



Ammonia emissions from inhibited urea fertilizers – Results on mitigation potential and wheat yield from a multisite experiment across six different regions in Germany

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ABSTRACT

The use of urease- and nitrification inhibitors (UI, NI) is widely accepted in agriculture. However, robust ammonia (NH₃) reduction factors for specific compounds and regions are missing. This study of coordinated field trials evaluated NH₃ emissions in Germany across 22 site-year combinations after the application of inhibited urea in winter wheat. Tested fertilizers were urea (U), urea with UI (U+UI), and double-inhibited urea (U+UI+NI). Ammonia emissions were determined using ALPHA samplers, inverse dispersion modeling, and semi-quantitative passive flux samplers. Improving the existing calibrated passive sampling approach, a linear mixed-effects model was developed, accounting for the placement of individual plots within the trial layout. Regardless of the fertilizer treatment, the weather covariates and the clay content significantly influenced the emission factors (EFs, expressed as NH₃-N per unit N applied). Average EFs for the treatments were 8.0, 3.1, and 3.8% for U, U+UI, and U+UI+NI, respectively. Compared to U, the emission reduction was affected by inhibitor treatment, soil clay content, and temperature, and was highest under high N-loss scenarios. Average reductions were 61% for U+UI and 52% for U+UI+NI. The results suggest a regionalization of EFs and reduction factors. Grain N yield was significantly influenced by inhibitor treatment and was highest for U+UI with 164 kg N ha⁻¹. U+UI+NI featured the highest absolute yield. With a reduced grain protein concentration, this resulted in a similar grain N yield when compared to U. Combining results of emission and yield measurements, recommendations for specific production targets in winter wheat production are derived.

1. Introduction

Ammonia (NH₃) is recognized as a major environmental pollutant with global impact. Long-range atmospheric transport and subsequent deposition of NH₃ can exceed critical N loads in sensitive ecosystems, causing eutrophication and acidification (Dentener et al., 2006).

Increased reactive N inputs in sensitive ecosystems drive biodiversity loss, reducing crucial values such as preserving the integrity of the biosphere (Dise et al., 2011). Emissions of NH₃ contribute to the formation of fine aerosol particles (PM_{2.5}), which are linked to premature mortality on a worldwide scale (Lelieveld et al., 2015). While NH₃ itself is not classified as a climate-relevant trace gas, its deposition can

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indirectly result in increased nitrous oxide (N₂O) emissions, a potent greenhouse gas (Bühlmann et al., 2015). Between 1990 and 2019, N deposition in Europe increased carbon sequestration, primarily in forests, offsetting the negative effects of indirect N₂O emissions (Vries et al., 2024). However, as soil organic carbon stocks cannot grow indefinitely this compensation cannot be projected for future periods.

Effectively addressing the challenges associated with NH₃ requires an integrated understanding of its emission, transport, and deposition processes. This has to be coupled with targeted interventions in the N-cycle. Focusing on N flows with the largest reduction potential or the simplest reduction options seems to be the most promising approach. With a share of 93%, agriculture is the primary source of NH₃ emissions in Europe, and substantial amounts of N are lost each year from arable land (EEA, 2024). Worldwide, urea is the most widely used synthetic N fertilizer, accounting for approximately half of the global N consumption of synthetic fertilizers (IFA, 2025). Simultaneously, urea is attributed the highest emission factor (EF, NH₃-N emission related to the N input) when compared with other synthetic N fertilizers (EEA, 2023). The interaction of these two facts makes urea highly relevant when reducing NH₃ emissions from synthetic N fertilizers. As the United Nations and the European Union have set ambitious reduction strategies in their Sustainable Development Goals and National Emission Ceilings (NEC) directive, the implementation of reduction measures in policy appears highly relevant (EU, 2016/2284 2001). However, implementing NH₃ mitigation measures by individual farmers is not easy to achieve, as the resulting benefits of reduced N losses and increased yields are too close to the implementation costs (Gu et al., 2023). The implementation of the NEC directive in German legislation has led to the amendment of the national fertilizer ordinance (DüV, 2020), which stipulates the use of urease inhibitors (UI) or the incorporation of urea into the soil within four hours after fertilizer application for surface-applied urea. Most recently, Ireland and England have implemented comparable rules, effectively banning the use of untreated urea in the main application seasons (Red Tractor, 2025; S.I. No. 42, 2025). With Germany being one of the first countries to implement the mandatory use of UIs on surface-applied urea, the abatement effect was derived from a meta-analysis of 25 studies (Schoof et al., 2025). For German emission inventory reporting, the EF for urea was reduced by 70% for incorporation and by 60% for the addition of UIs (Bittman et al., 2014; Schoof et al., 2025).

Even though there are occurring UIs in nature, the most widely used UIs applied to synthetic N-fertilizers are synthetic chemical substances. (Matczuk and Siczek, 2021; Svane et al., 2020). The active ingredients of the most researched UIs are N-(n-butyl) thiophosphoric triamide (NBPT) and a mixture of NBPT with N-(propyl) thiophosphoric triamide (NPPT) (Fan et al., 2022; Matse et al., 2024). Moreover, N-(2-Nitrophenyl) phosphoric triamide (2-NPT) is of importance, which is less researched, and only a handful of incubation and even fewer field studies are available on this comparatively new active ingredient (Matse et al., 2024). NBPT, NPPT, and their degradation products are known to block the active site of the urease enzyme, avoiding the entry of urea into the active site and therefore its further hydrolysis into ammonium (NH₄⁺) (Mazzei et al., 2019; Peters and Thiele-Bruhn, 2022; Svane et al., 2020). Active ingredients of NIs are more diverse, and most of them prevent the oxidation of NH₄⁺ by the ammonia monooxygenase enzyme (Ruser and Schulz, 2015). Of global importance are, among others DMPP, DMPSA, DCD, and triazole compounds (Akiyama et al., 2010). However, also less known active ingredients are available in regional markets such as N-(3 (5)-Methyl-1H-pyrazole-1-yl)methyl)acetamide (MPA) in Germany. To date, no field studies exist for this active ingredient.

NH₃ emissions from urea vary based on soil and weather conditions, due to their effects on urea hydrolysis and the chemical equilibrium between NH₄⁺ and NH₃. Known weather factors influencing NH₃ emissions include, among others, temperature (Drame et al., 2023; Siman et al., 2020), soil water content and its change by rainfall, irrigation, or drying of moist soils (Fröbl et al., 2025b; Holcomb et al., 2011;

Sanz-Cobena et al., 2011) and wind (Sommer et al., 2004). The most frequently described soil properties influencing NH₃ emissions are soil pH (Dawar et al., 2011; Ruser et al., 2008), texture (Kissel et al., 2008) and cation exchange capacity (CEC) (Ohnemus et al., 2021).

In summary, the general principles of the influence of site and weather conditions on NH₃ emissions or the emission potential of soils are well described. However, the information on the same influencing factors on the reduction ability of mitigation measures, such as UI, is scarce. Schoof et al. (2025) concluded in their meta-analysis that the influence of soil and weather covariates on reduction potential by UI was not significant, which they attribute to unbalanced data, missing ancillary data, and large site-specific influences. In a meta-analysis of Matse et al. (2024) the mean reduction potential of the commonly used UI NBPT was shown to be 61%, with a confidence limit between 57% and 64%. In the meta-analysis of Silva et al. (2017), the lowest reduction potentials were observed when the absolute emissions of untreated urea were already low. This was the case when substantial rainfall occurred shortly after fertilizer application. When UI was combined with other effective NH₃ mitigation measures, such as deep placement of urea, its additional mitigation effect was minimal. Because of the complex interactions of effects controlling NH₃ emissions, initial soil properties such as soil organic carbon, pH, and texture did not directly affect the NH₃ reduction efficacy of NBPT (Silva et al., 2017). Contrastingly, a meta-analysis of Fan et al. (2022) found correlations of UI efficacy with soil pH, soil texture, and temperature; however, only soil pH proved to be significant. UI was shown to be most effective in neutral soils. Alkaline soils favored volatilization by shifting the NH₄⁺/NH₃ equilibrium towards NH₃, while acidic soils led to faster degradation of UI and reduced inhibitor efficacy (Fan et al., 2022).

NIs are commonly applied with synthetic amides, NH₄⁺-N, or organic N fertilizers to increase N use efficiency as they can reduce nitrate (NO₃) leaching and N₂O emissions. In recent years, the addition to urea fertilizer in combination with UI has been suggested, and commercial products are available. NIs retard the microbial oxidation of NH₄⁺ to NO₃ thus resulting in higher NH₄⁺ concentrations when compared to a fertilizer without NI. As a consequence, the addition of NI to UI treated urea can increase NH₃ emissions (Castellano-Hinojosa et al., 2020; Fröbl et al., 2025b). Makary et al. (2020) showed that for sites with low NO₃ leaching during the cropping season, the number of split applications can be reduced without adverse effect on wheat protein content. Therefore, an N fertilization strategy with only two N doses in combination with double-inhibited urea fertilizer (UI + NI) seems to be a promising option to reduce the environmental impact of wheat production without yield and quality losses.

The first aim of the study was to determine NH₃ emission from application of urea to winter wheat in different regions of Germany and to analyse effects of weather condition, soil properties and timing of fertilization on N input related NH₃-N losses. Another aim was to determine the effects of single (UI: 2-NPT) and double (UI+NI: 2-NPT+MPA) inhibition of urea with comparatively new active ingredients on NH₃ emission at different sites, and to analyse effects of weather condition and site properties on inhibitor effects. Moreover, it was the objective to assess the effects of inhibitor application with urea on yield and protein concentration of winter wheat. Featuring an integrated assessment of NH₃ emissions from inhibited urea fertilizers and their agronomic effects on winter wheat yield in harmonized field trials across different German soils and climate zones under ceteris paribus conditions, this study is a major novelty. This study with its consistent trial layout and measurement methods as well as data-availability on the highest level, are advantages when compared to meta-analyses. The following hypotheses were tested:

- i) N input related NH₃ emission induced by the application of urea and inhibited urea exhibit distinct regional trends due to geographic differences in climate, soil, and management patterns.

