factors varied between 0.05% and 0.51% (Fig. 1G–I) with one exception: the one-year N_2O emission from AS at site BIL with 0.94% N loss of the nitrogen applied (Fig. 1H), which resulted in significantly higher N_2O emissions compared to the other N fertilizer treatments. On two of three fields (LAV and MUE) no significant difference in cumulative one-year N_2O emission was detected between different fertilizer forms, although by tendency the emission followed the order urea > AS > CAN at field LAV (Fig. 1G).

3.2 Daily N_2O emission

For each field the N_2O emission pattern during the growth period of winter wheat was similar for all N forms and differed only in the magnitude of the peak. The seasonal dynamics in N_2O emissions differed between the fields (Fig. 2A–C).

In 2011 at site LAV, major N_2O emissions occurred during the early growth period between DOY (day of year) 85 (March 26) and DOY 120 (April 30; Fig. 3A), while at site BIL almost all relevant N_2O fluxes occurred during the later growth period between DOY 180 (June 29) and DOY 205 (July 24; Fig. 2B). At site MUE, the main emissions occurred between DOY 100 (April 9) and DOY 127 (May 7; Fig. 2C). Peak events at site BIL were not related to N fertilizer application events, but rather appeared about 1 month after the 3rd N fertilizer application (Fig. 2B). In contrast, at site LAV mineral N fertilizer-related emission peaks were observed 3–2 weeks after the 1st and 2nd N-fertilizer application event, respectively (Fig. 2A). In 2012 at site MUE, a similar emission pattern to the pattern of LAV was detected, when the main N_2O emissions occurred after the 2nd N fertilizer application (80 kg N ha⁻¹) around DOY 118 (Fig. 2C).

Although no direct N fertilizer application-related N_2O emissions were observed at site BIL (Fig. 2B), emissions differed between N fertilizer forms towards the end of the growth sea-

son (DOY 170–210) with higher N_2O emissions from urea and AS fertilizer. In contrast, at site LAV (Fig. 2A) differences in N_2O emissions between N-fertilizer forms appeared after the 1st and 2nd N fertilizer application in spring (DOY 80–130) with a faster and slightly higher emission peak development from urea and AS fertilizer compared to the emission after CAN fertilizer application. At site MUE no clear differences in N_2O emissions between N fertilizer forms were observed during the growth period of winter wheat (Fig. 2C).

The post-harvest emissions displayed in Fig. 3 show that the seasonal dynamics in N_2O emissions varied strongly between LAV and BIL even though they had similar rainfall patterns (Fig. 3A, B). The emissions at site BIL (Fig. 3B) strongly increased for AS compared to the other N-fertilizer forms and remained high for a period of about 6 weeks after harvest of winter wheat (DOY 213–260). In contrast, at site LAV almost no higher N_2O emission was observed from fertilized plots after harvest compared to the control treatment (Fig. 3A). A slight and temporary emission was detected only from the urea treatment at about four weeks after harvest (DOY 240–260). In 2012 at site MUE, the main emission during the post-harvest season occurred between DOY 265 (September 21) and DOY 326 (November 21), whereas no difference could be detected in N_2O emissions between the different N fertilizer forms (Fig. 3C).

Emissions at the end of the one-year measurement period increased shortly after a rise in soil temperature from around –5°C to +3°C, at field site BIL and LAV (DOY 38–60; Fig. 3A, B). In 2013 at site MUE, no increase in N_2O emission after thawing was observed.

The mineral N content 45 d before harvest showed higher NH_4^+ -N content in 0–15 cm soil depth for AS compared to the other N fertilizer treatments at site BIL (not shown), whereas at the time of harvest almost no difference in the soil mineral N content occurred between the different N form treatments. At site LAV no differences in mineral N content between the N fertilizer treatments as well as between fertilized treatments and the control were found for the upper soil layer (0–15 cm) before and at harvest time. Also at field site MUE in 2012, no difference in the mineral N content between fertilized treatments was detected.

