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ORIGINAL ARTICLE

Split N application and DMP based nitrification inhibitors mitigate N_2O losses in a soil cropped with winter wheat

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Abstract Nitrogen (N) fertilization to crops might lead to formation and release of reactive N—e.g. nitrate, ammonium, ammonia, nitrous oxide (N_2O) —, contributing to eutrophication, atmospheric pollution, and climate change. Use of nitrification inhibitors and splitting of N fertilizer may reduce the N_2O emission from arable soils cropped with winter wheat. We tested different N fertilizers treated with 3,4-dimethylpyrazol phosphate (DMPP) and 3,4-dimethylpyrazol succinic acid (DMPSA) by applying 180 kg N ha^{-1} in different N splitting strategies in a full annual field experiment on a loamy soil in Southwest Germany. A threefold split fertilization led to an emission of 2.3 kg N_2O–N ha^{-1} a^{-1} (corresponding to a reduction of 19%) compared to a single application of ammonium sulphate nitrate (ASN) ($p=0.07$). A single application rate of ASN with DMPP resulted in an emission of 1.9 kg N_2O–N ha^{-1} a^{-1} and reduced N_2O emissions from an ASN treatment without NI by 33%. Calcium ammonium nitrate (CAN) with DMPSA reduced N_2O emissions during the vegetation period by 38% compared to CAN without a nitrification inhibitor, but this was offset by high emissions after harvest, which was driven by soil tillage with an annual reduction of 26% (CAN: 2.9 kg N_2O–N ha^{-1} a^{-1}; CAN + DMPSA: 2.1 kg N_2O–N ha^{-1} a^{-1}; $p=0.11$). Among our tested treatments, a twofold split application of ASN with DMPP efficiently reduced N_2O emissions and maintained grain yield when compared to the traditional system with threefold application without nitrification inhibitor. Despite resulting in lower protein contents in the twofold split application, this treatment should be further investigated as a potential compromise between wheat yield and quality optimization and climate protection.

Keywords N_2O emission · DMPP · DMPSA · N fertilizer splitting

Introduction

Nitrous oxide (N_2O) is a climate-relevant trace gas which also contributes to the depletion of stratospheric ozone (Ravishankara et al. 2009; IPCC 2021). More than half of the anthropogenic N_2O emissions are released from agricultural soils (Canadell et al. 2021). It is generally agreed that N_2O production in agricultural soils is mainly controlled by the microbiological processes of nitrification and denitrification (Robertson and Groffman 2015), whereas the contribution of other processes such as autotrophic

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nitrifier-denitrification to the release of N_2O is currently under discussion (Wrage-Mönnig et al. 2018).

The use of nitrification inhibitors (NIs) can raise fertilizer N use efficiency (NUE) in agriculture and thus reduce N surpluses. Commercially available NIs are substances capable of retarding the first step of nitrification—the oxidation of ammonia (NH_3) to hydroxylamine (NH_2OH). Besides the delay of nitrification, this also results in a reduction of the availability for further nitrite (NO_2^-) oxidation to nitrate (NO_3^-), thus lowering substrate supply for denitrification (Ruser and Schulz 2015). The use of NIs with ammonium (NH_4^+)-based fertilizers is supposed to keep NH_4^+ for a longer period in its reduced form; NH_4^+ is then mainly adsorbed to negatively charged soil particles in upper soil layers for a longer period, reducing NO_3^- leaching losses.

Another way of increasing NUE in wheat (*Triticum aestivum* L.) production is the splitting of N fertilization. Traditional N fertilization strategies for wheat comprise a splitting of fertilizer application in order to adapt N supply to the physiological needs of wheat plants. Wheat breeding schemes in the last decades have developed more flexible cultivars, which are less prone to yield losses through stress events and show a higher influence of N translocation during the grain-filling period than older cultivars (Makary et al. 2020). Due to these traits, wheat N uptake and N utilization of current cultivars is much higher when compared to older cultivars, and new fertilization strategies adapted to regional climatic and soil conditions must be developed. In a series of field experiments on medium to heavy textured soils in South Germany, Schulz et al. (2015) found no differences in grain yield or crude protein content when N fertilization was applied in one, two, or three application rates and soil mineral N (N_{min}) contents did not differ after harvest. Since splitting can lead to lower soil N_{min} contents throughout the vegetation period (Arregui and Quemada 2006; Guardia et al. 2018)—and since soil N_{min} often correlates with N_2O release (Granli and Bøckman 1994)—lower N_2O emissions can be expected when N fertilizer is split.

3,4-dimethylpyrazole phosphate (DMPP) is a widely used NI in Europe, which releases 3,4-dimethylpyrazole (DMP) as active compound. Because of its chemical characteristics, DMPP cannot be sprayed on calcium ammonium nitrate (CAN), the most frequently used N fertilizer in Western and Central Europe in 2018 (23% of the N fertilizer market; IFA 2021). 3,4-dimethylpyrazole succinic acid (DMPSA) is a novel NI that also provides DMP as active inhibitor after the microbial degradation of succinic acid (Pacholski et al. 2016). Because of its non-polar chemical nature, DMPSA can be sprayed on CAN, increasing the scope of applicability of DMP (Pacholski et al. 2016). As CAN contains a higher portion of the highly mobile NO_3^--N than ASN, synchronization of an early high N demand of wheat and N availability right after fertilizer application can be better achieved when compared to ASN. Simultaneously, the NH_4^+-N is stabilized and thus prevented from leaching.

Since weather and soil conditions as well as the presence of fresh organic matter in soil can greatly influence soil redox potential and therefore potential nitrification and denitrification, it seems rather impossible to predict N_2O emissions induced by different fertilizer types. For example, Lebender et al. (2014a) reported similar N_2O losses after application of ammonium sulphate (AS) and CAN at two sites and higher losses in the AS treatment at a third site with different N_2O emission patterns for the growth and post-harvest period.

In their meta-analysis on the effect of NIs on soil N_2O emission, Ruser and Schulz (2015) calculated a 35% emission reduction as compared to a conventionally fertilized control treatment without NI. This was the mean N_2O reduction over all NIs tested. For DMPP, they reported a 38% to 40% reduction. So far only few studies investigated the effect of DMPSA on N_2O release. Under humid Mediterranean conditions, N_2O emission from wheat fields was reduced by DMPSA (Huérfano et al. 2016). In an incubation experiment with DMPP and DMPSA, Torralbo et al. (2017) reported similar N_2O reduction for both NIs.

Most of the field studies investigating DMPSA were conducted under Mediterranean conditions in irrigated systems with mild and rainy winters. In contrast, winter wheat production in South Germany is rainfed, although soils may dry very strongly in the summer months. Rewetting of dry soil in this period after heavy rainfall as well as thawing of frozen soil in winter were shown to induce N_2O bursts highly relevant for annual balances (Flessa et al. 1995; Guzman-Bustamante et al. 2019). The latter can be significant in the context of NI application because some studies showed N_2O reduction after DMPP usage a long time after harvest in winter (Pfab et al. 2012; Guzman-Bustamante et al. 2019).

We aimed to quantify the effect of different N splitting strategies and of the NIs DMPSA and DMPP on N_2O emissions, yield, and N utilization in winter wheat under Southern Germany conditions. We hypothesized that (i) N_2O emissions from a winter wheat field can be decreased in a conventional N fertilization system with three N application rates when compared to a single N application since temporally high mineral N availability which serves as substrate for N_2O production is minimized. (ii) We also assumed lower N_{min} concentrations that serve as substrate for N_2O production in the split NI fertilization treatments. Consequently, annual N_2O emissions can be even further mitigated than a single NI application without any decrease in crop yield or protein concentration; lastly, (iii) the NI DMPSA shows similar N_2O reduction under field conditions compared to DMPP, due to the same active compound (DMP).