- ii) Addition of UI 2-NPT to urea shows a uniform relative reduction in NH₃ emission regardless of site and weather conditions.
- iii) Addition of MPA to U+UI increases NH₃ emissions compared to U+UI because of higher soil NH₄⁺-N concentrations after fertilizer application.
- iv) Reduced NH₃ emissions increase wheat yield, grain protein concentration, and grain N yield.

2. Materials and methods

2.1. Trial design

Investigations in the joint project NH₃-Min were based on coordinated multi-plot field trials conducted across six different German regions, which represent typical wheat production areas. Each region featured up to two field sites (Fig. 1). Eight different fertilizers, receiving the same site-specific annual amount of N, as well as one unfertilized control, were tested. The different treatments were allocated to a

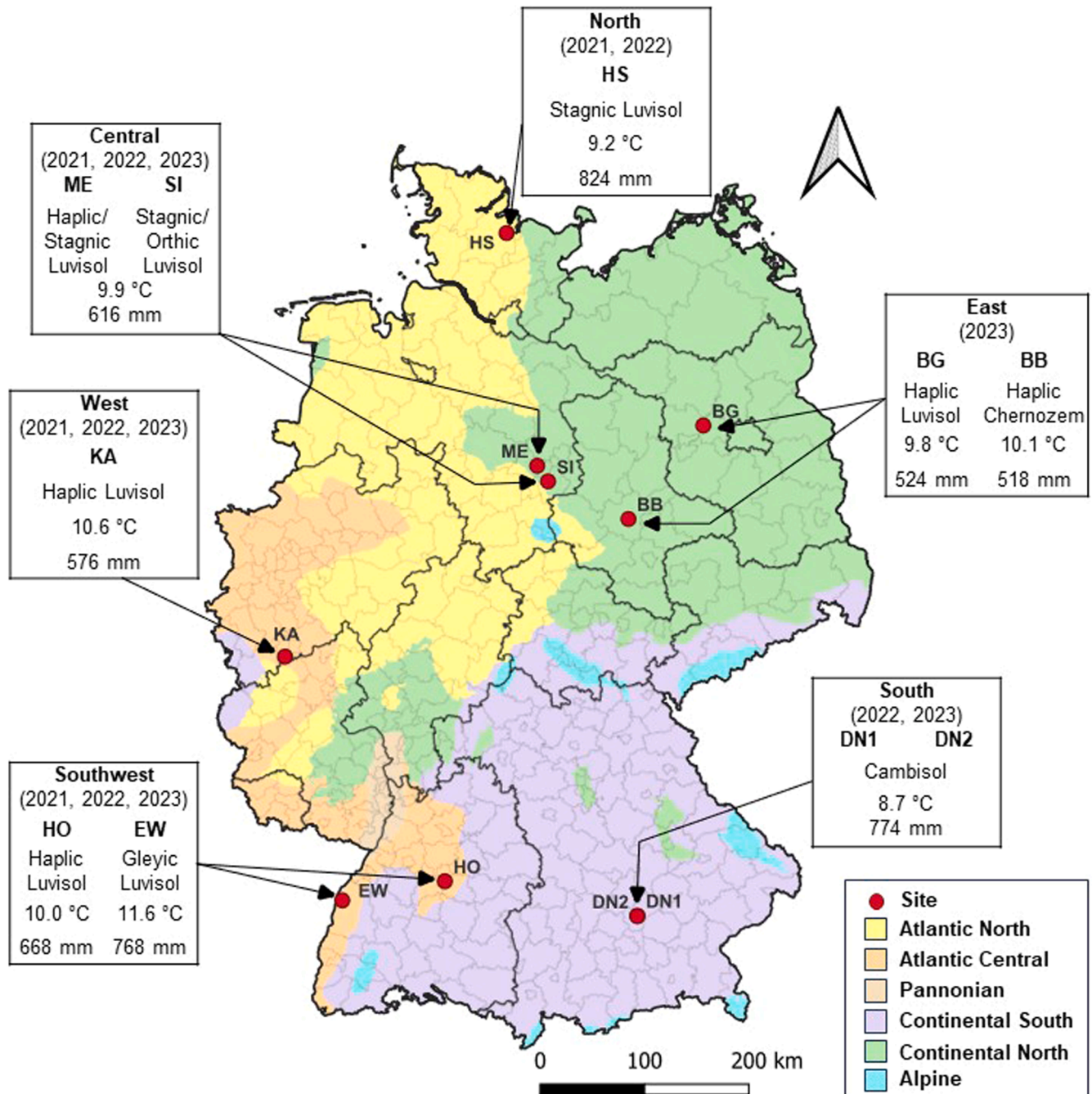


Fig. 1. Geographical locations of NH₃-Min trial with abbreviation of field site name (HS = Hohenschulen, BG = Berge, BB = Bernburg, DN1 + DN2 = Dürnast, HO = Hohenheim, EW = Eckartsweier, KA = Klein Altendorf, ME = Meine, SI = Sickte), respective study years, soil type, mean annual temperature, and rainfall. Soil types according to the World Reference Base for Soil Resources (FAO, 2014). Mean annual temperature and rainfall are based on the years 1991–2020 and were retrieved from the closest weather station of the German meteorological service (DWD, 2024). The map also shows environmental zones in Germany that have been grouped and modified based on Metzger et al. (2005).

randomized complete block design with four repetitions. This paper will focus on three of the tested fertilizers: untreated urea (U), urea with UI (U+UI), and urea with UI and NI (U+UI+NI). The unfertilized control (N0) was used to correct for background emissions within the trial. The size of the square experimental plots was 9 × 9 m with a 9 m buffer area between each plot, fertilized with the non-NH₃-emitting calcium nitrate fertilizer.

Winter wheat (*Triticum aestivum* L. var. RGT Reform) was cultivated at all sites, and timing of seeding, as well as crop protection measures, were decided based on best management practices and executed by the respective research stations.

2.2. Site descriptions

Experimental sites with varying environmental conditions for evaluating fertilizer performance were dispersed across Germany (Fig. 1). Soil samples for the site characterization were taken before fertilizer application in spring. Samples were sieved, air-dried, and analyzed collectively in the same central laboratory. The main site characteristics are given in Table 1.

2.3. Fertilizers

The granular fertilizers used in this study were urea (U), urea with the UI 2-NPT (U+UI), and double-inhibited urea with 2-NPT and the NI MPA (U+UI+NI). All fertilizers are commercially available (“PIAGRAN 46” (U), “PIAGRAN pro” (U+UI), and “ALZON neo-N” (U+UI+NI)), produced and marketed by the “SKW Stickstoffwerke Piesteritz GmbH”. According to the producer, the concentration of the active ingredient 2-NPT in treatments U+UI and U+UI+NI accounted for 0.075% of the N-content of the fertilizers. For the U+UI+NI fertilizer, the corresponding MPA concentration was 0.1% of the fertilizer N-content. The fertilizers were obtained every spring from agricultural distributors to avoid inhibitor degradation during storage over several years.

The annual amount of fertilizer applied was indicated by the site-specific maximum given by the German fertilizer ordinance (DüV, 2020). Spring soil mineral N (0–0.9 m depth) and potential site-specific mineralization during the vegetation period was subtracted from the N requirement for a five-year average wheat yield at the experimental sites (DüV, 2020). The fertilizer amounts differed across sites and years (Table S1) because of diverging yield potentials, pre-crops and soil

organic carbon concentrations. Fertilizer application was split into three applications for U and U+UI. The first N application was applied in early spring, during tillering of the wheat plants (ca. BBCH 23). During stem elongation (ca. BBCH 32) the second split application was applied. The third application was applied between ear emergence and flowering (ca. BBCH 49).

The split applications and subsequent NH₃ measurements are referred to as “campaign” or measurement campaign” in the following text.

The ratio between the three split applications was determined by the respective research stations (Table S1). For U+UI+NI the same annual amount of fertilizer was applied as for the other treatments but it was split evenly only between the first two applications, except for the region north in 2021 with three applications. In region south, all fertilizers were applied only in two split applications. For each NH₃ measurement campaign, fertilizers were applied at the same day using a tractor mounted pneumatic fertilizer spreader or plot experimental equipment.

2.4. NH₃ measurement

2.4.1. Measurement method

The NH₃-Min multi-plot field trials used the method of calibrated passive sampling (CPS) for emission calculation (Pacholski, 2016), by using Inverse Dispersion Modelling (IDM) in combination with ALPHA samplers for calculation of absolute ammonia fluxes recently validated in a study by Götze et al. (2025). As passive samplers (Vandré and Kaupenjohann, 1998) only produce relative treatment differences, they need to be scaled by a quantitative method (Pacholski, 2016). Employing IDM (Loubet et al., 2018; Nikolajsen et al., 2020) in combination with ALPHA samplers (Tang et al., 2001) absolute NH₃ emissions were estimated from atmospheric NH₃ concentrations, wind speed and wind direction at 2 m height. Passive samplers were used in every plot, ALPHA samplers only in the U treatment, where the highest emissions were expected. Additionally, in three out of the four unfertilized control plots, ALPHA samplers were used to capture the NH₃ background emissions. The described method of IDM with ALPHA samplers was recently described by Götze et al. (2025). This is the first paper using this novel approach for comparison of NH₃ emissions with different fertilizer treatments on large, coordinated field trials across Germany.

