

**Ammonia Emission from Field-Applied Synthetic Fertilizer –
Processes, Methods and Mitigation**

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I. Abbreviations

NH ₃	Ammonia
N ₂ O	Nitrous oxide
GHG	Greenhouse gas
EF	Emission Factor
EMEP	European Monitoring and Evaluation Programme
NEC	National Emission Ceilings Directive
IPPC	Integrated Pollution Prevention and Control
UI	Urease Inhibitor
NI	Nitrification Inhibitor
2-NPT	N-(2-Nitrophenyl) Phosphorsäure-Triamid
NBPT	N-(n-Butyl) thiophosphoric triamide
MPA	N-[3(5)-methyl-1H-pyrazol-1-yl) methyl] acetamide
bLs	backwards Lagrangian stochastic
pK _b	Base dissociation constant
pK _a	Acid dissociation constant
Alpha samplers	Adapted low- cost passive high absorption diffusive samplers
Polytetrafluoroethylene	PTFE

II. Abstract

Ammonia (NH_3) emissions affect the environment, climate and human health and originate mainly from agricultural sources such as synthetic nitrogen fertilizers. Accurate and replicable field measurements of these NH_3 emissions are crucial for research, inventories and particular the evaluation of mitigation measures. Due to the specific application limitations of NH_3 emission measurement techniques and the high variability between studies, different measurement methods for small plots used in replicated multi-plot field trials are debated.

In this thesis different mitigation techniques to avoid NH_3 losses from urea fertilizer were analysed in two incubation trials. In an in vitro microcosm approach with open dynamic incubation chambers NH_3 emissions were monitored using sulfuric acid washing bottles. Pollution swapping due to nitrous oxide (N_2O) emissions was studied in parallel by slow throughflow mesocosm set ups with continuous gas chromatographic measurements.

Three different principles of fertilizer incorporation methods were compared:

- shallow mixing at 2 cm
- injection with the closed slit technique at 5 cm
- deep complete incorporation at 5 cm simulating plow incorporation

Also, the effectiveness of inhibitor use was analysed and compared to incorporation:

- urease inhibitor (N-(2-Nitrophenyl) phosphoric triamide, 2-NPT) alone
- urease inhibitor in combination with nitrification inhibitors (N-[3(5)-methyl-1H-pyrazol-1-yl) methyl] acetamide, MPA)
- closed slit incorporation of urea fertilizer into the soil

All urea incorporation techniques showed great potential for mitigating NH_3 emissions on the clayey soil with slit injection showing the greatest effect. For sandy and drier soils, only deeper or closed slit injection were consistently effective. Slit injection showed the greatest effect on NH_3 emission reduction also compared to the use of urease inhibitor and urease inhibitor combined with nitrification inhibitor, highlighting the need for studies on understanding their individual inhibitors efficacy. Regarding the right moment of fertilizer application, the results of this thesis highlight the risk that under specific soil conditions, in particular high soil moisture, surface incorporation synthetic fertilizers like urea can increase N_2O emission.

Finally, small plot NH_3 measurement approaches based on a comprehensive dataset throughout Germany were developed and compared. Two small plot methods were employed, the dynamic chamber Dräger Tube Method and Inverse Dispersion Modelling combined with atmospheric concentrations obtained from Alpha samplers applied in a novel experimental setup. Both were assessed by comparison to the Integrated Horizontal Flux method with Alpha sampler, as micrometeorological reference method on parallel large plot trials. The Dräger Tube Method showed good agreement compared to the reference method. However, due to its severe limitations, particularly regarding the required load of fieldwork, its use should be carefully considered. With respect to Alpha sampler with Inverse Dispersion Modelling, deviations occurred and could be related to the specific weather thresholds of air temperature and wind speed. An empirical correction factor of 0.28 was derived, which can be considered for same weather soil and canopy conditions. Given the more practical applicability should be prioritized for future small-plot emission studies. In similar studies in the future, additional verification within a multi-plot set up can be achieved by carrying out a supplementary reference like a large plot trial with Integrated Horizontal Flux method, either as a reference or for quantitative scaling.