Material and methods

Field experiment

From a fully randomized block experiment (Guzman-Bustamante et al. 2019) located at the experimental station of the University of Hohenheim "Heidfeldhof", in Stuttgart, Germany (48° 42′ 59″ N; 9° 11′ 42″ E), 24 plots of 3 m x 5 m were selected. An overview of climatic conditions and soil properties is given in the supplementary online material. Plots were divided into a sampling and a harvest subplot (1.5 m x 5 m each). Gas and soil samples were taken from the sampling subplot, while the harvest subplot was used for grain and straw yield determination as well as for plant analysis (C and N). The winter wheat variety "Schamane" was sown 6 October 2011 after winter wheat as previous crop. Total fertilizer amount was 180 kg N ha^{-1}, calculated according to the German Fertilizer Ordinance ("good agricultural practice", DüV, 2006). The first N application took place 29 March 2012 (BBCH 28) as CAN with or without DMPSA ([1]CAN and [1]CAN + DMPSA), or ammonium sulphate nitrate (ASN) with or without DMPP ([1]ASN and [1] ASN + DMPP). For the twofold application treatments, 108 kg N ha^{-1} was applied as ASN + DMPP on 29 March 2012, with the second application of 72 kg N ha^{-1} as ASN + DMPP on 23 May 2012 (BBCH 39) or CAN on 31 May 2012 (BBCH 49/51) ([2]ASN + DMPP and [2]ASN + DMPP/CAN). The threefold split treatment ([3]ASN/CAN/CAN) was fertilized on 29 March 2012 with ASN (54 kg N ha^{-1}; BBCH 28), and with CAN on 15 May 2012 (72 kg N ha^{-1}; BBCH 39) and 31 May 2012 (54 kg N ha^{-1}; BBCH 49/51). An unfertilized control treatment was included ([0]control). An overview of the treatments and N fertilization rates is given in the supplementary online material.

Soil N_2O fluxes

Between 6 March 2012 and 14 March 2013, gas measurements took place weekly, with additional sampling during high emission events (after N fertilization, after heavy rain, after tillage, and during freeze/thaw cycles) as recommended by Flessa et al. (2002). N_2O fluxes were determined using the closed chamber method, for which circular PVC bases with an inner diameter of 0.3 m and a height of 11 mm were installed at a depth of ca. 70 mm in the middle of the sampling subplot. In order to account for the growth of the wheat plants inside of the soil rings, additional PVC extensions of 0.3 or 0.6 m height were used during gas sampling in the vegetation period. Closed chambers and extensions were fitted on the rings only when measurements took place. A closer description of the dark chambers fitted with a vent and identical in construction to our chambers was provided by Flessa et al. (1995).

During each gas sampling, four gas samples were taken out of the chamber's atmosphere with evacuated vials (22.4 mL) through a double cannula inserted into a sampling port with a septum in the chamber`s top at time intervals of 15 min. N_2O gas concentration in the vials was measured with a gas chromatograph (5890 series II, Hewlett Packard) equipped with a ^{63}Ni electron capture detector (ECD) and an autosampler (HS40, Perkin Elmer). A linear regression (concentration enrichment over time) was used in order to calculate N_2O fluxes as described by Flessa et al. (1995).

Air temperature and precipitation data was retrieved from weather station "Hohenheim" located 600 m south from the experimental site (Landwirtschaftliches Technologiezentrum Augustenberg 2015).

Soil measurements

Soil samples were taken weekly from a composite sample of eight soil cores (0.3 m depth and 14 mm diameter) per treatment in the sampling subplot outside of the chamber base ring. Soil samples were kept cold in the field and frozen after field sampling until extraction in the lab. 40 g of soil were extracted with 160 mL of 0.5 M K_2SO_4 solution for one hour to determine N_{min} concentration. NO_3^- and NH_4^+ concentrations in the extracts were measured with a flow injection analyser (3 QuAAtro.AQ2.AACE, SEAL Analytical, UK). Soil moisture was calculated gravimetrically after drying the samples at 105 °C for at least 24 h. Water-filled pore space (WFPS) was calculated after Ruser et al. (1998) using the mean measured bulk density (1.25 Mg m^{-3}) in the A_p-horizon during our experimental period.

In order to assess the transport of N_{min} in deeper soil layers, soil in three depths (0–0.3; 0.3–0.6 and 0.6–0.9 m) was sampled at three dates: before fertilization (6 March 2012), after harvest (8 August 2012), and at the end of the experiment (14 March 2013). At the first date, samples were taken as a composite for each treatment; at the second and third dates, samples were taken separately in each plot. For calculation of N_{min} amounts, we assumed a bulk density of 1.5 Mg m^{-3} for the 0.3–0.6 m soil layer and 1.6 Mg m^{-3} for the 0.6–0.9 m layer.

The NH_4-N/NO_3-N ratio was calculated in order to follow inhibitory effect of treatments with NI.

Yield and plant analysis

All measurements on yield and yield components took place in the harvest subplot. Spike number per m^2 was calculated by counting the wheat spikes in a circular area of 0.6 m diameter. Wheat grain was harvested using a plot harvester. Straw and grain samples were taken for each subplot. Samples were dried for 48 h at 60 °C and ground using a cutting mill. C- and N- analyses were conducted with an elemental analyser (vario MAX CN, Elementar Analysensysteme, Hanau, Germany). Thousand grain mass (TGM) was determined gravimetrically after weighting 100 grain subsamples (n = 3) counted by a seed counter (Contador, Pfeuffer GmbH, Kitzingen, Germany). N surplus—the balance between N fertilizer input and N removal through N in the harvest—was calculated subtracting grain-N from fertilizer-N.

Seasonal and annual N_2O emission and statistical analysis

Cumulative N_2O emissions were calculated using a step function, i.e. the flux at a given date was assumed to be constant until the next sampling date (Flessa et al. 1995). This was done for each *"Season",* which represents the experimental time interval *vegetation period* (6 March—9 August 2012), *tillage* (10 August—29 November 2012) and *winter* (30 November 2012–21 March 2013), and for the whole experimental year.

Statistical analyses were performed with SAS (SAS Institute Inc., Cary, NC, USA). For N_2O fluxes, a repeated measures model was implemented using PROC MIXED with block, season, weekly dates (nested in season) and treatments as fixed effects, weekly date as repeated term with plot as subject and season as grouping variable. A spatial power correlation matrix was used in order to avoid serial autocorrelation and to consider differing sampling dates. For a better distribution of residuals, N_2O fluxes were transformed using the *boxcox* SAS Macro (Box and Cox 1964; Piepho 2017).

The effect of treatments and seasons on cumulative emissions was assessed using a repeated measures model with block, season and treatments as fixed effects, and season as repeated term, with plot as subject. An autoregressive correlation matrix was used. Effect of treatments on annual emissions and yield parameters were calculated with linear models. A logarithmic transformation was used when necessary to improve residual distribution.

The effect of different variables (soil NH_4, soil NO_3, soil temperature, WFPS and ΔWFPS) on N_2O fluxes was calculated using PROC GLMSELECT and PROC GLM with the Akaike information criterion (AIC value) as selection parameter. To improve residual distribution, all variables were log transformed. The interaction between N_{min} and use of NI was also assessed by including NI as a dummy variable. The relative importance of variables was calculated dividing the type I sum of squares of each variable by the sum of squares of the model.

Using PROC MIXED the effect of depth, date and treatment on soil NO_3^- content was assessed using a repeated measures model, with depth and date as repeated terms and plot as subject. An autoregressive correlation matrix was used. Because the first soil sampling was done as composite, the model was used with the data of the second (after harvest) and third soil sampling (end of experiment, after winter).

Adjusted means were calculated using the LSMEANS and SLICE statements in PROC PLM, with letter display for pairwise comparisons at $\alpha = 5\%$ using the Student–Newman–Keuls method for all linear models (Büchse and Zenk 2013). All graphs were done with the graphical R package *ggplot2* (Wickham 2009).