Table 1

Main site characteristics. Values are rounded to a single digit. EW2023, DN2023, and SI2023: trial on the same respective field but plots shifted to avoid overlap with the 2021 trial. C_{org} = soil organic carbon, N_t = total soil nitrogen, CEC = soil cation exchange capacity. pH determination in 0.01 mol l⁻¹ CaCl₂ (ratio soil/extraction solution = 1/5, w/v). For site abbreviations, see Fig. 1.

Region	Site	Year	Latitude	Longitude	Texture		Clay	C _{org}	N _t	pH	pH buffer capacity	CEC	Urease activity
			degr. N	degr. E	Sand	Silt							
North	HS	2021	54.313407	9.993680	59.4	27.6	13.0	1.1	0.11	6.9	38.7	10.6	23.5
	HS	2022	54.211040	9.983022	52.5	32.0	15.5	1.2	0.11	6.8	39.3	12.0	22.6
East	BB	2023	51.832900	11.693100	15.5	65.2	19.3	1.8	0.16	7.1	32.7	17.9	28.0
	BG	2023	52.619600	12.784900	71.6	19.9	8.5	0.8	0.09	6.4	21.9	6.9	11.0
South	DN1	2022 + 2023	48.407058	11.694203	13.8	64.7	21.5	1.2	0.13	6.8	23.9	13.8	23.3
	DN2	2022	48.407058	11.694203	15.9	57.0	27.1	1.3	0.14	6.5	24.2	17.8	23.9
Southwest	EW	2021 + 2023	48.545250	7.851324	38.6	41.3	20.1	1.0	0.11	6.8	30.5	13.9	16.1
	EW	2022	48.518299	7.869955	33.7	50.0	16.3	1.0	0.08	6.0	29.5	7.4	13.3
	HO	2021	48.710884	9.193204	8.1	68.0	23.9	1.8	0.18	6.6	39.7	16.8	37.7
	HO	2022	48.716286	9.188530	7.9	69.3	22.8	1.4	0.14	6.8	34.6	13.9	30.4
	HO	2023	48.713643	9.195351	3.2	72.0	24.8	1.1	0.13	7.1	36.2	15.6	30.4
West	KA	2021	50.616390	6.996154	6.4	75.5	18.1	1.1	0.11	6.4	31.9	11.3	21.3
	KA	2022	50.620352	6.988096	6.3	77.0	16.7	1.0	0.10	6.9	29.1	10.7	19.3
	KA	2023	50.617860	6.988583	7.4	76.0	16.6	0.9	0.10	6.7	29.5	10.7	15.1
Central	ME	2021	52.370582	10.547239	74.6	19.9	5.5	1.5	0.11	5.5	26.7	5.4	15.8
	ME	2022	52.387282	10.562512	68.6	24.2	7.2	1.4	0.11	6.6	23.8	7.0	20.5
	ME	2023	52.366386	10.491218	79.1	12.0	8.9	1.2	0.12	6.6	20.5	8.3	21.6
	SI	2021 + 2023	52.190478	10.686515	17.6	69.4	13.0	1.6	0.16	6.3	45.2	13.5	23.7
	SI	2022	52.202587	10.635506	48.6	37.3	14.1	1.6	0.14	6.4	33.5	13.2	24.1

2.4.2. Management of NH₃ samplers in the field and laboratory

Triplicates of ALPHA samplers and one passive sampler were fastened on steel rods 0.25 m above the canopy in the center of the respective square plot. Sampling intervals ranged from approximately 24 h when emissions occurred to up to 72 h at the end of a measurement campaign with very low emissions and atmospheric NH₃ concentrations. Measurement campaigns lasted from one to three weeks, with both types of samplers being changed simultaneously. The passive samplers consisted of 0.25 dm³ square-bottom PE bottles with two 0.02 m diameter holes on each side. The holes were covered with a fine mesh to allow for easy air exchange and to exclude insects and debris. For NH₃ measurement, the samplers were filled with 0.02 dm³ of sulfuric acid (0.05 mol l⁻¹). After exposition, the volume of the remaining solution in the samplers was sampled, quantified, and the samples were then frozen until analysis. ALPHA samplers capture NH₃ diffusing through a PTFE membrane using citric-acid-coated filter paper. After exposition, the filter paper was removed from the ALPHA sampler body and frozen until analysis. For the determination of NH₄⁺-N uptake, the ALPHA filter papers were extracted with 0.005 dm³ of deionized water. For NH₄⁺-N measurement of the extracts and sulfuric acid solutions from the passive samplers, NH₃-selective electrodes or colorimetric analyzers were used. A list of NH₄⁺-N measurement devices at the individual sites is given in Table S2. An interlaboratory test confirmed the accuracy and comparability of the individual laboratories and measurement devices.

2.4.3. NH₃ emissions estimation from ALPHA samplers by inverse dispersion modelling

Atmospheric NH₃ concentration of ALPHA samplers was calculated based on the effectively sampled air volume and the amount of absorbed N (Tang et al., 2001). Inverse dispersion modelling performed by using a backward Lagrangian stochastic (BLS) model (Flesch et al., 2004). The open source software “WindTrax” (Thunder Beach Scientific, Nova Scotia, Canada) mapped the experimental plot as an emission source and the ALPHA sampler as a concentration sensor. Using wind speed, friction velocity, and atmospheric stability, the BLS model estimates half-hourly fluxes. The actual emissions based on ALPHA samplers is the result of dividing the measured atmospheric NH₃ concentration by the simulated concentration-to-emission ratio.

The process of IDM modelling and the derivation of input parameters for the WindTrax software is described in detail in Götze et al. (2025). When compared to integrated horizontal flux measurements as a micrometeorological reference method (Kemmann et al., 2025), Götze et al. (2025) recently confirmed that this approach, which includes a correction for low wind speed and high temperature conditions, resulted in accurate measurements. This comparison of NH₃ measurement methods was part of the NH₃-Min project, which aimed to validate small-scale replicate plot NH₃ loss measurements against the integrated horizontal flux method as a reference. It was integrated in the field trials described here.

2.4.4. Derivation of transfer coefficient

In calibrated passive sampling, a correction is necessary for semi-quantitative passive sampler measurements using quantitative emission data. This scaling was done in past studies by a simple transfer coefficient (TC) calculation. The TC is the quotient that is obtained by dividing absolute NH₃ emissions by passive sampler concentrations. However, background emissions have a substantial influence on TC calculation and were shown to differ across plots in multi-plot field trials (Huf et al., 2023a). Huf et al. (2023a) suggested to use the treatment means of cumulative emissions at the end of the trial for a robust TC calculation. Differing meteorological conditions and crop growth stages tend to influence the TC (Huf et al., 2023a). As the NH₃-Min field trials represented a large diversity of such conditions, TC calculation was not always successful. Comparatively small passive sampler concentrations or high ALPHA sampler emissions resulted in biased TCs, thereby overestimating NH₃ emissions. Measurement campaigns for

slow-emitting synthetic fertilizers tend to last longer than those for organic fertilizers, where the concept of calibrated passive sampling was developed. To improve standard TC calculation, multiple statistical models were tested on a subset of six site-year combinations. The models were fitted separately for each measurement campaign. The root mean square error between the model-predicted emissions and the input measured emissions was used to assess the goodness of fit. The campaign-specific linear mixed model (Equation 1) gave the lowest root mean square errors across campaigns.

Equation 1: Linear mixed model for transfer coefficient estimation.

$$y_{ijklm} = \mu_{klm} + \beta_{klm}x_{ijklm} + \beta_{jklm}x_{ijklm} + \rho_{iklm} + e_{ijklm}$$

Where y_{ijklm} is the absolute emission (kg ha⁻¹) in the i^{th} plot in the j^{th} sampler exposure period of the k^{th} measurement campaign at the l^{th} site in the m^{th} year. μ_{klm} is the general intercept for the k^{th} measurement campaign at the l^{th} site in the m^{th} year. β_{klm} is the fixed slope for the k^{th} measurement campaign at the l^{th} site in the m^{th} year. x_{ijklm} is the measured passive sampler concentrations (mg N l⁻¹) in the i^{th} plot in the j^{th} sampler exposure period of the k^{th} measurement campaign at the l^{th} site in the m^{th} year. β_{jklm} is a random slope for the j^{th} sampler exposure period of the k^{th} measurement campaign at the l^{th} site in the m^{th} year. ρ_{iklm} is a random plot effect for the i^{th} plot in the k^{th} measurement campaign at the l^{th} site in the m^{th} year. e_{ijklm} is the random error of y_{ijklm} .

The general intercept μ and the fixed slope β explain the primary passive sampler's influence on absolute emissions. The random slope β_{jklm} is specific to the sampler exposure period and gives an estimate of the influence of the specific meteorological conditions on the relationship between passive samplers and NH₃ emissions based on ALPHA samplers connected with IDM. The random plot effect estimation was not feasible for plots without ALPHA samplers and was set to zero in these plots. Comparable to a standard TC, the proposed linear mixed model was fitted individually for each NH₃ measurement campaign, using the “lmer” function from the R-package “lme4” (Bates et al., 2015). The function “predict” from the R-package “stats” was used to calculate absolute emissions from passive sampler concentrations (R Core Team, 2023). The standard error of absolute emissions was estimated by 10,000-fold bootstrapping using the function “bootMer” from the R-package “lme4” (Bates et al., 2015).

This novel approach to TC calculation based on a linear mixed model has the following advantages: i) The placement of the plots within the multi-plot trial and thus the associated background emissions are statistically considered in the calculation. ii) A factor for the correlation between ALPHA IDM emissions and passive sampler NH₃ uptake during the sampler's exposure period is included in the model. This is especially important for long measurement campaigns under changing meteorological conditions, as is often the case for emission trials involving inhibited synthetic fertilizers. iii) The prediction error can be considered as the standard error of the emissions for further calculations, rendering the need for error propagation calculation during ALPHA IDM unnecessary.