3.3 Grain yield and N_2O emissions per ton of grain yield (yield-scaled)

Cumulative emissions in relation to crop yield were also determined for all fields and all N fertilizer forms. No effect of N form on grain yield was detected, whereas the grain yield from the fertilized treatments was significantly higher compared to the control (Table 3). At site LAV, no difference in yield-scaled N_2O emissions were detected between N-fertilizer forms, whereas significantly higher yield-scaled N_2O emissions were detected from the control treatment compared to the fertilized treatment. At field BIL, AS caused the highest yield-scaled N_2O emission compared to the other N fertilizer forms as well as to the control. In 2012 at field MUE, no differences in yield-scaled emissions between N forms as well as between the control treatment were detected (Table 3).

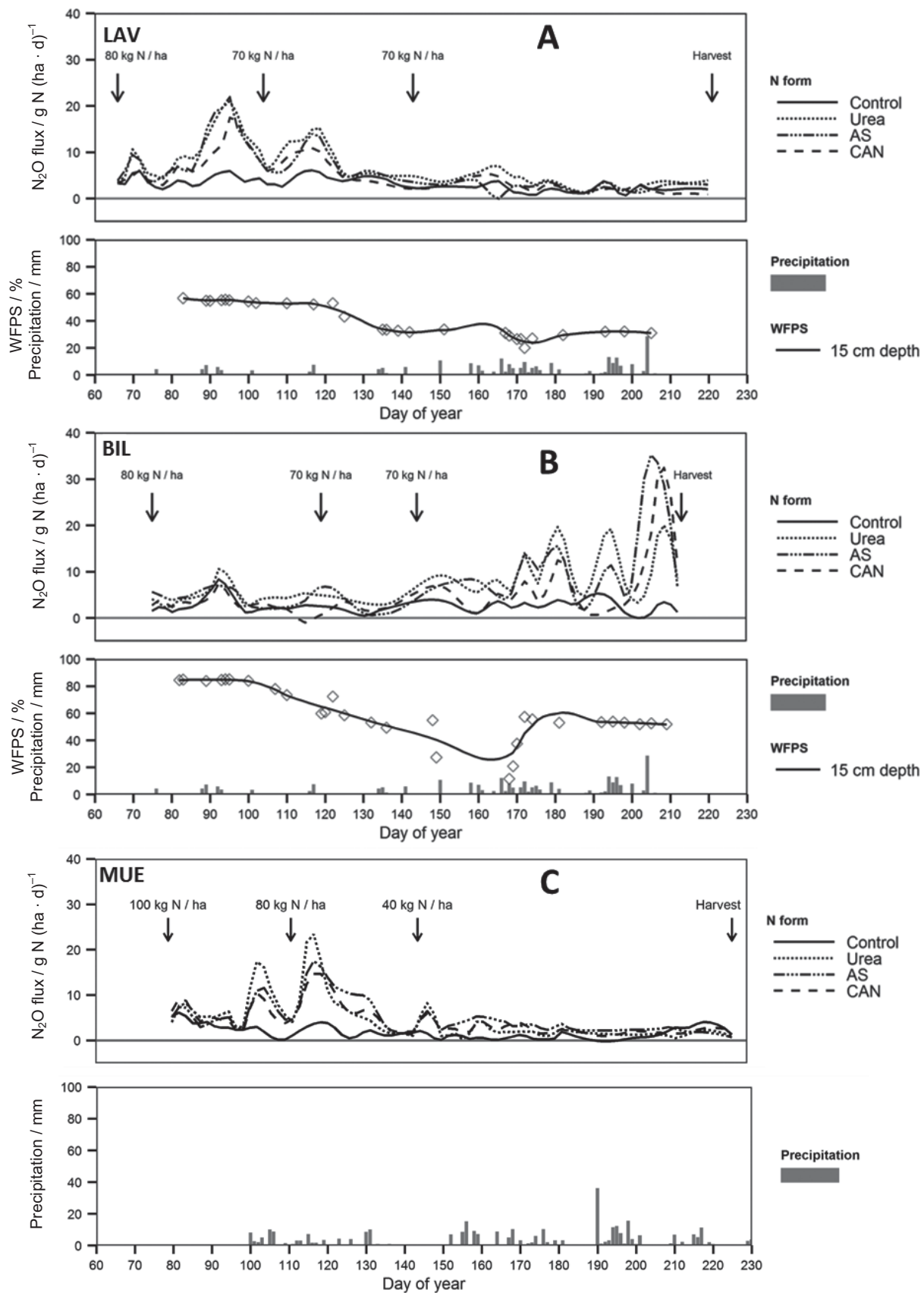


Figure 2: Daily calculated N₂O emissions (top graph), precipitation and WFPS (bottom graph) during the experimental period (March–August; ≈ 140 d) for three different field sites under winter wheat: BIL (A), LAV (B), and MUE (C). Total N amount = 220 kg N ha⁻¹; arrows represent the N fertilizer application splits; *n* = 3.