Weather conditions

After sowing, precipitation summed up to 44 mm during October 2011. A dry November was followed by a mild, rainy winter with a median daily temperature of 3.9 °C and a total precipitation of 170 mm during December 2011 and January 2012. From the end of January, temperature dropped down (lowest mean daily temperature: -12.4 °C) without a snow cover for two weeks (S1, supplementary online material). Vegetation period started beginning of March with low precipitation and consequently low soil moisture (Fig. 1). To avoid drought stress due to the lack of rain, the field experiment was irrigated on 29 May 2012 with 17 mm. Precipitation was higher during June and July (172 mm), nevertheless, its clustered distribution led to dry soil conditions by the end of June (30% WFPS) and a rewetting event two days after (42% WFPS after 46 mm of rain). Before harvest, wheat plants showed signs for leaf rust infection—orange-red pustules on leaf surface.

After harvest ("tillage" season), precipitation continued while temperature dropped from 20 °C to 0 °C (end of November 2012), leading to higher soil

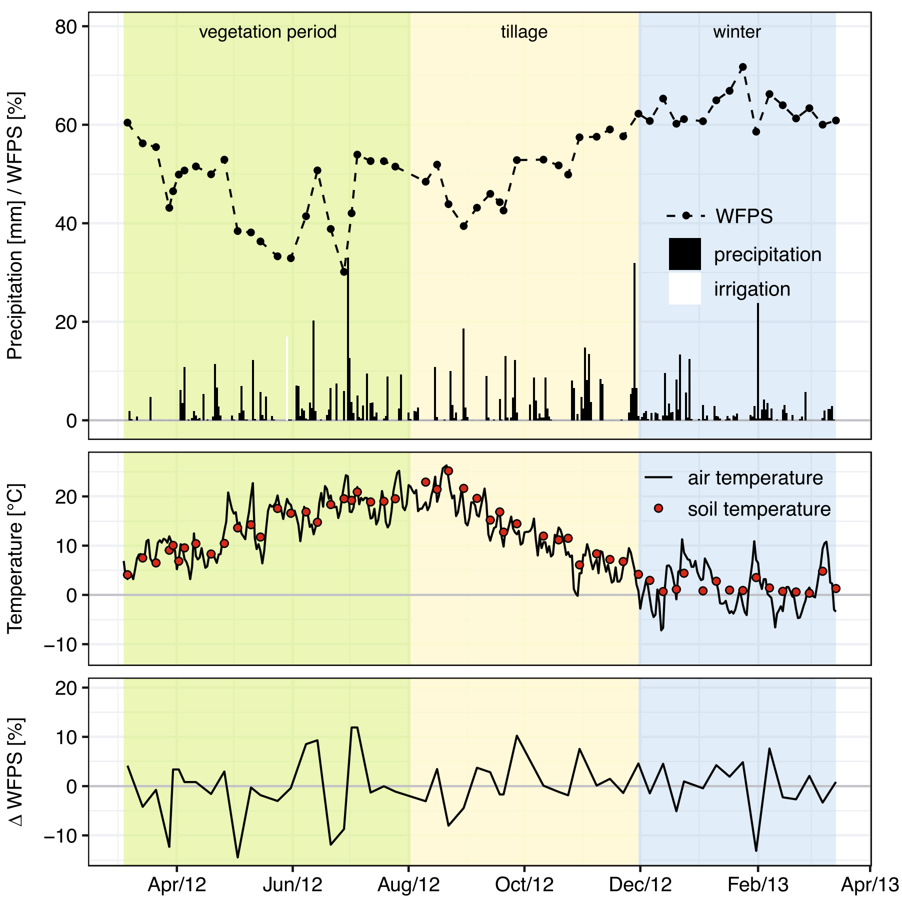

Fig. 1 Daily precipitation and mean water filled pore space (WFPS) of all treatments (upper panel), mean daily temperature (2 m; middle panel), and ΔWFPS (weekly change of WFPS value; lower panel). Experimental time periods "vegetation period", "tillage" and "winter" are represented as coloured blocks. Irrigation took place once (29 May 2012, white bar)

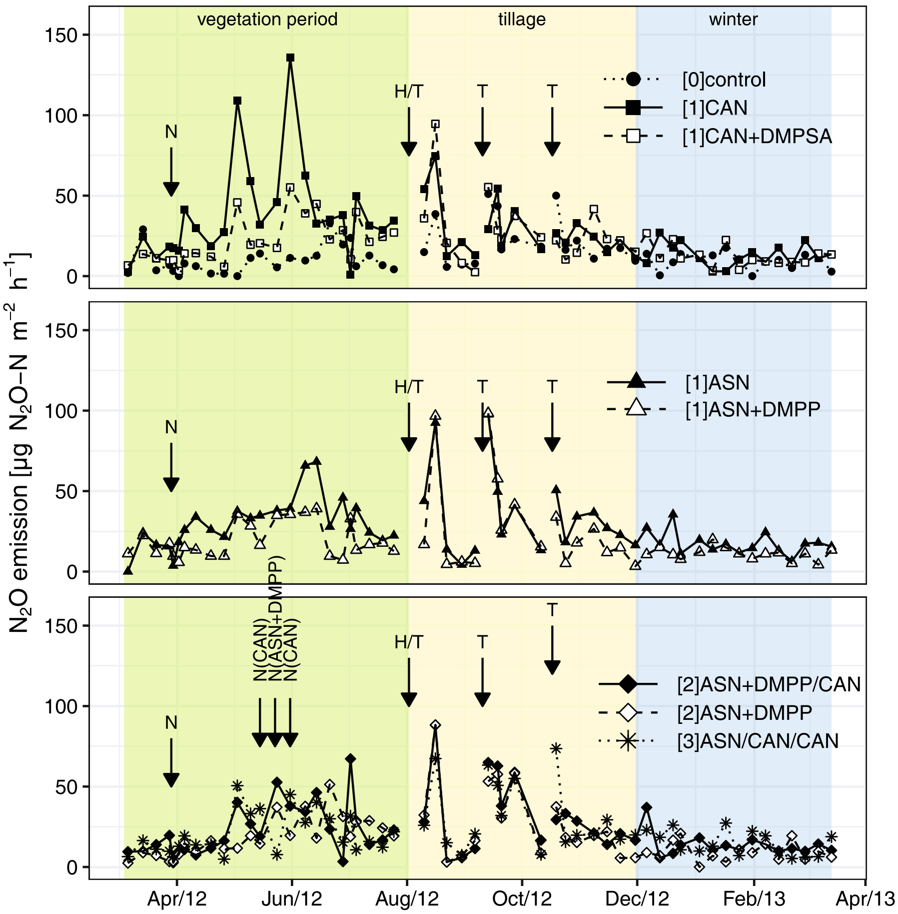

Fig. 2 Course of the median N_2O emission (n = 4). Arrows represent nitrogen (N) fertilization (N = all treatments; N* = only three application rates treatment), harvest (H) and tillage (T). Experimental time periods "vegetation period", "tillage" and "winter" are represented as coloured blocks. The number of application rates is given in square brackets. ASN: ammonium sulphate nitrate; CAN: calcium ammonium nitrate; DMPP: 3,4-dimethylpyrazol phosphate; DMPSA: 3,4-dimethylpyrazol succinic acid

moisture (60% WFPS) at the beginning of the winter season (December 2012). The relatively harsh winter (104 days) was characterized by continuous precipitation with changing temperatures, nevertheless, in a small range (-7 to 11 °C) and with 21 ice days (daily maximum air temperature below 0 °C) (Fig. 1).