2.5. Soil sampling

Soil samples were taken using stainless steel soil corers to determine soil mineral N (NO₃-N and NH₄⁺-N) concentrations and budget. In early spring, a pooled sample from four plots per treatment was taken to a depth of 0–0.9 m. From these samples the average soil mineral N concentration for fertilizer requirement calculation was determined. During the NH₃ measuring campaigns, soil samples were taken from 0 to 0.1 m at least once a week, with the first sampling conducted one day after fertilizer application. The shallow sampling depth was chosen to capture soil pH effects during urea hydrolysis.

Each sample consisted of at least three individual subsamples of 0.1 l per plot, which were homogenized and pooled into a single sample. The samples were transported to the laboratory in cooled containers and

stored frozen until analysis. The individual laboratories analyzed the soil samples according to VDLUFA (1991): For each sample, soil and extraction solution (CaCl_2 , $0.0125 \text{ mol l}^{-1}$) were filled into shaker bottles (1:4 w/v) and were mechanically shaken for one hour at 30–35 rpm. After shaking, the extract was filtered, and the clear filtrate was frozen until colorimetric analysis of $\text{NH}_4^+\text{-N}$ and $\text{NO}_3^-\text{-N}$. Instruments used for mineral N concentration measurements in soil extracts differed across regions and are given in Table S2.

As demonstrated by Li et al. (2012), soil extraction with K_2SO_4 (0.5 mol l^{-1}) yields in higher $\text{NH}_4^+\text{-N}$ concentrations when compared to extracts with CaCl_2 (0.01 mol l^{-1}). Therefore, we additionally extracted soil from the U and U+UI+NI treatment (0–0.1 m) with K_2SO_4 solution (0.5 mol l^{-1} , 1:4 w/v).

The soil sampling during the vegetation period took place in a dedicated area of the plots, which was not used for agronomic measurements thereafter.

2.6. Agronomic measurements

Plants in the individual plots were harvested at BBCH 89. For the manual harvest, an area of 0.5 m^2 was cut at 0.02 m above the soil surface, and the above-ground fresh matter was determined. The number of ears was determined, and the ears were separated from the straw. The fresh and dry matter of the straw and ear samples were determined before and after air drying at 60°C until a constant weight was achieved. After drying, the ears were threshed and the grain separated from the spelt and chaff. Carbon and N concentrations were determined in milled straw and grain. Additionally, wheat was harvested using a small plot combine harvester to determine the grain yield (Mg ha^{-1}). Grain dry matter of the plot combine sample was determined after forced air drying at 105°C . Grain N yield was calculated by multiplying the grain dry matter grain yield of the combine harvester with the grain N concentration.

2.7. Weather conditions

Air temperature, precipitation, and wind speed were determined by weather stations at every field site. Wind speed was additionally measured at the same height as the ALPHA samples. Temperature and wind speed were averaged per campaign. Standardized rainfall (mm d^{-1}) was calculated by dividing the cumulative rainfall for each campaign by its duration in days, providing a measure of rainfall intensity. In case of missing site-specific weather data, gaps were filled from nearby stations of the German meteorological service (DWD).

2.8. Statistical analysis

2.8.1. Outline

Daily emissions were cumulated for each plot as well as for measured background emissions in the control plots. The control treatment was submitted to the model, similar to the other treatments. This approach was chosen because control subtraction from treatments before modeling would result in correlation of background-subtracted emission, voiding a fundamental premise of statistical evaluation. Due to the unbalanced nature of the data between sites, treatments, and years, as well as the repeated measuring of emissions on the same plots during one experimental year, a linear mixed effects model was used for analysis of the data. Normality of the residuals was checked visually using QQ-plots of the residuals. As the emission data were not normally distributed, the data were log-transformed before statistical analysis. After fitting the mixed model and selecting covariates, back-transformed estimates were obtained to subtract background emissions from treatment emissions. Input-related $\text{NH}_3\text{-N}$ emissions were calculated based on background-subtracted emissions and the fertilized N amount per treatment. Significant differences between treatments on the back-transformed scale were indicated by the log scale p-values of the

pairwise differences.

2.8.2. Linear mixed effects models for emissions and yield parameters

To analyze the influence of fertilizer treatment and covariates on NH_3 -emissions, the baseline mixed model given in Equation 2 was formulated and fitted to the data according to Piepho et al. (2004).

Equation 2: Linear mixed effects model for analysis of NH_3 -emissions.

$$\begin{aligned} \eta_{ijklm} = & \mu + \tau_i + \alpha_j + (\tau\alpha)_{ij} + B_{m(lk)} + Y_k + L_l + (\tau Y)_{ik} + (\tau L)_{il} + (YL)_{kl} \\ & + (\tau YL)_{ikl} + B_{m(jlk)} + (\alpha Y)_{jk} + (\alpha L)_{jl} + (\tau\alpha Y)_{ijk} + (\tau\alpha L)_{ijl} + (\alpha YL)_{jkl} \\ & + (\tau\alpha YL)_{ijkl} + e_{ijklm} \end{aligned}$$

where η_{ijklm} is the log-transformed NH_3 -emission cumulated per campaign in the j^{th} campaign from the i^{th} treatment applied in the m^{th} block at the l^{th} location and in the k^{th} year. Here, μ is the intercept, τ_i is the main effect of the i^{th} treatment, α_j is the main effect of the j^{th} campaign, $(\tau\alpha)_{ij}$ is the interaction effect of the i^{th} treatment with j^{th} campaign, $B_{m(lk)}$ is the main effect of the m^{th} block effect nested within the l^{th} location in the k^{th} year, Y_k is the main effect of the k^{th} year, L_l is the main effect of the l^{th} location, $(\tau Y)_{ik}$ and $(\tau L)_{il}$ are the interaction effects of the i^{th} treatment with k^{th} year and l^{th} location, respectively, $(YL)_{kl}$ is the interaction effect of the l^{th} location and k^{th} year, $(\tau YL)_{ikl}$ is the interaction effect of the i^{th} treatment with l^{th} location and k^{th} year, $B_{m(jlk)}$ is the deviation from the main block effect at the j^{th} campaign, $(\alpha Y)_{jk}$ is the interaction effect of the j^{th} campaign and the k^{th} year, $(\alpha L)_{jl}$ is the interaction effect of the j^{th} campaign and the l^{th} location, $(\tau\alpha Y)_{ijk}$ is the interaction effect of the i^{th} treatment with the j^{th} campaign and the k^{th} year, $(\tau\alpha L)_{ijl}$ is the interaction effect of the i^{th} treatment with the j^{th} campaign and the l^{th} location, $(\alpha YL)_{jkl}$ is the interaction effect of with the l^{th} location and the k^{th} year, $(\tau\alpha YL)_{ijkl}$ is the interaction effect of the i^{th} treatment, the j^{th} campaign, the l^{th} location, and the k^{th} year, and e_{ijklm} is the random plot error associated with η_{ijklm} .

Here, treatment effect τ_i , campaign effect α_j and treatment by campaign interaction $(\tau\alpha)_{ij}$ were fitted as fixed effects and remainder of the effects in model (Equation 2) were fitted as random effects with $Y_k \sim N(0, \sigma_Y^2)$, $L_l \sim N(0, \sigma_L^2)$, $B_{m(lk)} \sim N(0, \sigma_B^2)$, $(\tau Y)_{ik} \sim N(0, \sigma_{\tau Y}^2)$, $(\tau L)_{il} \sim N(0, \sigma_{\tau L}^2)$, $(YL)_{kl} \sim N(0, \sigma_{YL}^2)$, $(\tau YL)_{ikl} \sim N(0, \sigma_{\tau YL}^2)$, $B_{m(jlk)} \sim N(0, \sigma_{B\alpha}^2)$, $(\alpha Y)_{jk} \sim N(0, \sigma_{\alpha Y}^2)$, $(\alpha L)_{jl} \sim N(0, \sigma_{\alpha L}^2)$, $(\tau\alpha Y)_{ijk} \sim N(0, \sigma_{\tau\alpha Y}^2)$, $(\tau\alpha L)_{ijl} \sim N(0, \sigma_{\tau\alpha L}^2)$, $(\alpha YL)_{jkl} \sim N(0, \sigma_{\alpha YL}^2)$, $(\tau\alpha YL)_{ijkl} \sim N(0, \sigma_{\tau\alpha YL}^2)$. As multiple NH_3 measurements were collected within single experimental plots in one year, the residual variance-covariance structure of the model was set to account for autocorrelation of experimental plots across campaigns. A heterogeneous autoregressive model of order 1 [ARH(1)] was fitted, which allowed the determination of a campaign-specific residual variance.

To incorporate the environmental covariates (x_1, \dots, x_p), the model (Equation 2) was extended, and covariate-specific slopes (β_1, \dots, β_p) on each covariate and their interaction with treatment were fitted. The available covariates were soil properties (soil pH, clay content, and soil $\text{NH}_4^+\text{-N}$ concentration) and weather data (average temperature, average wind speed, and standardized rainfall). The soil pH and clay content were location-specific, and the rest of the covariates were campaign-specific. All covariates were standardized to a mean of 0 and a standard deviation of 1 prior testing, ensuring stable estimates for explanatory variables. The model's assumptions were checked using diagnostic plots. All subset regression was used for model selection, and the model with the lowest Akaike Information Criterion (AIC), calculated with full likelihood, was selected. However, the final selected model was re-fitted using the residual maximum likelihood (REML).

For each of the yield components dry matter grain yield, grain protein concentration, and grain N yield, a linear mixed effects model (Equation 3) was fitted separately.