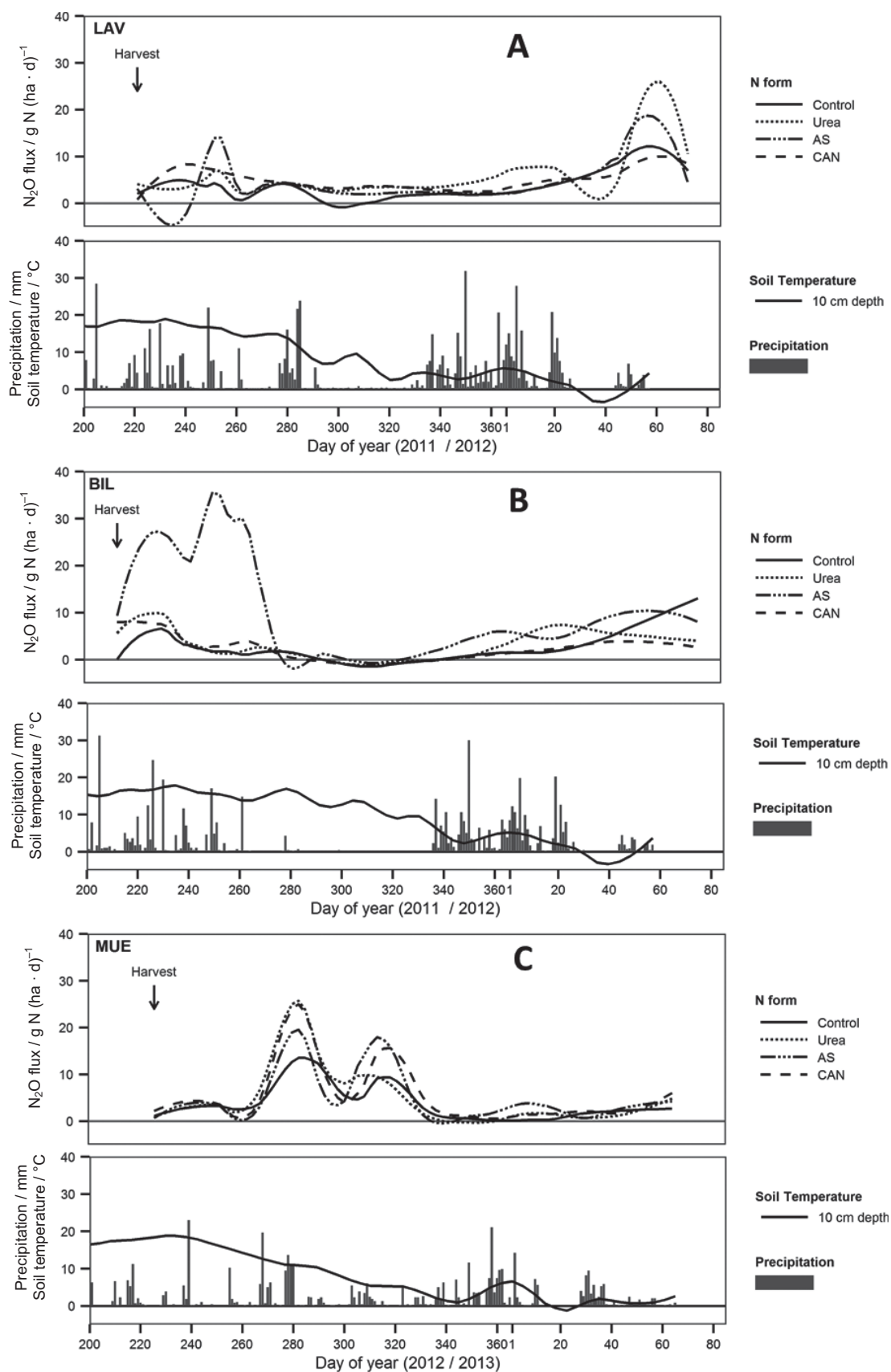


Figure 3: Daily calculated N₂O emissions (top graph), precipitation and soil temperature (bottom graph) during post-harvest season (August 2011–March 2012; ≈ 217 d) for three different field sites: BIL (A), LAV (B), and MUE (C) with winter wheat. Total N amount = 220 kg N ha⁻¹; arrows represent the winter wheat harvest; *n* = 3.

Table 3: Grain yield and yield-scaled N₂O emissions at sites BIL, LAV and MUE for different N fertilizer forms (application rate = 220 kg N ha⁻¹) in winter wheat; *n* = 3, mean ± SE, different letters indicate statistically significant differences between treatments for each field.