Results

N_2O fluxes and cumulative N_2O emission

Temporal dynamics and drivers of N_2O fluxes

Average N_2O fluxes before the first N application were 13 (± 11) µg N_2O-N m^{-2} h^{-1} (Fig. 2). After the first N application, only CAN treatment showed elevated fluxes (41 µg N_2O-N m^{-2} h^{-1}) one week after N application. Two peaks with flux rates higher than 100 µg N_2O-N m^{-2} h^{-1} were registered in the CAN treatment in a period of rising temperatures and in conjunction with rainfall on 3 May 2012 and due to the irrigation, which had taken place two days before the second N_2O flux measurements on 31 May 2012. The other fertilized treatments showed rather low fluxes during the vegetation period, ranging from 3 to 68 µg N_2O-N m^{-2} h^{-1} and with a rise of fluxes in June and reduction at harvest.

After harvest, fluxes were high after each tillage event. With 98 µg N_2O-N m^{-2} h^{-1} in the ASN and ASN + DMPP treatment, highest flux in this period was measured after seeding (13 October 2012). During winter fluxes were low, ranging between 0 and 37 µg N_2O-N m^{-2} h^{-1} (Fig. 2).

Soil temperature was a main driver for N_2O fluxes (Table 3). A comparison of soil temperature and fluxes shows a similar course, with higher fluxes during the warmer period between May and September 2012 (Figs. 1 and 2). Soil NH_4-N and NO_3-N were the second and third main drivers for N_2O fluxes, followed by the weekly change of WFPS (ΔWFPS) and WFPS (Table 3).

Effect of N fertilization, splitting and N fertilizer type

N fertilization significantly increased N_2O fluxes during the vegetation period, with treatment [1]CAN showing the highest fluxes (4.3 times higher fluxes compared to [0]control, Table 1). Fertilization significantly increased cumulative emissions only during vegetation period (Table 2).

The type of N fertilizer (ASN or CAN) did not significantly influence fluxes or emission. Nevertheless, higher cumulative emissions were observed during the vegetation period for [1]CAN (Table 2, also supplementary online material). Compared to a single application of CAN, [3]ASN/CAN/CAN treatment lowered N_2O fluxes by 11 µg N_2O-N m^{-2} h^{-1} (Table 1) and consequently also cumulative emission by 38% during the vegetation period (Table 2). Nevertheless, this effect did not have a repercussion on the cumulative annual emissions ($p=0.13$).

Splitting of fertilization had a significant influence on the flux behaviour during seasons, with highest fluxes during the tillage period, followed by vegetation and winter period. In the single application treatments winter fluxes were significantly lower than during the rest of the seasons (Table 1).

Effect of nitrification inhibitor

Nitrous oxide fluxes were significantly reduced using DMPP and DMPSA, mostly during the vegetation period and, in the case of DMPP, also on an annual basis (Table 1). During the vegetation period [1]CAN + DMPSA reduced fluxes by 12 µg N_2O-N m^{-2} h^{-1}, compared to [1]CAN, and [1]ASN + DMPP reduced fluxes by 10 µg N_2O-N m^{-2} h^{-1} compared to [1]ASN. The two highest emission peaks of the [1]CAN treatment (3 and 31 May 2012) were reduced by approx. 60% when DMPSA was used (Fig. 2).

This reduction of N_2O fluxes induced a reduction of cumulative N_2O emissions by 38% in treatments which used DMPSA and DMPP at the single

Table 1 Type 3 tests of fixed effects and back transformed adjusted means of significant effect *"treatment"* (annual) and significant interaction *"season x treatment"* for N_2O fluxes

Effect	NumDF	denDF	F-value	*p*-value
Block	3	799	0.27	0.8498
Season	2	327	86.07	< 0.0001
Season × date	53	1463	12.70	< 0.0001
Treatment	7	456	13.76	<0.0001
Season × treatment	14	450	2.45	0.0024

	Season[1]			
	Vegetation period	Tillage	Winter	Annual
Treatment[2]	[µg N_2O-N m^{-2} h^{-1}]			
[0]control	$6.8^{D\ b}$	$17.7^{B\ a}$	$7.7^{B\ b}$	8.0^{D}
[1]CAN	$29.4^{A\ a}$	$27.7^{AB\ a}$	$10.1^{AB\ b}$	17.7^{AB}
[1]CAN + DMPSA	$17.5^{BC\ a}$	$24.3^{AB\ a}$	$10.2^{AB\ b}$	13.9^{BC}
[1]ASN	$25.7^{AB\ a}$	$31.5^{A\ a}$	$15.3^{A\ b}$	19.9^{A}
[1]ASN + DMPP	$15.9^{C\ ab}$	$20.4^{AB\ a}$	$9.6^{AB\ b}$	12.3^{BC}
[2]ASN + DMPP/CAN	$17.2^{C\ ab}$	$25.0^{AB\ a}$	$10.6^{AB\ b}$	14.1^{BC}
[2]ASN + DMPP	$13.7^{C\ a}$	$22.2^{AB\ a}$	$7.9^{B\ b}$	11.3^{C}
[3]ASN/CAN/CAN	$18.0^{BC\ ab}$	$26.9^{AB\ a}$	$11.9^{AB\ b}$	15.3^{B}

1. Adjusted mean N_2O fluxes followed by a common capital letter are not significantly different within treatments (Student–Newman–Keuls; $\alpha=5\%$)

2. Adjusted mean N_2O fluxes followed by a common small letter are not significantly different within seasons (Student–Newman–Keuls; $\alpha=5\%$)

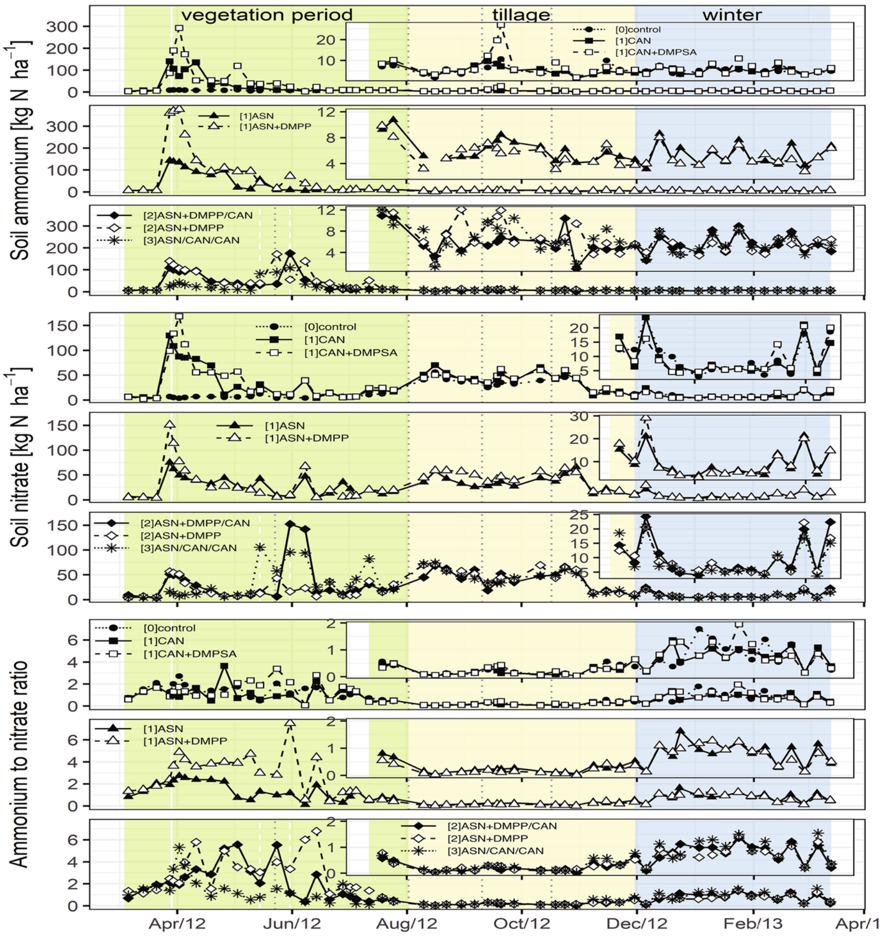

Fig. 3 Course of the soil mineral nitrogen (N_{min}) amounts, as soil ammonium content (first three panels), soil nitrate content (panels four to six) and the ammonium to nitrate ratio (ammonium-N/nitrate–N; last three panels). Experimental time periods "vegetation period", "tillage" and "winter" are represented as coloured blocks. White vertical lines represent N fertilization (solid = all treatments; dashed = only three application rates treatment), grey vertical dotted lines represent tillage events. Note inlets for each panel. The number of application rates is given in square brackets. ASN: ammonium sulphate nitrate; CAN: calcium ammonium nitrate; DMPP: 3,4-dimethylpyrazol phosphate; DMPSA: 3,4-dimethylpyrazol succinic acid