In conclusion, this thesis contributes significant knowledge about the measurement and reduction of NH_3 emissions from mineral fertilizers, proving the efficacy of readily available agricultural procedures. Furthermore, the presented results on simple, field-applicable methods for quantification of NH_3 emissions verify their suitability and facilitate future research and monitoring. Nevertheless, investigation on different inhibitors should be continued, as technical implementation of incorporation can be difficult in agricultural practice also due to limited machinery availability. Furthermore, factors like crop nitrogen uptake and rainfall would further modify the overall effect on emissions and need to be considered in field trials also for final pollution swapping estimation. Next to the potential of inhibitor use little is known about the possibility pose any threat to the environment, food safety and human health. Achieving the goals of nitrogen efficiency and climate protection guidelines requires a combination of advanced, site-specific fertilization practices and continuous validation and improvement of measurement methods.

1 Introduction

The topic of this thesis originates at the intersection of food security and environmental protection. Excessive ammonia (NH_3) emissions from agricultural sources such as mineral fertilizers are a significant environmental problem affecting various ecosystems and human health. Taking the example of Germany, the majority of NH_3 emissions are generated in the agricultural sector. The agricultural NH_3 inventory reports annually (EMEP/EEA, 2023) on emissions from animal husbandry (stables, storage of farm manure) and soils (application of farm manure, mineral fertilizers, sewage sludge and other organic fertilizers; grazing). In 2021, the agricultural sector alone emitted around 482300 t of NH_3 with 34900 t originating from synthetic nitrogen fertilizers (Hu et al., 2024).

Emitted NH_3 in the atmosphere, reacts with other air pollutants forming harmful particular matter (Griffith et al., 2015; Wang et al., 2016) and leads to eutrophication through nitrogen input (Bergström et al., 2008) in near-natural ecosystems and subsequent loss of biodiversity (Clark and Tilman, 2008). As a result of consecutive conversion processes, NH_3 contributes to soil acidification, groundwater pollution and formation of the indirect greenhouse gas emissions in form of nitrous oxide.

Globally agreed critical NH_3 levels were defined in an amendment to the Convention on Long-Range Transboundary Air Pollution (CLRTAP) agreement in 2012, becoming effective in 2019. However, in 2018 the stated levels have been exceeded for a significant number of protected ecosystems in Europe (Schaap et al., 2018). With the aim of reducing emission of air pollutants and the resulting negative effects on human health and environment, the European Union (EU) passed the National Emission Ceilings Directive (NEC Directive) (European Parliament, 2016). It contains compulsory national emission ceilings for certain air pollutants for each member state. Under the NEC Directive, Germany has committed to reducing NH_3 emissions by 29% till 2030 compared to 2005 levels.

To achieve these reduction targets, agricultural mitigation measures such as fertilizer incorporation or chemical inhibition must be applied. However, to date effectiveness of NH_3 mitigation measures has not been sufficiently assessed in field trials with replicates nor does a European standard on measuring NH_3 emissions in such trials exist. This is primarily due to the

reactive nature and volatility of NH_3 , making its detection under real environmental conditions challenging as it requires sophisticated measuring techniques.

Overall, the two main objectives are first, the investigation of incorporation techniques and inhibitors products as mitigation measures for NH_3 emissions to analyse their effectiveness, taking into account soil types, soil moisture contents and considering also pollution swapping in form of N_2O losses in laboratory trials. And second, the evaluation of measurement methods for quantifying NH_3 emissions which can be applied in replicated agronomic field plot trials and to be able to statistically compare different fertilizers and measures.

Therefore, at first this work focuses on the effectiveness of urea incorporation compared to the mitigation measure urease and nitrification inhibitor for reducing NH_3 emissions. Microcosm experiments were conducted, mimicking and investigating three incorporation methods: surface incorporation by cultivating, deep incorporation by ploughing, and the slit application followed by closing the slit. Furthermore, rarely investigated urease inhibitor and nitrification inhibitor are evaluated and compared to incorporation. The effectiveness of these measures is analysed, taking into account soil types, soil moisture contents. Additionally, pollution swapping in form of N_2O losses is considered as well. This allows for a statement about the applicability and the limitations under different environmental conditions.