Equation 3: Linear mixed effects model for analysis of yield com-

ponents.

$$\xi_{iklm} = \mu + \tau_i + Y_k + L_l + B_{m(lk)} + (\tau Y)_{ik} + (\tau L)_{il} + (YL)_{kl} + (\tau YL)_{ikl} + e_{iklm}$$

where ξ_{iklm} is the response (dry matter grain yield, grain protein concentration or grain N yield) from the i^{th} treatment applied in the m^{th} block in the l^{th} location and in the k^{th} year. Here, the treatment effect, i.e. τ_i , is fitted as a fixed effect and the rest of the effects as random effect like in model (1). However, to account for heterogeneity among environments (location \times year), an environment-specific error variance was fitted.

The models were fitted using the R-packages “asreml” (Butler et al., 2023) and “asreml-Plus” (Brien, 2025). The emission reduction between treatments and the related standard errors were calculated using “Abbott’s formula” according to Piepho et al. (2024). Compact letter displays were produced manually according to Piepho (2004).

3. Results

3.1. Overall NH₃ emissions

Averaging across all measurement campaigns, years, sites, and covariates, the highest NH₃-N emissions per unit N input were found in the U treatment with an EF of 8.0% (Table 2). The EF for U+UI decreased by 61% when compared to U and was found to be 3.1%. Treating urea with UI and NI (U+UI+NI) decreased the EF to 3.8%, a reduction of 52% compared to the U treatment. As U+UI+NI was not measured at all experimental sites, and therefore in a smaller number of plots, the emission reduction due to the inhibitor addition showed a higher standard error when compared to U+UI. Background subtracted absolute NH₃-N emissions were 4.2, 1.7, and 2.0 kg NH₃-N ha⁻¹, for the treatments U, U+UI and U+UI+NI, respectively.

3.2. Campaign-specific NH₃ emissions

Emissions were significantly affected by the application campaign, regardless of the fertilizer treatment (Table S3). Emissions were found to be highest after the first split application during tillering and lowest after the second split application during stem elongation (Table 3). The emissions after the third split application between ear emergence and flowering were slightly higher than those observed during stem elongation.

Average input related campaign specific emissions across years and sites for U ranged between 7.4 and 15.3 kg NH₃-N ha⁻¹, which corresponded to 5.8 and 12.2% of the applied N (Table 3), while the addition of UI reduced emissions to range between 5.5 and 11.4 kg NH₃-N ha⁻¹, which corresponded to 2.3 and 4.7% of the applied N. Input related

Table 2

Number of measured plots included in the analysis, estimated, back-transformed NH₃-N emissions, input-related NH₃-N emissions, and emission reductions by inhibitor-treated urea compared to untreated urea. All values \pm standard error of the estimate. Treatments: Control = unfertilized control (background emissions), U = urea, U+UI = urea with urease inhibitor, U+UI+NI = urea with urease- and nitrification inhibitor. Estimates of NH₃-N emissions that do not share any letter are significantly different according to the Tukey test at the 5% level of significance. NA = not applicable.

Treatment	Number of plots	Estimated NH ₃ -N emissions (kg NH ₃ -N ha ⁻¹)	Input related NH ₃ -N emissions (% of N applied)	Emission reduction compared to U (%)
Control	252	5.8 \pm 0.9 c	NA	NA
U	252	10.1 \pm 1.6 a	8.0 \pm 1.3	NA
U+UI	249	7.5 \pm 1.2 b	3.1 \pm 0.5	61.0 \pm 8.0
U+UI+NI	106	7.8 \pm 1.3 b	3.8 \pm 0.7	52.0 \pm 12.0

Table 3

Number of measured plots included in the analysis, estimated, back-transformed NH₃-N emissions per measurement campaign, and input related NH₃-N emissions per measurement campaign. All values \pm standard error of the estimate. Treatments: Control = unfertilized control (background emissions), U = urea, U+UI = urea with urease inhibitor, U+UI+NI = urea with urease- and nitrification inhibitor. NA = not applicable. Campaign I = first fertilizer split application during tillering, campaign II = second fertilizer split application during stem elongation, campaign III = third fertilizer split application between ear emergence and flowering.

Treatment	Campaign	Number of plots	Estimated NH ₃ -N emissions (kg NH ₃ -N ha ⁻¹)	Input related NH ₃ -N emissions (% of N applied)
Control	I	88	8.8 \pm 3.2	NA
Control	II	84	4.2 \pm 1.0	NA
Control	III	80	5.2 \pm 2.2	NA
U	I	88	15.3 \pm 5.5	12.2 \pm 4.4
U	II	84	7.4 \pm 1.6	5.8 \pm 1.3
U	III	80	9.0 \pm 3.8	7.2 \pm 3.0
U+UI	I	87	11.4 \pm 4.1	4.7 \pm 1.7
U+UI	II	83	5.5 \pm 1.2	2.3 \pm 0.5
U+UI	III	79	6.7 \pm 2.8	2.8 \pm 1.2
U+UI+NI	I	51	11.9 \pm 4.3	5.8 \pm 2.2
U+UI+NI	II	47	5.7 \pm 1.3	2.8 \pm 0.7
U+UI+NI	III	8	7.0 \pm 3.0	3.4 \pm 1.5

emissions of U+UI+NI were between the other treatments and were found to be between 5.7 and 11.9 kg NH₃-N ha⁻¹, which corresponded to 2.8 and 5.8% of the applied N. Campaign specific measurements of covariates are given in Table S1.

3.3. Influence of covariates on NH₃ emissions

One soil covariate and three weather covariates, as well as two interaction terms were identified during the covariate selection process. Soil clay content, mean campaign wind speed, standardized rain, mean campaign air temperature, the interaction of soil clay content with treatment, and the interaction of temperature with treatment were the covariates that significantly decreased the AIC and increased the quality of the model (Table S8). As the addition of the treatment campaign interaction increased the AIC, it was not included in the final model (Table S8).

Absolute emissions were found to increase with increasing wind speed with a fixed effect of 0.44 on the log scale (Table S4). Increasing rainfall was found to decrease absolute emissions by -0.18 on the log scale. Increasing clay content resulted in reduced absolute emissions across treatments (Table 4). However, when comparing input related emissions this held only true for the U treatment. The U+UI and U+UI+NI treatments showed an increase in input related emissions, when the soil clay content increased from 5% to 15%. With a further increase from 15% to 25%, both inhibitor treatments showed a decrease of input related emissions. Higher temperature increased absolute emissions for the U treatment (Table 5). Contrastingly, both inhibitor treated urea fertilizers showed decreasing emissions with increasing temperature, resulting in an increase emission reduction by both inhibitor types with increasing temperature.

3.4. Soil mineral N contents (K₂SO₄ extractable) after fertilizer application

At the southwest, south, and east sites, soil samples for U and U+UI+NI plots were extracted with K₂SO₄ (0.5 mol l⁻¹). Fig. 2 shows the NH₄⁺-N to NO₃-N ratio of soil samples at the respective sites, pooled for each specific measurement campaign, as well as the number of samplings per campaign. Ratios in the third campaign are not shown, as

Table 4

Influence of soil clay content on estimated, back-transformed NH₃-N emissions, input related NH₃-N emissions, and emission reductions by inhibitor-treated urea compared to untreated urea. All values ± standard error of the estimate. Treatments: Control = unfertilized control (background emissions), U = urea, U+UI = urea with urease inhibitor, U+UI+NI = urea with urease- and nitrification inhibitor. NA = not applicable.

Treatment	Clay content	Estimated NH ₃ -N emissions	Input related NH ₃ -N emissions	Emission reduction compared to U
	(%)	(kg NH ₃ -N ha ⁻¹)	(% of N applied)	(%)
Control	5	10.0 ± 2.3	NA	NA
Control	15	4.4 ± 0.8	NA	NA
Control	25	2.0 ± 0.8	NA	NA
U	5	14.6 ± 3.4	8.7 ± 2.1	NA
U	15	8.3 ± 1.6	7.3 ± 1.4	NA
U	25	4.8 ± 2.0	5.2 ± 2.2	NA
U+UI	5	11.5 ± 2.7	2.9 ± 0.7	66.9 ± 15.6
U+UI	15	6.0 ± 1.1	3.0 ± 0.6	59.6 ± 7.9
U+UI	25	3.1 ± 1.3	2.2 ± 0.9	58.2 ± 11.3
U+UI+NI	5	11.3 ± 2.8	2.5 ± 0.9	71.9 ± 25.6
U+UI+NI	15	6.5 ± 1.3	4.0 ± 0.8	46.0 ± 10.3
U+UI+NI	25	3.8 ± 1.6	3.4 ± 1.5	34.5 ± 16.4

Table 5

Influence of temperature on estimated, back-transformed NH₃-N emissions, input related NH₃-N emissions, and emission reductions by inhibitor-treated urea compared to untreated urea. All values ± standard error of the estimate. Treatments: Control = unfertilized control (background emissions), U = urea, U+UI = urea with urease inhibitor, U+UI+NI = urea with urease- and nitrification inhibitor. NA = not applicable.

Treatment	Temperature	Estimated NH ₃ -N emissions	Input related NH ₃ -N emissions	Emission reduction compared to U
	(°C)	(kg NH ₃ -N ha ⁻¹)	(% of N applied)	(%)
Control	2	6.8 ± 4.5	NA	NA
Control	12	5.8 ± 0.9	NA	NA
Control	22	4.9 ± 3.3	NA	NA
U	2	8.6 ± 5.7	3.4 ± 2.3	NA
U	12	10.1 ± 1.6	8.1 ± 1.3	NA
U	22	11.9 ± 8.0	13.0 ± 8.7	NA
U+UI	2	8.2 ± 5.5	2.6 ± 1.8	22.7 ± 41.5
U+UI	12	7.4 ± 1.2	3.1 ± 0.5	61.4 ± 7.9
U+UI	22	6.8 ± 4.6	3.5 ± 2.3	73.4 ± 9.4
U+UI+NI	2	8.0 ± 5.4	2.3 ± 1.6	32.9 ± 47.6
U+UI+NI	12	7.8 ± 1.3	3.9 ± 0.7	52.3 ± 12.0
U+UI+NI	22	7.7 ± 5.2	5.2 ± 3.6	60.2 ± 16.9

for the sites with three split applications, the annual N-amount for the U+UI+NI treatment was split evenly between the first two fertilizer applications. Values are only shown for sites featuring U+UI+NI treatments and soil sample extraction with K₂SO₄. With little exceptions, soil

Table 6

Dry matter grain yield, grain protein concentration and grain N yield of different inhibited urea fertilizers. All values ± standard error of the estimate. Treatments: Control = unfertilized control (background emissions), U = urea, U+UI = urea with urease inhibitor, U+UI+NI = urea with urease- and nitrification inhibitor. Estimates (per column) not sharing any letter are significantly different by the Tukey-test at the 5% level of significance.