Table 2 Adjusted means for seasonal and annual N_2O cumulative emissions as affected by fertilization treatments (n = 4)

	Season[1]			
	Vegetation period [149 d]	Tillage [119 d]	Winter [112 d]	Annual [380 d]
Treatment[2]	[g N_2O–N ha^{-1}]			
[0]control	$436^{\text{D ab}}$	$605^{\text{B a}}$	$282^{\text{A b}}$	1322^{C}
[1]CAN	$1564^{\text{A a}}$	$911^{\text{AB b}}$	$375^{\text{A c}}$	2850^{A}
[1]CAN + DMPSA	$963^{\text{BC a}}$	$821^{\text{AB a}}$	$331^{\text{A b}}$	2116^{ABC}
[1]ASN	$1223^{\text{B a}}$	$1089^{\text{A a}}$	$508^{\text{A b}}$	2820^{A}
[1]ASN + DMPP	$761^{\text{C a}}$	$765^{\text{AB a}}$	$359^{\text{A b}}$	1886^{BC}
[2]ASN + DMPP/CAN	$914^{\text{BC a}}$	$959^{\text{AB a}}$	$357^{\text{A b}}$	2230^{AB}
[2]ASN + DMPP	$759^{\text{C a}}$	$805^{\text{AB a}}$	$319^{\text{A b}}$	1883^{BC}
[3]ASN/CAN/CAN	$963^{\text{BC a}}$	$895^{\text{AB a}}$	$414^{\text{A b}}$	2271^{AB}

1. Adjusted mean N_2O cumulative emissions followed by a common capital letter are not significantly different within treatments (Student–Newman–Keuls; $\alpha = 5\%$)

2. Adjusted mean N_2O cumulative emissions followed by a common small letter are not significantly different within seasons (Student–Newman–Keuls; $\alpha = 5\%$)

Table 3 Parameters of the linear-logarithmic regression model of N_2O flux rates as affected by soil and weather variables after a stepwise regression. The interaction between use of NI and soil NO_3 and NH_4 was included in a second regression model. All initial variables had a significant effect on N_2O fluxes and were not excluded from the final model. The relative importance of the explained variance is given for regression variables

Variable	Estimate	Standard error	t Value	*p* value	Relative importance (%)
Without NI as dummy variable (23% explanation of variance)					
Intercept	89.9	24.5	3.66	0.0003	
Log soil temperature	3.4	1.1	3.25	0.0013	68
Log NH_4	−4.3	0.8	−5.18	< .0001	14
Log NO_3	3.7	0.9	3.9	0.0001	12
Log ΔWFPS	5.4	2.2	2.42	0.0158	4
Log WFPS	−22.8	6.1	−3.74	0.0002	2
With NI as dummy variable (24% explanation of variance)					
Intercept	85.5	24.6	3.48	0.0006	
Log soil temperature	3.4	1.1	3.24	0.0013	65
Log $NH_4 \times +NI$	−3.9	1.0	−3.98	< 0.0001	16
Log $NH_4 \times -NI$	−4.0	1.3	−3.12	0.0019	
Log $NO_3 \times +NI$	3.2	1.1	2.9	0.0039	12
Log $NO_3 \times -NI$	4.3	1.1	3.8	0.0002	
Log ΔWFPS	5.6	2.2	2.51	0.0124	5
Log WFPS	−22.1	6.1	−3.62	0.0003	2

application rate. At an annual cumulative basis, only ASN + DMPP independent of the number of applications significantly reduced emissions by 33% ([1] ASN + DMPP and [2]ASN + DMPP compared to [1] ASN).

Nitrous oxide fluxes of split treatments which included DMPP were in the same order of magnitude as [1]ASN + DMPP during vegetation period. When compared to [1]CAN and [1]ASN, these treatments significantly lowered fluxes during the vegetation period. Although this effect was not seen during tillage, in the case of [2]ASN + DMPP fluxes were significantly lower compared to [1]ASN also during winter (Table 1). This effect did not translate into lower cumulative emissions for the vegetation period; nevertheless, compared to [1]CAN and [1]ASN, treatments with split N application emitted less N_2O during vegetation period, with the [2]ASN + DMPP treatment emitting 51% less than [1]CAN and 38% less than [1]ASN (Table 2). On an annual basis, [2] ASN + DMPP performed as [1]ASN + DMPP and emitted 34% less than [1]CAN and 33% less than [1] ASN; but it did not differ from the [3]ASN/CAN/CAN treatment (Table 2).

Several logarithmized soil variables influenced N_2O flux rates, with soil temperature and NH_4-N and NO_3-N content being the most influential ones (Table 3). Positively correlated variables were soil temperature, NO_3-N, and ΔWFPS; NH_4-N and WFPS were negatively correlated with N_2O fluxes.

Soil N_{min}

Highest NH_4^+ amounts in the upper soil layer (0–0.3 m) were measured after fertilization in the single application treatments with DMPP or DMPSA (Fig. 3). Highest NO_3^- amounts were found in the single application treatments and after the third CAN application in the [3]ASN/CAN/CAN treatment on 31 May 2012.

The highest NH_4-N/NO_3-N ratio was found in the [1]ASN + DMPP and [2]ASN + DMPP treatments during most of the vegetation period (Fig. 3). During tillage period the NH_4-N/NO_3-N ratio was < 1 for