Field site	N-form	Grain yield		Yield-scaled N ₂ O emission	
		/ t ha ⁻¹		/ g N ₂ O-N (t grain) ⁻¹	
LAV 2011	Control	3.7	b	342.8	± 17.8
	Urea	10.2	a	234.8	± 8.4
	AS	11.2	a	175.7	± 9.8
	CAN	10.6	a	167.3	± 24.7
BIL 2011	Control	5.0	b	208.1	± 49.2
	Urea	8.7	a	198.2	± 20.7
	AS	7.8	a	399.7	± 45.2
	CAN	8.2	a	142.3	± 25.0
MUE 2012	Control	4.8	b	212.5	± 20.0
	Urea	9.0	a	196.7	± 31.6
	AS	9.1	a	201.8	± 12.7
	CAN	9.1	a	201.1	± 6.0

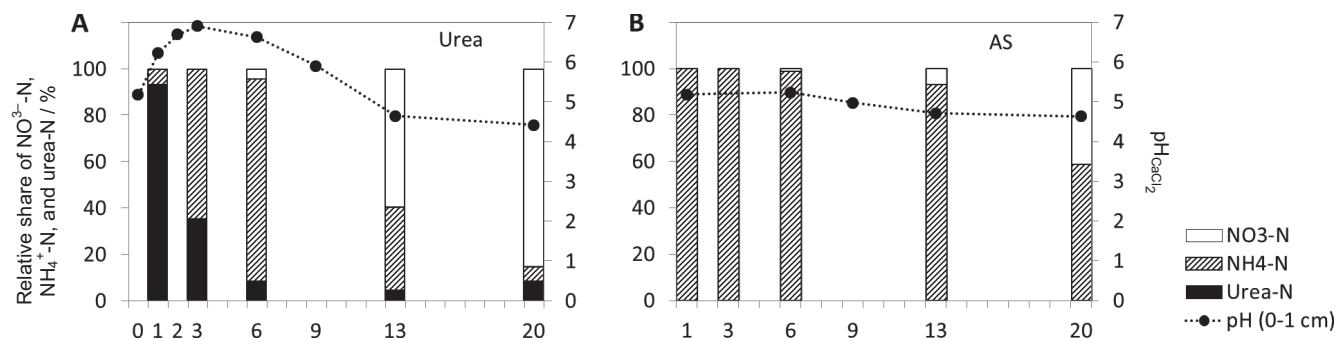
3.4 Incubation experiment to measure the nitrification rate