Treatment	Dry matter grain yield	Grain protein concentration	Grain N yield
	(Mg ha ⁻¹)	(%)	(kg N ha ⁻¹)
Control	4.40 ± 0.55 b	9.30 ± 0.36 c	65.7 ± 9.8 b
U	7.67 ± 0.55 a	12.66 ± 0.36 ab	155.2 ± 9.8 a
U+UI	7.86 ± 0.55 a	13.14 ± 0.36 a	163.9 ± 9.8 a
U+UI+NI	7.96 ± 0.56 a	12.42 ± 0.39 b	155.5 ± 10.2 a

samples in the U+UI+NI treatment showed higher NH₄⁺-N to NO₃⁻-N ratios when compared to the U treatment at the respective site and campaign. Long campaigns resulted in higher interquartile ranges compared to short campaigns, which sometimes consisted of only one soil sampling after fertilizer application. The lowest ratios were found at the BB1 site. This site expressed comparatively high NH₄⁺-N as well as NO₃⁻-N values. High ratios after the first fertilizer application were likely followed by high ratios after the second fertilizer application for the respective site and treatment. Ratios differed between sites but were not correlated with site characteristics, such as clay content or soil organic matter.

3.5. Yield and NUE

The unfertilized control treatment always exhibited the lowest dry matter grain yield, grain protein concentration and grain N yield (Table 4). Dry matter grain yield of the fertilized treatments was lowest for U, highest for U+UI+NI with U+UI in between. However, the differences in dry matter grain yield between the three treatments were not statistically significant. Grain protein concentration in this group was highest for U+UI. Though not significant, U showed lower grain protein concentrations when compared to U+UI. U+UI+NI with only two split applications showed the lowest grain protein concentrations of the fertilized treatments and was also significantly lower when compared to the other fertilized treatments. Grain N yield once again proved not to be significantly different for all three fertilized treatments. The lower grain protein concentration in the U+UI+NI treatment was compensated by a higher dry matter grain yield, resulting in a grain N yield of 156 kg ha⁻¹, which is almost similar when compared to the U treatment with 155 kg ha⁻¹. The combination of higher dry matter grain yield and higher grain protein concentration in the U+UI treatment resulted in the highest grain N yield (164 kg ha⁻¹). Adding cumulative NH₃ emissions over all campaigns as a covariate to the yield model did not improve the model, it was not significant in the Wald Test for fixed effects (Table S5–7). Other covariates were not tested, as this would be beyond the scope of this study.

4. Discussion

4.1. Absolute NH₃ emissions and influencing factors

N input related NH₃-N emissions were 8.0% for untreated urea, and thus noticeably lower when compared to the default values of the IPCC with 14.2% and EEA with 16.1% (EEA, 2023; IPCC, 2019). However, when compared to the study of Ni et al. (2014) who found a mean input-related emission of 8.4% the values are comparable. This might be due to the many similarities in trial design, such as the use of winter wheat as the crop type and the same location in the northern region of this trial. The observed emission factors were also close to the ones reported by Abalos et al. (2012), who reported an EF of 6.7% after the spring application of urea to a winter barley field. Using inverse dispersion modeling, Huo et al. (2015) determined an EF of 12.0% after the application of urea on a winter wheat crop in the North China Plain.

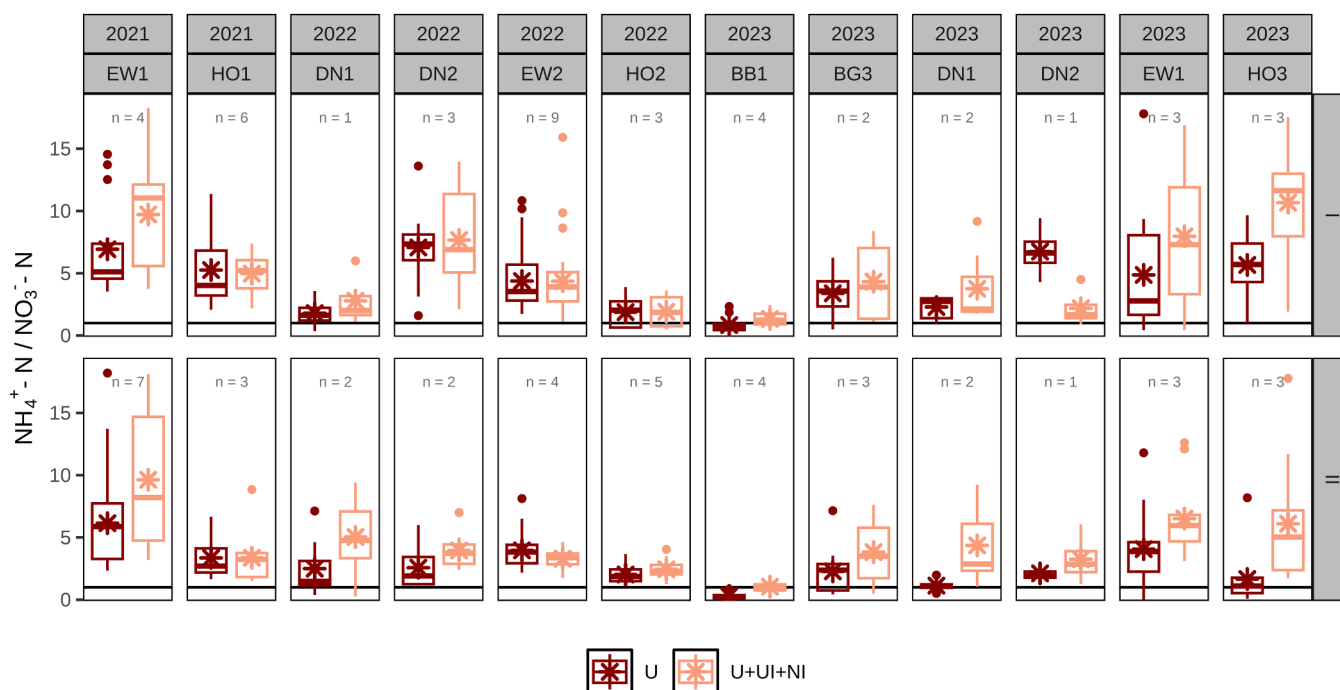


Fig. 2. Box plots of measured $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$ ratios for U (urea) and U+UI+NI (urea with urease- and nitrification inhibitor) in 0–10 cm K_2SO_4 soil samples after fertilizer application. I = samples after the first fertilizer application. II = samples after the second fertilizer application. n = number of soil sampling dates per campaign. Horizontal black lines represent a 1:1 ratio of $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$. For site abbreviations, see Fig. 1.

Recio et al. (2020) observed lower emissions of only 5.5% after the urea application in an irrigated corn crop. After applying urea to a corn crop, Drury et al. (2024) found NH_3 emissions to be 11.8% of the applied N amounts. These differences may be due to varying environmental conditions, as numerous covariates are known to influence NH_3 emissions from urea-based fertilizers. Variables that were shown to affect NH_3 emissions are e.g. soil texture, pH, CEC, urease activity, or pH buffer capacity (Fan et al., 2022; Ni and Pacholski, 2022; Ohnemus et al., 2021). Also, weather conditions after fertilizer application can influence NH_3 emissions.

Wind speed has a major influence on the difference in partial pressure between soil and air, which is the main driving force of NH_3 emissions (Bouwman et al., 2002). Air movement exchanges the NH_3 -enriched air at the soil surface with less saturated air, resulting in an increased difference in partial pressure and amplifying NH_3 emissions from the soil. In a separate evaluation of micrometeorological measurements in our field trials, employing the integrated horizontal flux method, Kemmann et al. (2025) found only a weak correlation between measured wind speeds and emissions in a circular urea plot. Extending this research from non-replicated circular plots to replicated small plots and from only urea to all tested mitigation techniques resulted, however, in a significant effect of wind speed on absolute emissions.

Water availability after fertilizer application is also known to play a crucial role in NH_3 emissions. As moisture is needed for granule dissolution and urea hydrolysis, urea-N is not transferred to $\text{NH}_4^+\text{-N}$ without available water (Ni and Pacholski, 2022). Due to the hygroscopic properties of urea, even relatively high air humidity can be sufficient to initiate hydrolysis. As urea is only mobile in the uppermost soil layer when sufficient water is available, low rainfall after fertilizer application can result in concentrated spots of urea and $\text{NH}_4^+\text{-N}$ in the closest proximity of the fertilizer granule (Cantarella et al., 2018). These hotspots of urea hydrolysis can cause a localized increase in soil pH, thereby forcing NH_3 emissions. With rainfall following fertilizer application, urea is dissolved and spread vertically and horizontally through a greater soil volume, thereby decreasing hydrolysis hotspots characterized by high NH_4^+ concentrations and increased pH (Dawar et al., 2011).