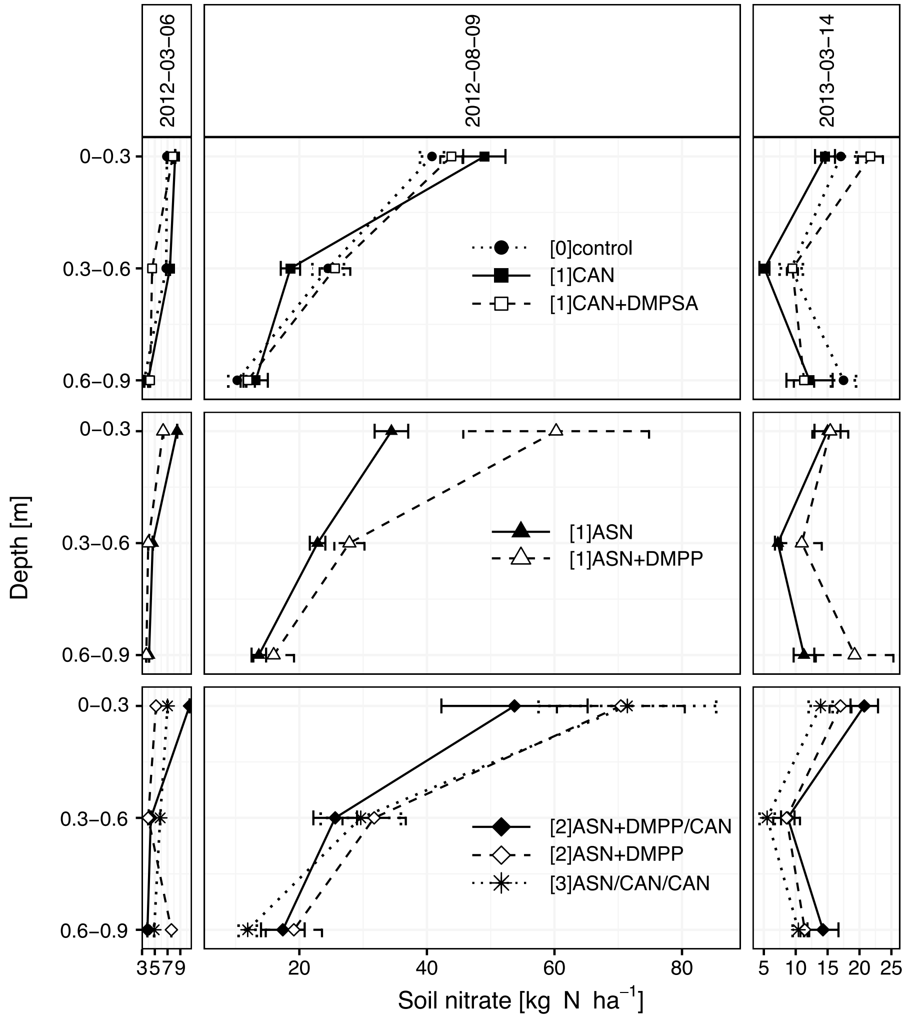

Fig. 4 Soil nitrate in three depths (0–0.3, 0.3–0.6 and 0.6–0.9 m) and for three time periods (beginning of experiment, after harvest and end of the experiment) as affected by fertilization. Values for the first date come from a composite sample. Second and third dates show back transformed least square means and standard error. The number of application rates is given in square brackets. ASN: ammonium sulphate nitrate; CAN: calcium ammonium nitrate; DMPP: 3,4-dimethylpyrazol phosphate; DMPSA: 3,4-dimethylpyrazol succinic acid

all treatments and rose slightly above 1 during the wintertime.

Before fertilization, the average NO_3^- amount in the uppermost layer was 7.5 (± 1.6) kg N ha^{-1}. After harvest, the median NO_3^- amount in the upper layer was 49.8 kg N ha^{-1}. Highest NO_3^- amounts after harvest were determined in the uppermost soil layer of the treatments [2]ASN + DMPP and [3]ASN/CAN/CAN (68.2 and 67 kg N ha^{-1}, respectively). In this layer, the only significant difference between treatments was found with amounts being higher in the treatments [2]ASN + DMPP and [3]ASN/CAN/CAN when compared to [1]ASN (Fig. 4).

After winter, [1]ASN + DMPP and [1]CAN + DMPSA showed the highest NO_3^- amount in the 0.3–0.6 m soil layer (9.9 and 9.4 kg N ha^{-1}) whereas highest amounts in the [0]control and [1]ASN + DMPP treatment were recorded in the 0.6–0.9 m soil layer (17.1 and 17.0 kg N ha^{-1}) (Fig. 4).

Yield and yield components

Fertilization was a main driver for yield and yield components, with significant effects on grain and straw yield, spike number as well as on N related variables such as N concentrations in grain and straw (and N amount in these wheat fractions). Among fertilized treatments, the N amount in straw ranged between 25 and 33% of applied N fertilizer and N surplus varied only between 49 and 65 kg N ha^{-1} (Fig. 5). Among the fertilized treatments, a single application of ASN yielded 21.4% more grain and

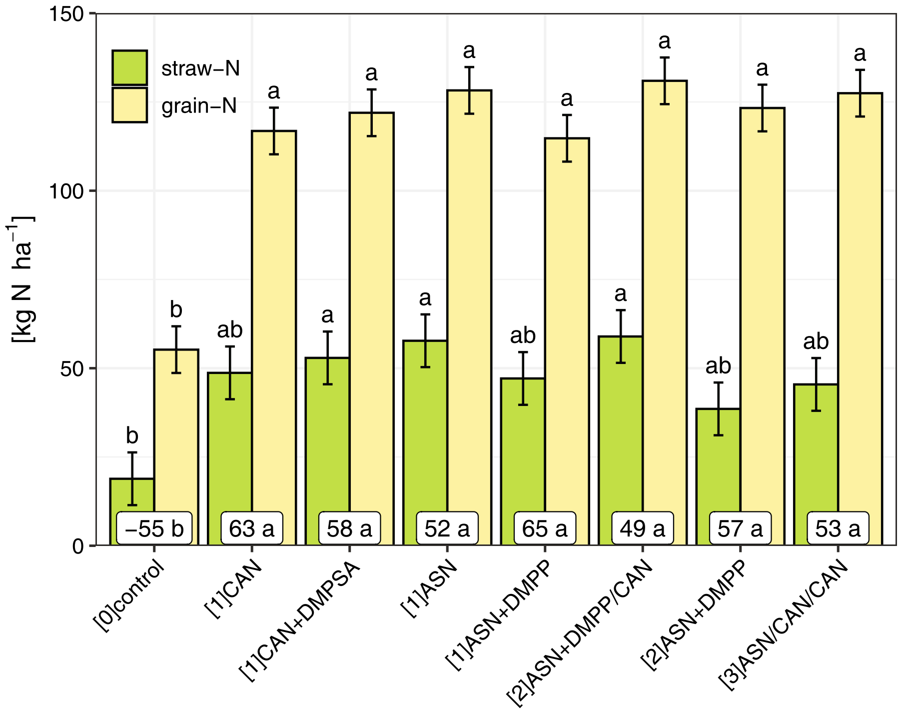

Fig. 5 Mean straw-N and grain-N as affected by N fertilization strategies (n = 4). N balance is given in the bottom of the bars. Error bars indicate standard error of the model mean estimates. Mean values followed by a common letter are not significantly different within variable (Student–Newman–Keuls; $\alpha = 5\%$)

had 32% more spikes per m^2 than the traditional [3]ASN/CAN/CAN treatment.

Crude protein content in grain was mainly affected by splitting, with the highest protein content in the [3]ASN/CAN/CAN treatment and decreasing protein content with less N applications (Table 4). Within fertilized treatments, N_2O emission per grain-N in the [2]ASN + DMPP treatment was 38% lower than in treatment [1]CAN.

Discussion

Main drivers for N_2O release

The positive correlation between temperature and N_2O flux rates can be explained not only by a direct effect of temperature on enzymatic activity, but also by an increased soil anaerobiosis after stimulation of soil respiration (Butterbach-Bahl et al. 2013). We found a negative correlation between the N_2O flux rates and the NH_4^+ contents, which were mainly high after fertilizer application. This might be a hint on nitrification as the main N_2O source in this period. However, we cannot exclude denitrification as another relevant N_2O source, since NO_3^-, the end product of nitrification, serves as a substrate for denitrification. This was indicated by a positive correlation between N_2O flux rates and NO_3^- contents. Using a stable isotope approach, Ruser et al. (2006) reported a contribution of denitrification of up to approx. 66%, at a low soil moisture (40% WFPS) in a soil similar in soil texture and humus content. They found this high ratio of denitrification to the total N_2O flux especially after the rewetting of dry soil, and explained this phenomenon by inferring that increased oxygen consumption and microbial growth after rewetting was due to an enrichment of easily available carbon under dry soil conditions, which induced anaerobiosis even at low soil moisture. This would also explain the positive correlation between N_2O fluxes and the change of soil moisture (ΔWFPS) between two sampling dates.

Soil tillage also stimulated N_2O flux rates. As summarized by Guzman-Bustamante et al. (2019), tillage increases C turnover in soil aggregates, nitrification and denitrification potential and enhances C and N availability of crop residues. Similarly, increased N_2O fluxes after tillage have also been reported e.g., by Mutegi et al. (2010) after winter barley harvest and by Lebender et al. (2014b) after winter wheat harvest.