After 20 d of incubation about 90% of the urea-N had been converted to nitrate. During the first 6 d after urea application an increase in pH was measured accompanied by an increase in NH₄⁺. After day 6 the pH decreased and the amount of NO₃⁻ increased. During the first 6 d after AS application no change in soil pH or nitrification was observed. At day 13, NO₃⁻ could be detected accompanied by a slight pH decrease. After day 13 the amount of NO₃⁻ increased. Twenty days after AS application about 40% of the applied AS was nitrified to NO₃⁻ (Fig. 4).

4 Discussion

The results from two of three fields (LAV and BIL) showed that differences in N₂O emissions from fertilizers occur during the growth period of winter wheat depending on the N fertilizer form applied. On these two fields higher N₂O emissions

were measured from urea compared to CAN (Figure 1A, B). This is in line with the evaluation of several N₂O measurements done by Bouwman et al. (2002) and data from others (Mulvaney et al., 1997; Bergstrom et al., 2001; Gagnon et al., 2011). A possible reason for the differences in emissions observed in the present study may be the short-term pH increase in soil after urea application, which was also determined in the incubation experiment over a period of 20 d (Fig. 4) and was also mentioned by Vilsmeier and Amberger (1980). This pH increase may result in an accumulation of NO₂⁻ (Wetselaar et al., 1972) as nitrite-oxidizing bacteria are inhibited under these conditions (Anthonisen et al., 1976; Van Cleemput et al., 1996; Hawkins et al., 2010). The possibility of nitrite accumulation after application of alkalizing fertilizers (e.g., urea) is well known (Chapman et al., 1952; Christianson et al., 1979; Magalhães et al., 1987; Venterea and Rolston, 2000). In addition, NO₂⁻ can in turn be a possible substrate for N₂O production (Minami et al., 1986; Baumgärtner et al., 1992; Venterea, 2007).

**Figure 4:** Relative share of the different N forms resulting from urea (A) and AS (B) conversion and the changes in pH during hydrolysis and nitrification. *n* = 3; N application = 55 mg kg soil⁻¹.

On two of the three fields, the daily pattern during the experimental period shows that the main N_2O emission events occurred during the vegetation period shortly after N-fertilizer application (LAV, MUE; Fig. 2A, C), which is in line to findings of *Venterea et al.* (2005) as well as *Senbayram et al.* (2009). However, at site BIL no N_2O emissions were measured after N-fertilizer application events. As WFPS at this site was initially very high (> 80%), there was no difference in N_2O emission between the control (nil N fertilizer) and nitrate-containing CAN fertilizer treatments (Fig. 2B). This indicates that either another factor (e.g., available carbon) for N_2O production from denitrification was limiting or that under these almost water-saturated soil conditions the denitrifying process continued further to N_2 and, therefore, decreased the $\text{N}_2\text{O} : \text{N}_2$ ratio, as the ratio usually decreases with increasing water content (*Rolston et al.*, 1982; *Davidson et al.*, 1991; *Schuster and Conrad*, 1992; *Weier et al.*, 1993). However, this is an assumption as both possibilities (i.e., available carbon, N_2 production) were not determined. The moisture content in soil, WFPS, declined over the experimental period at sites BIL and LAV. Such declines of WFPS over the growth season can be expected as the climatic water balance becomes increasingly negative with increasing temperatures and crop water evapotranspiration. But at field BIL, the main emission occurred after rainfall events in the late growth season triggered by an increase in WFPS from 18% to 50% (Fig. 2B), which is supported by similar findings of *Smith et al.* (1998) and *Dobbie et al.* (1999). It is known that wetting dry soil typically results in a flush of C and N mineralization (*Birch*, 1958; *Kieft et al.*, 1987), which can enhance the microbial activity and, therefore, also N_2O emissions (*Murakami et al.*, 1987; *Davidson et al.*, 1992; *Priemé et al.*, 2001).