However, under drying and evaporation conditions, mass flow in the soil is diverted towards the soil surface, increasing the rate of NH_3 volatilization (Kirk and Nye, 1991). The increased air-filled porosity in dry soils facilitates the gaseous diffusion of NH_3 to the soil surface (Drame et al., 2023). The tested dataset comprised a wide range of different soil moisture and rainfall patterns. Some campaigns with low soil moisture prevented granule dissolution until further rainfall occurred, resulting in negligible emissions during that period. Fertilizer application after rainfall on moist soils, followed by warm conditions without further rain, supplied enough initial moisture for fast granule dissolution, urea hydrolysis, and drying of the upper soil layers, resulting in substantial emissions. Moreover, the distribution of rainfall after fertilizer application was observed to have an impact on NH_3 emissions. All the previously described observations were pooled into the standardized rain (cumulative rainfall per campaign divided by the campaign length) to facilitate model data analysis. Standardized rain proved to significantly reduce absolute NH_3 emissions in our mixed model analysis, which is in accordance with previous literature (Fröbl et al., 2025b; Hurtado et al., 2024; Ruser et al., 2008; Sanz-Cobena et al., 2011).

The chemical equilibrium between NH_3 and NH_4^+ , which is the primary pathway for transferring soil N to NH_3 emissions, depends, among other factors, on temperature (Kirk and Nye, 1991). With increased temperature, the equilibrium is shifted towards higher NH_3 proportions (Burch and Fox, 1989; Drame et al., 2023), resulting in increased NH_3 emissions in the U treatment. This effect can be attributed to an increase in urease activity at higher temperatures (Burch and Fox, 1989; Ni and Pacholski, 2022).

Higher soil clay content proved to lower NH_3 emissions, which is in accordance with Ohnemus et al. (2021). However, clay content proved to be correlated to CEC and pH in our analysis, which are both known to influence the chemical equilibrium between NH_3 and NH_4^+ , as well as the availability of cations in the soil solution (Ohnemus et al., 2021).

Even though the final model accounted for all the weather covariates tested in the stepwise selection process, as well as one soil covariate, the effect of the measurement campaign still remained significant. This fact proves that the remaining influence on campaign emissions is neither

sufficiently explained by weather covariates nor better explained by the addition of soil covariates. The factor campaign likely encompasses hidden variables that were not explicitly measured but may nevertheless be of importance. Such factors could be the effect of the development stage and the canopy of the wheat. As winter wheat follows a distinct course of N-uptake depending on its development stage, N-applications are usually split to achieve a higher NUE (Sieling et al., 1998). Higher physiological activity, growth, and thus soil N uptake during stem elongation could be an explanation for the comparatively low emissions during stem elongation. Additionally, for the first fertilizer application, the wheat canopy was less developed compared to later applications. With higher crop stands, NH₃ emitted at the soil surface is less likely to be emitted to the atmosphere, as it can be absorbed by the plants while being transferred from the soil through the canopy (Fröbl et al., 2025a; Schjørring et al., 1998). As plant height for the first N-application usually ranged between 5 and 10 cm, and physiological activity and N-uptake were supposedly low, this could explain the higher emissions observed in the first measurement campaign. Canopy absorption proved to be higher during stem elongation, when compared to the grain filling period in a field study conducted at the Hohenheim site in the second experimental year (Fröbl et al., 2025a), possibly contributing to the lower emissions in the second measurement campaign when compared to the third measurement campaign. However, N-fertilizer application during heading or grain filling is usually associated with a lower N-use efficiency, as plants are reducing the root N-absorption and increase translocation of N within the plant. Another cause might be the impact of higher temperatures and drier soil conditions, limiting N-transformation processes in the soil and reducing N-availability to the plants (Makary et al., 2020; Meloni et al., 2024; Schulz et al., 2015). Another effect of increased plant height at later development stages could be a reduced influence of wind. As the wind speed measurement was fixed at the height of 2 m, such differences within the canopy could not be examined. As the influence of weather and soil covariates proved to significantly influence the emissions after application of all fertilizers tested, hypothesis i) can be accepted.

Influencing variables, such as land use, could not be tested in this study, as measurements were only conducted on winter wheat. As some covariates possibly have a non-linear effect on emission reduction, they could not be tested by the chosen mixed model. To reliably model non-linear relationships, a larger test size would have been advantageous.

Background emissions in the non-fertilized control plots were higher when compared to natural background deposition (Schellenberger Costa et al., 2022; UBA, 2024). This is likely due to the nature of the small plot trial design and is known as a multi-source problem where emissions from one source are captured by multiple samplers (Crenna et al., 2008). As it is known, that different measurement techniques have an influence on absolute emission measurements (Kamp et al., 2024), this issue of uncertainty was addressed in multiple ways in this study. As it is internationally accepted, the NH₃-Min trials included measurements with the IHF method at most locations that showed a comparable emission factor of 8.5% for urea (Kemmann et al., 2025). Based on the IHF measurements and multiple other measurement techniques the comparability of IHF emissions with ALPHA sampler based emission measurements was shown by Götzte et al. (2025). Additionally, an improved method for TC calculation was introduced in this publication, accounting for the placement of the ALPHA plots in the trial layout. Moreover, the new method of TC calculation enabled the inclusion of the unfertilized control as a treatment in statistical evaluation, thus disclosing background emissions rather than subtracting them early during calculations, showing only input related emissions, and not addressing this obvious problem.

4.2. NH₃ emission reduction by inhibitors

4.2.1. Effects of urease inhibitor

The NH₃ emission reduction by UI in field studies was reported to

vary between 51% and 70% when compared to untreated urea (Fan et al., 2022; Matse et al., 2024; Misselbrook et al., 2014; Pan et al., 2016; Schoof et al., 2025; Silva et al., 2017). The mentioned studies mainly focused on the most widely used active ingredient NBPT. In a meta-analysis, covering only two publications on field trials, Matse et al. (2024) calculated a reduction of 70% for the active ingredient 2-NPT. With a mean reduction of 61%, the results of our field trials confirm the first part of our first hypothesis, that the application of a UI significantly reduces NH₃ emissions.

While the general effectiveness of UI on NH₃ emission reduction is well studied, the interfering effect of environmental conditions on the reduction is currently not well described. In their evaluation of literature datasets, Schoof et al. (2025) employed a linear mixed effects model to check possible covariates that might influence the relationship between NH₃ loss from inhibited and untreated urea. The input data used in this meta-analysis were filtered to match Western European conditions closely. No covariates proved significant in the analysis, while there was a tendency of a reduced inhibitory effect with increasing temperature (Schoof et al., 2025). A reason for the reduced effectiveness of UIs at higher temperatures could be the increased degradation rate of the active ingredient (Carmona et al., 1990; Soares et al., 2012). This is supported by the findings of Fan et al. (2022), who observed a decrease in UI effectiveness with increased seasonal mean air temperature. A reduced effectiveness of UIs with increasing temperature under low soil moisture conditions was also confirmed in an incubation study by Drame et al. (2023).

In our study, the interaction between treatment and temperature also proved to be significant. However, as temperature increased, so did the reduction effect. Upon closer inspection, this increased reduction appears to be due to the different development of absolute emissions at higher temperatures for the respective treatments. U showed increasing emissions with increasing temperature, whereas U+UI and U+UI+NI showed decreasing emissions. Consequently, the difference between the inhibitor-treated urea fertilizers and U increased with temperature, resulting in an increased reduction effect. One possible reason for the increase in U emissions at higher temperatures can be an increased urease activity (Moyo et al., 1989). A degradation and thus lower inhibitory effect at higher temperatures cannot be assumed in our study. Conversely, the results highlight the ability of the tested inhibitors to reduce emissions, particularly under high temperature, high N emission scenarios.

Increasing clay content decreased absolute emissions across all treatments tested. When comparing to input related emissions, this only holds true for the U treatment. This is likely due to soil properties correlated to clay content such as water holding capacity, soil porosity, and CEC, reducing emissions (Fan et al., 2022; Ohnemus et al., 2021). The input related emissions for U+UI and U+UI+NI were less affected by clay content and were highest at a medium clay content of 15%. Here again, it is shown that the inhibitor effect was highest at high emission scenarios.

Numerous studies have shown that soil pH has no effect on the reduction of NH₃ emission by UI (Li et al., 2017; Schoof et al., 2025; Silva et al., 2017), whereas Fan et al. (2022) showed a distinct effect in their meta-analysis. They reported the strongest effectiveness of UI at soil pH 7 and a decrease in effectiveness in acidic and alkaline soils. Decreased effectiveness of inhibitors in acidic soils can likely be attributed to an increased degradation rate, which was shown for the active ingredient NBPT (Engel et al., 2015; Engel et al., 2013). Contrastingly, in an examination of 27 German cropland soils for NH₃ emission potential, Ohnemus et al. (2021) reported no correlation of initial soil pH before fertilizer application and emission potential. However, they reported a significant correlation between CEC, which is usually correlated to soil texture, and NH₃ emission potential (Ohnemus et al., 2021). Our study could neither confirm an effect of soil pH nor CEC on absolute emissions nor on the effectiveness of the inhibitors. For pH, this fact is likely attributed to the lower number of sites and thus smaller range of soil pH

levels when compared to the comprehensive meta-analysis of Fan et al. (2022). As pH levels and CEC are closely correlated with soil type, the design of this study, with repeated measurements in specific regions across different years, resulted in even less variation in pH levels and CEC.

In our evaluation, the interaction between treatment and temperature, as well as treatment and soil clay content proved significant. The reduction ability after inhibitor addition to urea was highest under high loss scenarios, which is in contradiction to our initial hypothesis, and suggests a regionalization of UI EFs.