Use of NI diminished the slope of Log NO_3^- (Table 3) indicating that DMP based NIs were

Table 4 Adjusted means for yield related variables as affected by fertilization treatments (n = 4)

Treatment	Grain yield [Mg ha^{-1}]	Straw yield	Spike number [n m^{-2}]	TGM [g]	C/N straw [ratio]	Crude protein content grain* [%]	N straw	NUE	N_2O per grain-N [g N_2O-N kg^{-1} grain-N]	N_2O per grain [g N_2O-N Mg^{-1}]
[0]control	3.29 ^{c}	3.80 ^{b}	311 ^{c}	42.5 ^{ab}	86.8 ^{a}	9.6 ^{d}	0.50 ^{c}		23.8 ^{a}	415
[1]CAN	6.06 ^{ab}	5.72 ^{a}	513 ^{ab}	40.3 ^{ab}	55.4 ^{b}	11.0 ^{c}	1.48 ^{a}	34.2	24.4 ^{a}	472
[1]CAN + DMPSA	6.13 ^{ab}	6.33 ^{a}	556 ^{a}	37.7 ^{b}	52.6 ^{b}	11.3^{c}	0.72 ^{bc}	37.1	17.2 ^{ab}	348
[1]ASN	6.58 ^{a}	6.01 ^{a}	577 ^{a}	38.7 ^{ab}	45.4 ^{b}	11.1 ^{c}	0.92 ^{bc}	40.6	22.1 ^{ab}	435
[1]ASN + DMPP	5.75 ^{ab}	5.25 ^{ab}	495 ^{ab}	40.0 ^{ab}	50.4 ^{b}	11.3 ^{c}	0.97 ^{bc}	33.1	16.1 ^{ab}	329
[2]ASN + DMPP/CAN	6.00 ^{ab}	6.01 ^{a}	513 ^{ab}	41.8 ^{ab}	50.5 ^{b}	12.4 ^{b}	0.89 ^{bc}	42.1	16.7 ^{ab}	373
[2]ASN + DMPP	5.57 ^{ab}	4.96 ^{ab}	431 ^{abc}	43.0 ^{a}	55.5 ^{b}	12.7 ^{b}	1.19 ^{ab}	37.8	15.2 ^{b}	341
[3]ASN/CAN/CAN	5.17 ^{b}	5.00 ^{ab}	394 ^{bc}	43.9 ^{a}	47.9 ^{b}	14.0 ^{a}	0.91 ^{bc}	40.1	17.6 ^{ab}	438

Adjusted means followed by a common small letter are not significantly different (Student–Newman–Keuls test; $\alpha = 5\%$)

TGM = thousand grain mass; *NUE* = Nitrogen use efficiency, also apparent N efficiency

*Grain N concentration × 5,7

able to lower N_2O fluxes by decreasing NO_3^- availability as a substrate for denitrification.

Although moisture plays a predominant role in triggering N_2O production, by filling soil pores with water thus limiting oxygen diffusion and consequently stimulating denitrification (Flessa and Beese 1995; Roman-Perez and Hernandez-Ramirez 2021), we found a negative correlation between WFPS and N_2O fluxes (Table 3). A negative correlation of these variables during the growing season was also found by Vitale et al. (2013), who hypothesized a limiting effect of high soil moisture on nitrification. Analog to the correlation between NH_4^+ and N_2O fluxes, WFPS in our study was higher during periods of time when other conditions were limiting, i.e., during winter, when WFPS reached ≈70%, but NO_3^- contents ranged only between 0.9 and 7.8 g N kg soil^{-1}. Additionally, Guzman-Bustamante et al. (2019) reported a temporal C limitation during the cropping season of winter wheat at the same study site and at the same time as the measurements presented here, overwriting moisture effects on N_2O flux rates. As pointed out by Granli and Bøckman (1994), fertilizer application, as a seasonal operation, which takes place when temperature is high and—in the case of South Germany—in periods with most precipitation, can mask the effect of soil-physical variables on N_2O fluxes and complicates the interpretation of field studies.

Effect of N fertilization and N splitting

Annual N_2O emissions of [1]CAN and [1]ASN (2.85 and 2.82 kg N_2O–N ha^{-1} a^{-1}) were in accordance with the range of N_2O emissions reported by Kaiser and Ruser (2000) who reported a mean N_2O emission of 2.8 kg N_2O–N ha^{-1} a^{-1} from 14 field experiments with wheat in Germany. Lebender et al. (2014b) found lower annual emissions at two sites in Germany cropped with winter wheat (1.7 and 1.8 kg N_2O–N ha^{-1} a^{-1}) although this experiment took place in the same year as our experiment (2012). In contrast to our study, soil texture at the study site of Lebender et al. (2014b) was characterized by higher sand and lower clay and silt contents.

Weather conditions before the vegetation period indirectly influenced N_2O fluxes and annual emissions of N fertilized treatments in our study. Due to a mild winter with a short cold period without snow cover, wheat plants tended to create more stems and straw biomass then usual (Guzman-Bustamante et al. 2019). The high straw biomass together with enhanced N concentrations in the straw induced relatively high N amounts in the straw remaining on the field after harvest (ASN: 32%; CAN: 27% of applied fertilizer N). Tillage operation promoted mineralization of wheat straw and a rapid nitrification resulted in increased soil NO_3^- amounts in the tillage period, thus, as indicated by the positive correlation between N_2O release and NO_3^- availability, stimulating N_2O production from denitrification. These high N_2O flux rates in the tillage phase were the reason for the high contribution of the emissions during the tillage period to the annual emissions (ASN: 57%; CAN: 45% of annual N_2O emissions after harvest).

Although the type of fertilizer can alter N_2O emissions (Shcherbak et al. 2014), we did not find statistical differences between the annual emissions of [1]CAN and [1]ASN. Despite lower N_2O emissions during the vegetation period for [1]CAN treatment, high fluxes of [1]ASN during tillage and winter offset the N_2O mitigation during vegetation period, indicating the need for whole annual measurements for the evaluation of N_2O reduction strategies. Similar results were reported from measurements in potatoes (Ruser et al. 2001) and in winter oilseed rape (Kesenheimer et al. 2021). The [1]ASN treatment contained more NH_4^+-N than [1]CAN (CAN: 50% as NO_3-N, 50% as NH_4-N; ASN: 29% as NO_3-N, 71% as NH_4-N). Desorption of higher amounts of fertilized NH_4^+ from clay minerals might have postponed N availability and the resulting substrate supply for N_2O production into the post-harvest period in the [1]ASN treatment (Lebender et al. 2014a).

Increasing NO_3^- and low NH_4^+ amounts during the tillage period indicate a rapid nitrification of mineralized N from N-rich straw. The turnover of easily degradable carbon fractions of the straw such as cellulose and hemicellulose might also have further contributed to O_2 consumption, thus increasing anaerobic conditions favouring denitrification and enhancing N_2O fluxes after harvest.

A comparison with other field experiments shows that grain yield of our fertilized treatments was rather low, between − 16% and − 26% (Pasda et al. 2001; Schulz et al. 2015). The reasons for the low yields might be related to year, as Makary et al. (2020) also reported low grain yields in the same experimental year. They attributed this result to the exceedingly warm winter, which led to an unfavourable high tiller density in spring.

A comparison between the single application in [1]CAN and the traditional threefold application in [3]ASN/CAN/CAN showed significantly decreased fluxes and 38% less emissions during the vegetation period in the traditional split fertilization treatment. Although statistically not significant on an annual basis, the t-test comparison of the annual N_2O emission between the treatments with single and three applications was very close to statistical significance ($p = 0.056$) and can at least be considered a substantial trend.