This study was conducted without ^{15}N -labeled fertilizers, therefore, it was not possible to distinguish between nitrification and denitrification-derived N_2O . According to *Davidson* (1991), WFPS $\geq 60\%$ triggers N_2O emissions from denitrification. This value has to be used with caution as it strongly depends on the soil type and different authors have suggested values of about 70% (*Ruser et al.*, 2006; *Bateman et al.*, 2005). Nevertheless, it is assumed that nitrification was the major process responsible for N_2O emission during the growth period. Possible reasons for this assumption are the 11–37% lower precipitation than the long-term average, which in turn resulted in relatively low WFPS ($\bar{\text{O}}$ of LAV and BIL: about 50%) during the experimental period and the very low N_2O emissions. Under conditions which favor denitrification, higher emissions from CAN (nitrate fertilizer) compared to urea might have been observed similar to results of *Velthof et al.* (1997), *Henault et al.* (1998) and *Smith et al.* (2012). Several results obtained under laboratory conditions showed a trend in N_2O emission of urea > NH_4^+ -based fertilizers > NO_3^- -based fertilizers under aerobic conditions, while NO_3^- -based fertilizers induced a greater N_2O production when soil conditions became anoxic (*Pathak and Nedwell*, 2001; *Tenuta and Beauchamp*, 2003).

No difference in cumulative post-harvest N_2O emissions between N fertilizer forms was detected in all fields except for the AS treatment at BIL. At site BIL, N_2O emissions increased for the AS treatment at the end of the growth period and re-

mained high for about 6 weeks after harvest of winter wheat, but this was not observed at site LAV in the same year. The difference between LAV and BIL cannot be explained with variations in the soil mineral N content at harvest as no difference was found in mineral N (NH_4^+ and NO_3^-) between either fertilizer forms or between the fertilized and non-fertilized treatments for both fields. The reasons for the higher emissions from the AS treatment at BIL are more or less speculative. As site BIL has a high clay content (clay-loam), the AS fertilizer (NH_4^+) could have been fixed to clay minerals and released during, e.g., soil tillage after harvest. Most emissions, also from other treatments, in the post-harvest season occurred shortly after harvest which might be related also to soil tillage activities as this can cause differences in the soil aeration status as reported by *Chatskikh et al.* (2007).

Emission peaks in the following year (around DOY 45) can be related to freeze–thaw effects inducing an increase in denitrification activity (e.g., *Priemé et al.*, 2001; *Dörsch et al.*, 2004; *Sharma et al.*, 2006). As there was no difference in grain yield between the N forms no difference was observed for the yield-related N_2O emissions either. The yield-scaled emissions for the fertilized treatments did not increase compared to the control due to 2–3 times higher grain yields for the fertilized treatments. Even higher yield-scaled emissions from the control compared to the fertilized treatments were detected at site LAV. No significant difference in yield-scaled emission between N forms was detected for all fields, except for the AS treatment at site BIL.

5 Conclusions

According to the results from three agricultural fields in North-West Germany it can be concluded that nitrification is the predominant process for N_2O under mainly dry conditions (26% less rainfall during March to end of July). Under these conditions and soil pH increase during urea hydrolysis, urea caused higher N_2O emissions during the growth period compared to AS and CAN. N fertilizer application irrespective of N fertilizer form significantly increased the cumulative N_2O emissions compared to the non-fertilized control. To assess the value of different N_2O -mitigation options, yield-scaled emissions should be considered. Since grain yield was about 2–3 times higher with fertilizer application, N_2O emissions per unit of grain yield (yield-scaled emission) did not increase. Based on the obtained results further investigations should be made to evaluate the impact of different N fertilizer forms on N_2O emissions across a range of soil types and climatic regions.

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