4.2.2. Effect of the combination of urease and nitrification inhibitor

In this study, the application of urea fertilizer with a combination of UI and NI increased NH_3 emissions in comparison to those from urea only treated with UI. This effect was often described in the results from field and laboratory studies, and in meta-analyses (Castellano-Hinojosa et al., 2020; Fan et al., 2022; Fröhl et al., 2025b; Soares et al., 2012; Zaman et al., 2008). Lasisi et al. (2020) attribute the increase in NH_3 volatilization of double-inhibited fertilizers not only to the increased persistence of NH_4^+ -N but also to a decreased reduction ability of the UI NBPT on urea hydrolysis.

The U+UI+NI treatment in our study featured a different N application splitting when compared to the other treatments at most sites. Therefore, the inhibitor effect and the split application regime are hard to be differentiated, as they are both confounded within the treatment factor.

When compared to U, the effect of the NI addition in treatment U+UI+NI can be clearly seen in the elevated NH_4^+ -N/ NO_3^- -N ratios, which suggest reduced nitrification. This effect is linked to the inhibition of the ammonia monooxygenase, the first enzyme in the oxidation path of microbial NH_4^+ oxidation during nitrification, by the NI, resulting in a decrease of nitrification rate and thus reducing NO_3^- -N concentrations in the soil (Ruser and Schulz, 2015). Moreover, the reduction of the nitrification rate results in an accumulation of NH_4^+ -N in the topsoil, which may be prone to NH_3 losses (Pan et al., 2016; Soares et al., 2012; Wang et al., 2020). In addition, the reduced nitrification rate extends the phase of increased soil pH around the fertilizer granule (Curtin et al., 2020; Janke et al., 2020), which was reported to be the main period of NH_3 emissions (Ohnemus et al., 2021). The results of these effects can clearly be seen in our evaluation and confirm hypothesis iii), that additional NI application increases the NH_3 emission when compared to the U+UI treatment. Nevertheless, the addition of a NI to a U+UI fertilizer reduced NH_3 emissions also to a high degree compared to a sole urea fertilizer. For a comprehensive evaluation of the environmental impact of different urea fertilizers, additional environmental aspects must be considered. It was shown that indirect greenhouse gas emissions via the leaching path can be reduced significantly with the help of NIs (Chen et al., 2023; Zaman et al., 2008) and they also have a high potential for the reduction of the release of N_2O from soils (Ruser and Schulz, 2015). Even though not tested in this study, the double-inhibited urea can likely reduce both NH_3 and N_2O emissions, which is a particular asset of double-inhibited fertilizers (Drury et al., 2024; Drury et al., 2017; Ni et al., 2023).

Increasing nitrogen use efficiency by synchronizing N-supply with crop N-uptake is often mentioned as a reason for splitting N-application in winter wheat production (Sieling et al., 1998; Sieling and Kage, 2021). However, this topic is controversially discussed, as a reduced number of split applications can, on the one hand, produce a similar yield but, on the other hand, also potentially increase N_2O emissions, when compared to a fertilization system with three split N doses (Guzman-Bustamante et al., 2022; Makary et al., 2020; Schulz et al., 2015). Consequently, the use of double-inhibited urea fertilizers can be recommended to facilitate fertilization regimes while simultaneously avoiding increased N emissions.

4.3. Yield effect of inhibitors

Yield levels were similar to those of other studies in winter wheat in Germany (Huf et al., 2023b; Sieling and Kage, 2021). The average value for the experimental years 2021–2023 of the whole of Germany is given as 7.4 Mg ha^{-1} by the Federal Statistical Office of Germany and is close to the yields obtained in this study (DESTATIS, 2025).

Cumulative NH_3 emissions were not significant when added as an explanatory variable to the yield model. In contrast, a small insignificant increase in yield was observed with 2.4% and 3.8% for U+UI and U+UI+NI, respectively. This result is similar to the findings of Fan et al. (2022) who could observe a minor yield increase of 3% for the addition of a UI to urea. As the observed EFs in this study were well below IPCC and EMEP values, emissions were comparatively low (EEA, 2023; IPCC, 2019).

Consequently, the absolute amount of reduced N availability resulting from NH_3 -N loss was likely not enough to impact the absolute yield significantly (Fan et al., 2022). As yields were not significantly affected by inhibitor addition the emission reduction must have been low, which again confirms the low EFs reported in this study. However, a tendential effect by use of inhibitors and the different fertilizer split applications on yield could be observed. Inhibitor addition increased dry matter grain yield, grain protein concentration, and grain N yield. The only decrease in protein concentration was observed in the U+UI+NI treatment, likely due to the different allocation of fertilizer N in the respective split applications. Here the annual N-amount was divided only between the first two application dates at most sites for U+UI+NI. It is likely, that available N was missing during the grain filling period for the formation of high grain protein concentrations (Alcoz et al., 1993; Fuertes-Mendizábal et al., 2018). The higher N-application in the first and second application supported the formation of the yield components ears per m^2 and kernels per ear, which are determined during tillering of the wheat (Alcoz et al., 1993). A higher second application dose during stem elongation supports the number of kernels per ear (Alcoz et al., 1993), also indicated in this study by a higher yield in the U+UI+NI treatment. This higher yield might also be a reason that grain protein was diluted and thus significantly lower when compared to U+UI. The lower dry matter grain yield in the U+UI treatment when compared to the U+UI+NI treatment can likely be attributed to the lower N amounts in the first two split applications. However, the lower amount in the first and second application was followed by a third application during ear emergence or grain filling, which increased the grain protein concentration (Fuertes-Mendizábal et al., 2018; Zörb et al., 2018). In this light, hypothesis iv) that a reduced NH_3 emission increases wheat yield, grain protein concentration and grain N yield can be confirmed only partially, as only grain protein concentration was significantly affected by inhibitor addition. The other measured yield components only showed a tendency of positive influence by the inhibitors.

These results highlight not only the beneficial effect of emission reduction but also the influence of inhibitors and N-allocation on the formation of yield components. With this knowledge, inhibitors and N-allocation can easily be used to achieve different objectives during wheat production. As wheat quality is differentiated into distinct classes mainly based on grain protein concentration, multiple strategies for inhibitor use can be differentiated. Use of U+UI resulted in a higher dry matter grain yield compared to U, and the highest grain protein concentration among all treatments tested. This strategy entails also the strongest reduction in NH_3 emissions. To produce high-yielding wheat, regardless of grain protein concentration, U+UI+NI applied in two split applications would provide a feasible option. With a reduced number of split applications and extended time windows for application (dependent on weather), this strategy can facilitate fertilizer management in field crops. With a significant reduction of NH_3 as well as N_2O this strategy can also reduce the environmental impact of field crop production. Another strategy could be a combination of U+UI+NI for the

first two split applications and a third split application of another low-emitting fertilizer (strategy not tested in this trial). This strategy will feature high dry matter grain yields, an additional boost for grain protein concentration, and a reduced environmental impact due to reduced N losses.

The described yield effects can also be achieved by choice of N fertilizers containing different N-forms. However, options like calcium ammonium nitrate or other nitrate-based fertilizers bear other disadvantages such as potential N₂O emissions, NO₃ leaching, higher emissions during production and transport to the field, and finally higher cost to the individual farmers.

5. Conclusion

A modified method of calibrated passive sampling for ammonia emission measurement with a novel approach to TC calculation, employing a linear mixed-effects model, was successfully used for the first time to estimate absolute NH₃ emissions. This establishes a new, robust method for NH₃ flux calculation from concentration measurements that can be employed on a small-scale replicated plot design. Overall ammonia emission levels for urea fertilizer application were considerably lower as in global meta-analyses. The results suggest that emission inventories can be improved by using site specific emission factors depending on windspeed, rainfall, soil clay content, and temperature. On average, the relative reduction for urea treated with UI was 61% of the applied N amount, whereas the average reduction for urea fertilizer treated with a combination of UI and NI was 52%. The reduction potential of inhibitors was influenced by soil clay content and temperature, implying that the relative reduction was highest under high emission scenarios. Consequently, the results suggest a regionalization of reduction factors for a better emission inventory reporting. In this light, knowledge of site properties and prevailing weather conditions during fertilizer application season is crucial for predicting absolute NH₃ emission levels and thus the expected mitigation potential of inhibitors. Grain N yield of winter wheat was not significantly influenced by inhibitor treatment of urea, whereas grain protein concentration was significantly reduced by the combination of U+UI+NI and a reduced number of split applications. The fact that grain N yield was not influenced by inhibitor treatment can likely be attributed to the adequate nutrient availability and high yield potential of the tested sites. Therefore, further studies are needed to test the economic, and yield effects, as well as the effect on grain protein concentration of reducing N-application amounts of inhibited urea fertilizer compared to non-inhibited urea.

Reporting emission inventories requires recognized abatement factors for inhibitors. Closing a knowledge gap for specific inhibitor compounds, regions, and the combination of UI and NI, this study gives valuable input for emission inventory calculation. While this study focused on the NH₃ emission, other detrimental N losses are also known to be influenced by inhibitors. Assessing N₂O emissions and NO₃ leaching should be considered in future studies to fully evaluate the impact of inhibitors on the environment. Further, evaluating the costs and benefits of inhibitors on an economic and eco-toxicological scale are encouraged.

CRedit authorship contribution statement

Sina Kukowski: Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization. **Heinz Flessa:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Andreas Pacholski:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Torsten Müller:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Alexander Kelsch:** Investigation, Formal analysis, Data curation. **Mareike Hofmeister:** Investigation, Data curation. **Waqas Ahmed Malik:** Formal analysis. **Björn Kemmann:** Visualization, Investigation, Data curation. **Reiner**

Ruser: Writing – review & editing, Supervision, Investigation, Conceptualization. **Hannah Götz:** Investigation, Formal analysis, Data curation. **Julian Brokötter:** Investigation, Formal analysis, Data curation. **Paul Heinemann:** Investigation, Data curation. **Jens Hartung:** Formal analysis. **Jonas Fröbl:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

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Appendix A. Supporting information

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Data availability

Data will be made available on request.

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