Possible reasons for lower N_2O emissions with increasing number of N splitting compared to a single application rate were (i) the generally lower soil NO_3^- contents in the treatments with fertilizer splitting and especially during the time of the first N_2O peak after rain, and (ii) the fact that fertilizer granules were only slowly dissolved due to relatively low soil moisture following the second and third application. As discussed by Knittel et al. (2007), the later fertilization occurs, the higher the probability that soil might be too dry for fertilizer granules to be dissolved.

The high soil NO_3^- amounts in the split treatments after the second and third application did not induce enhanced N_2O fluxes; this might be the result of the low soil moisture and the corresponding good aeration in this period which limited denitrification. Mainly because of different precipitation patterns and the occurrence of heavy rainfall events after N applications, the success of splitting as a N_2O reduction strategy can strongly vary as shown by Guardia et al. (2018) and others.

In our experiment, grain yield and quality were influenced by splitting of the N-fertilizer with higher grain yield in the treatment without splitting when compared to the traditional fertilization with three application rates and higher crude protein contents in treatments with split application. Neither Schulz et al. (2015) nor Makary et al. (2020) found differences in yield or N content for split N fertilization on similar study sites in Southwest Germany. Both recommended to consider one single CAN application in a late (shooting) stage when modern wheat varieties are grown on soils with low NO_3^- leaching during the growing season. In contrast, our results recorded under unusually dry conditions (19% lower rainfall from March to July when compared to the long-term annual mean) seem to be more similar to the ones reported under Mediterranean conditions: we observed slightly higher grain yields with one application rate (Guardia et al. 2020) and a higher N grain content when N fertilizer was split (Ercoli et al. 2013). Yield components such as spike number and TGM followed a similar trend as found by Pasda et al. (2001), with smaller spike numbers and higher TGM when N fertilizer was split. Since results from a previous experiment on the same field showed higher grain yields for a fertilization with three application rates (Guzman-Bustamante et al. 2012) and no difference between protein contents (data not shown), the comparatively milder winter and dryer vegetation period together with the high N amount might have driven spike numbers on [1]ASN and [1]CAN and so elevated competition among wheat plants and decreased grain yield (Maidl et al. 1998). In this sense, split fertilization was not able to contribute to yield formation, since the spike number was too high (Scharf and Alley 1993).

Effect of nitrification inhibitors

Both NIs in our study reduced the mean annual N_2O emission (DMPSA: 26%; DMPP: 33%), with the reduction for DMPP being statistically significant. For [1]CAN + DMPSA the tillage operation after harvest might have masked N_2O reduction during the vegetation period (Corrochano-Monsalve et al. 2020).

Similar reduction potentials for DMPP and DMPSA were reported for field studies by Ruser and Schulz (2015) and by Huérfano et al. (2016). The reduction of N_2O emissions after the application of ammonium containing fertilizers with NIs was explained directly by lower N_2O production during nitrification as well as indirectly by the lower substrate availability for denitrification (Ruser and Schulz 2015). Additionally, Torralbo et al. (2017) detected an increased N_2O reduction during denitrification after NI application which also decreased net N_2O release from soil.

A direct comparison between DMPP and DMPSA cannot be drawn with our dataset, as we used different N fertilizers for the two inhibitors. Differences between the two products (ASN + DMPP vs. CAN + DMPSA) might result either from different efficiencies of the inhibiting compounds or from the different share of NH_4^+ and NO_3^- in CAN and ASN. The latter was reflected by the soil NH_4-N/NO_3-N ratio, which was higher in the ASN + DMPP treatment (vs. ASN) for approximately 3.5 months, whereas it did not differ that clearly for CAN + DMPSA (vs. CAN).

Twofold split application of ASN + DMPP treatment performed similarly to a single application of ASN + DMPP leading to 33% lower annual N_2O emissions compared to a single application of ASN. One of the reasons for this reduction was the same as for the [3]ASN/CAN/CAN treatment: lower soil NO_3^- amounts were registered for split treatments during periods with conditions favourable for high N_2O production.

Similarly to our results, splitting NI fertilizers did not further mitigate N_2O emissions compared to a single N application under Mediterranean conditions (Huérfano et al. 2016; Corrochano-Monsalve et al. 2020), because soil conditions during the second fertilizer application were not favourable for N_2O production (WFPS $< 48\%$). Contrarily, if the second NI application occurs when denitrification conditions are optimal (high water content and high soil temperature), high N_2O fluxes might raise emissions to the same level as soil fertilized without NI (Huérfano et al. 2015).

Despite lower N_2O flux rates in the [2]ASN + DMPP treatment during winter, cumulative N_2O emissions from [2]ASN + DMPP and [1]ASN were not significantly different. The lower N_2O flux rates in the [2]ASN + DMPP treatment might hint on long-term effects of NIs on N transformation processes in soil. A significant effect was shown by Pfab et al. (2012) and Guzman-Bustamante et al. (2019) for the same study site as in our experiment. The reasons for possible long-term effects on N_2O emissions as reported by Pfab et al. (2012) and Guzman-Bustamante et al. (2019) from our study site as well as DMPP-induced changes in microbial function diversity in a study site in Italy (Tedeschi et al. 2020) clearly show the need for further verification.

In this regard, determination of the inhibiting compound and metabolites might be interesting, since it was shown that approx. 16% of DMPP were still present in a topsoil under winter wheat at the end of the vegetation period (Benckiser et al. 2013).

In terms of winter wheat yield and quality, our results agree with Pasda et al. (2001) and Huérfano et al. (2015), who did not find an effect of split NI on winter wheat grain yield, whereas protein content was increased in a twofold ASN + DMPP application compared to all single application treatments. Since our single application treatments with and without NI were all in a lower crude protein class (≈ 11.2%) compared to the treatments with split application (12.4–14%), splitting seems to be the main factor influencing crude protein in wheat grain as discussed before.

As enhanced-efficiency fertilizers are more expensive than regular mineral fertilizer, its use might not be profitable in a wheat system. From a climate protection point of view, farmers could waive its use when an appropriate N fertilization management is implemented (Li et al. 2018). However, due to expiration of patent protections, NI-containing fertilizers became cheaper on the European market in the last years, and an economical re-evaluation of the use of NIs seems worthwhile.

Conclusion

Our first hypothesis—that a threefold split N application can decrease N_2O emission compared to a single N application—can be partially corroborated ($p < 0.1$) as [3]ASN/CAN/CAN reduced annual N_2O emission compared to one application of CAN and ASN. The second hypothesis—that split application of a NI fertilizer can further mitigate N_2O emissions, compared to a sole NI application—must be rejected, as N_2O emission levels of both split NI treatments ([2]ASN + DMPP and [2]ASN + DMPP/CAN) showed the same emission levels as a single application of ASN + DMPP. Nevertheless [2]ASN + DMPP contributed to significantly higher grain protein content. Our third hypothesis—that DMPSA used with CAN shows a similar N_2O reduction as ASN + DMPP—must be rejected as well, since a single application of CAN + DMPSA mitigated N_2O emissions from CAN only during the vegetation period but not on an annual basis. Only DMPP was able to lower N_2O fluxes during the vegetation period and winter, thus mitigating annual emissions. Our results support the splitting of N fertilizer in order to achieve high grain quality when appropriate wheat varieties are sown by simultaneously lowering N_2O emissions. As a result of climate change, precipitation patterns (with more heavy rain events during the cropping season) will change more frequently in the future. Such strong rainfall events can trigger N_2O production after N application, and thus the use of DMP-based nitrification inhibitors could be a powerful tool to mitigate N losses in these periods. Future studies should focus on the effects of DMPSA on N transformation in soils, especially after harvest. Determination of long-term effects on nitrification and probably also on denitrifiers may help to improve our understanding in this context.

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Declarations

Conflict of interest None.

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