Second, different methods for quantifying NH_3 emissions are evaluated: two small plot methods the dynamic chamber Dräger Tube Method and Inverse Dispersion Modelling combined with Alpha samplers applied in a novel experimental setup. Both were assessed by comparison to the Integrated Horizontal Flux method, as micrometeorological reference on parallel large plot trials. The validation field trials are carried out at six sites with different soil and climate conditions across Germany against a reference micrometeorological method. The evaluation of these methods involves consideration of several factors, including spatial scale, cost, measurement frequency, precision, accuracy, detection limits.

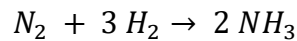
Finally, recommendations are made for both, measuring methods for field trials with replicates and efficient practical mitigation measures serving and supporting emission regulation at a political level.

2 State of the Art - Ammonia emissions

2.1 Origination of NH₃ emissions from urea as mineral fertilizer

Nitrogen is a basic building block of plant life as it is an essential component of proteins, including chlorophyll. In agricultural production in the past, reactive nitrogen availability was limited by nitrogen from organic sources such as animal manure. Due to the development of the Haber-Bosch process in the early 20th century, Nitrogen has become accessible in large quantities due to processing of NH₃ into nitrogen fertilizer urea. In the Haber Bosch process, NH₃ is produced under high pressure and temperatures using hydrogen from natural gas and atmospheric nitrogen from air (Equation 1). This is followed by the urea synthesis, in which NH₃ reacts with carbon dioxide to form urea, a stable, and easily transportable form of nitrogen.

Equation 1 NH₃ production with Haber Bosch process



Due to the increased availability of plant available nitrogen through urea production, agricultural productivity increased globally. Particularly during the decades following the 2nd world war the global food supply significantly improved. Compared to other mineral nitrogen fertilizers such as calcium ammonium nitrate, urea has the advantages of high nitrogen content of 46% at a low cost per unit of nitrogen due to lower production costs, wide availability in most markets, flexible use in dry or liquid form, fast availability to plants and a high water solubility of 1 kg L⁻¹ at 20°C (Silva et al., 2017). Due to these advantages, urea is currently the most important mineral nitrogen fertilizer in the world. The annual consumption of nitrogen fertilizer in EU countries was approximately 11.7 x 10⁶ t N year⁻¹ between 2016 and 2020 (Hu and Schmidhalter, 2024). The Food and Agriculture Organisation of the United Nations reports a consumption of around 190 million tons of inorganic fertilizers for 2023, with Asia (especially China and India) and America (including the US and Brazil) accounting for the largest share (United Nations, 2024). Local hotspots for the use of organic fertilizers (slurry/manure) are found in regions with intensive livestock farming, but the available data sets indicate that mineral fertilizers account for the largest share of nutrients applied worldwide.

Currently, 95% of German NH₃ emissions are generated in the agricultural sector (Hu et al., 2024). The agricultural NH₃ inventory reports annually on emissions from animal husbandry (stables,

storage of farm manure) and soils by application of farm manure, mineral fertilizers, sewage sludge and other organic fertilizers. Agriculture alone emitted around 482300 t of NH_3 in 2021 with 34900 t from synthetic nitrogen fertilizers application (Figure 1) (Hu et al., 2024). The agreed maximum limits for NH_3 emissions are increasing the political pressure to take action to introduce measures to reduce emissions, particularly in the agricultural sector. Global fertilizer consumption is expected to increase, with Asia likely to account for the largest share of this increase, followed by Latin America. In Europe, particularly in Western and Central Europe, fertilizer consumption has been declining in recent years. This is primarily due to stricter environmental regulations (EMEP/EEA, 2023). In Germany, following peak NH_3 emissions in 2016 from synthetic nitrogen fertilizers of around 100,000 t NH_3 , NH_3 emissions decreased between 2016 and 2021, reaching approximately 65% of the 2016 peak level. This decline coincided with amendments to the German Fertilizer Application Ordinance from 2017 onwards, which introduced measures such as urease inhibitor use or urea fertilizer incorporated within four hours. (Figure 1).

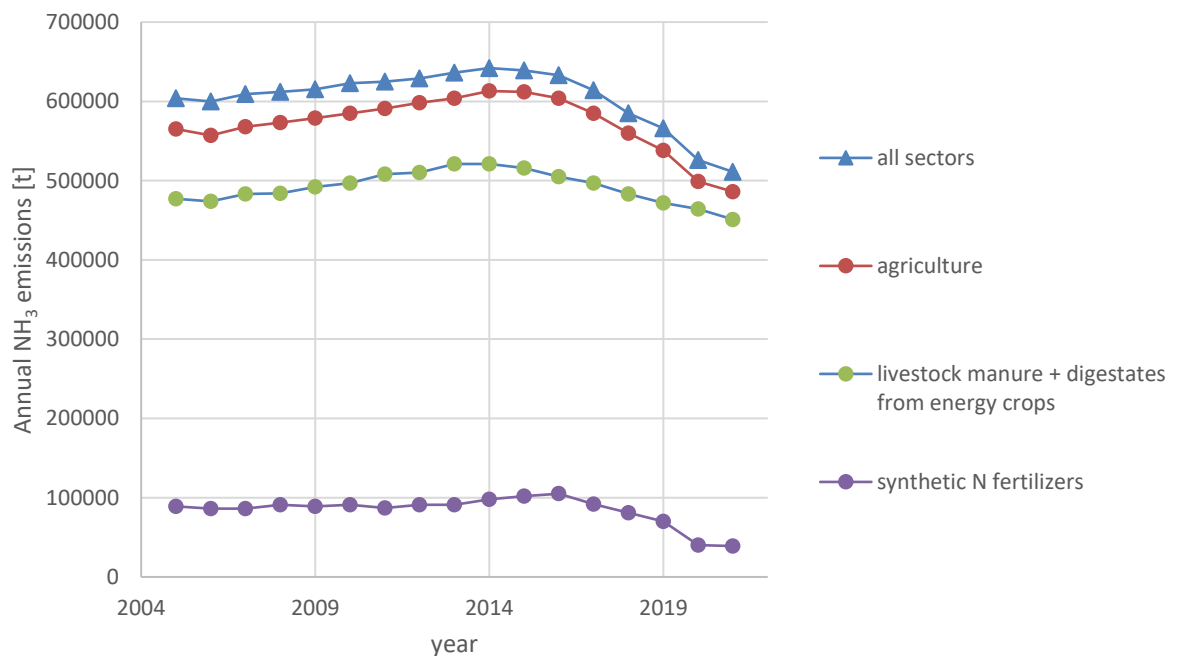


Figure 1 Annual NH_3 emissions from different sources in Germany between 2005 and 2021 (adapted from Hu et al., 2024)

2.2 Environmental impacts of nitrogen fertilization and NH_3 emissions

Often, nitrogen applied through fertilization cannot be fully utilized by the plant. Depending on soil properties and weather conditions, nitrogen leaching and gaseous nitrogen losses occur (Sutton et al., 2008). In consequence, elevated levels and deposition of both oxidized and reduced nitrogen compounds can lead to various detrimental effects. Nitrogen is primarily leached from the root zone as nitrate, thus entering the groundwater and potentially impairing drinking water quality (Aneja, 2001). Furthermore, its deposition after NH_3 emission can contribute to eutrophication of water bodies and acidification of soils and surface waters (Sutton et al., 2008). Additionally, it can stimulate the occurrence of harmful algal blooms and a decline in water quality (Aneja, 2001). It can also indirectly contribute to global warming through the soil's production of nitrous oxide following deposition (Zhu et al., 2013). Nitrous oxide (N_2O) is one of the three important atmospheric greenhouse gases (GHGs) originating from agricultural activities, with about 265 times the global warming potential of carbon dioxide (IPPC, 2019). In plant production, nitrous oxide emissions are mainly due to the use of nitrogen fertilizers.

Ammonia emissions exhibit a high dry deposition velocity, ranging from 0.5 to 5 cm s^{-1} , with the highest rates observed under humid conditions (Finlayson-Pitts, 2000). This results in a significant portion of NH_3 depositing near its source of origin due to its relatively short atmospheric lifetime which typically falls within the range of 1 to 5 days. In contrast, aerosols containing NH_4^+ exhibit a longer atmospheric lifetime, lasting from 1 to 15 days, and can travel greater distances from their point of origin (Aneja, 2001). In natural and semi-natural ecosystems the deposition of nitrogen can cause an ecological shift in species diversity and a loss of biodiversity due to the fertilizing and acidifying effects of NH_3 (Clark and Tilman, 2008). Apart from the environmental impacts, NH_3 also poses a risk to the human health. Particularly fine particles have a detrimental impact on human health with NH_3 and NH_4^+ salts in the atmosphere playing a significant role in the formation of harmful particulate matter with a diameter $< 2.5 \mu\text{m}$ (PM 2.5) (Griffith et al., 2015; Wyer et al., 2022).

In conclusion, the atmospheric pollutant NH_3 has detrimental impacts on ecosystems, as well as on health of both humans and animals. However, the reduction of NH_3 and N_2O emissions is not only of environmental importance, but also of great agricultural interest. Avoided emissions are connected with enhanced nitrogen utilization contribute to resource conservation and lower the amount of purchased fertilizers. This conservation of resources therefore lowers costs, as the

nitrogen remains within the farm. Additionally, increasing fertilizer demand due to population growth with concomitant low nitrogen fertilizer efficiencies calls for increasing nitrogen effectiveness. This is becoming increasingly important due to the resulting increase in fertilizer prices. Thus, mineral nitrogen fertilization of arable land undoubtedly plays a leading role in the conflict between resource efficiency and environmental impact.

2.3 Political measures for reducing NH₃ emissions from mineral fertilizer

International and European Union

The Convention on Long-Range Transboundary Air Pollution (CLRTAP) is an international framework agreement that defines common objectives for reducing air pollution and is implemented through voluntary protocols. In the European Union, the National Emission Ceilings (NEC) Directive translates these objectives into binding law by negotiating enforceable national emission reduction commitments for Member States. The NEC Directive establishes emission reduction targets for Member States and the EU regarding five key air pollutants: nitrogen oxides, non-methane volatile organic compounds, sulphur dioxide, NH₃ and particulate matter. These pollutants are known to contribute to poor air quality, resulting in significant adverse effects on both human health and the environment. Therefore, methane is excluded as it is regulated as a greenhouse gas under EU and international climate agreements. Implemented on December 31, 2016, the NEC Directive (2016/2284/EU) supersedes earlier legislation (Directive 2001/81/EC) and outlines emission reduction commitments for 2020 and 2030. These commitments, agreed upon by the EU and its Member States under the revised 2012 Gothenburg Protocol, aim to halve the health impacts of air pollution by 2030 compared to 2005 levels. Germany has fulfilled the emission reduction commitments of the NEC Directive (2016/2284/EU) for 2020, achieving a reduction of 5% compared to the base year 2005 (Umweltbundesamt, 2025).

Member States are required to develop National Air Pollution Control Programs to support the implementation of air quality plans established under the EU Air Quality Directive. Additionally, the directive mandates regular reporting of air pollutant emission inventories by Member States to monitor progress and compliance with emission reduction commitments. In addition to annual emission reporting, every two years emissions projections for the specified pollutants have to be reported. Within national air quality programs, member states present their historical, current and future planned strategies and measures to achieve the reduction commitments. These programs are to be updated at least every four years. For reporting purposes, there are emission factors (EF) that indicate the mass of a specific greenhouse gas emitted per unit of a given activity. Regarding the assessment of NH₃ emissions, there is a need for regional EFs linked to the application of synthetic nitrogen fertilizers within Germany (Umweltbundesamt, 2018).

The emission factor used for NH₃ emission reporting varies among the reporting organizations. The IPCC states that 14.2% of the applied nitrogen from urea is lost as NH₃ (IPPC, 2019), while the

current European Monitoring and Evaluation Program (EMEP) guidebook reports an EF for urea of 16.1% (EMEP/EEA, 2023). Furthermore, Member States must submit policies and measures aimed at meeting emission reduction commitments for the periods 2020-2029 and beyond 2030.

Germany

Under the European National Emission Ceilings Directive (NEC Directive) of 2016/2284, Germany has committed to reducing its national NH_3 emissions by 5% till 2020 and by 29% till 2030, compared to the 2005 levels. This reduction will follow a linear trajectory between 2020 and 2030. Within the domain of synthetic nitrogen fertilizers, urea-based fertilizers play a crucial role (Figure 2).

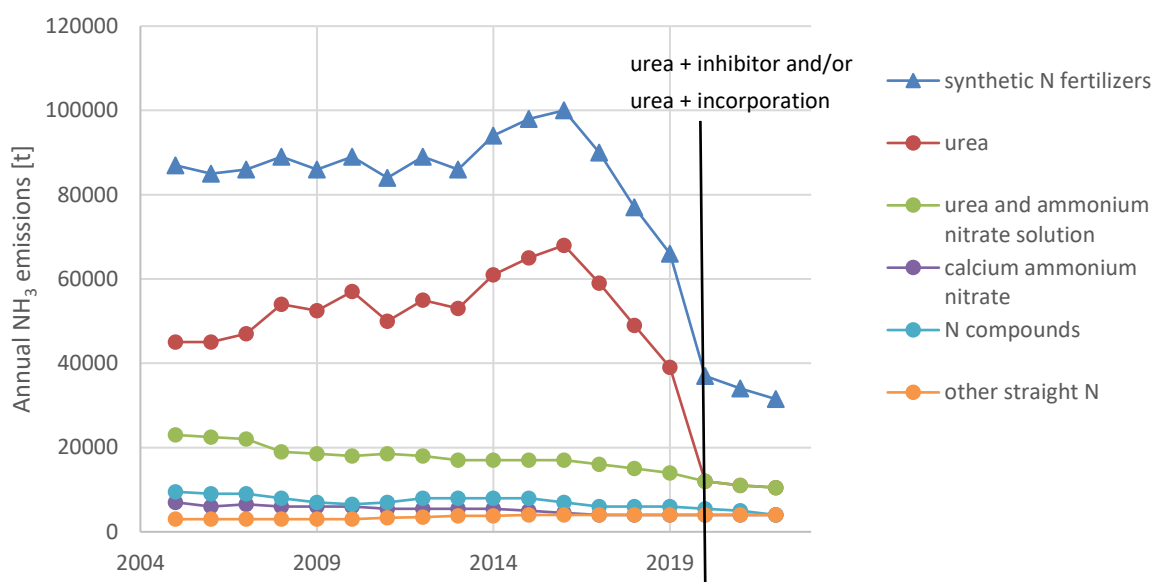


Figure 2 Annual NH_3 emissions from synthetic nitrogen fertilizers in Germany between 2005 and 2022 with NH_3 emissions calculated based on their annual consumption and emission factors (adapted from Hu et al., 2024)

When urea is surface applied, the potential loss of total applied nitrogen through volatilization can reach up to 68% (Drury et al., 2017; Rochette et al., 2009). To address this issue, measures have been implemented in the amendment of the German fertilizer ordinance (DüV20). Since spring 2020, urea fertilizer is required to be applied in combination with a urease inhibitor (UI) or alternatively incorporated into the soil within four hours. In the German annual NH_3 emissions, urea accounted for 52–67% of the total NH_3 emissions from synthetic nitrogen fertilizer between

2005 and 2019 and around 31% between 2020 and 2022 (Figure 2) based on annual consumption and emission factors (Hu et al., 2024). This reduction shows the impact of the German fertilizer ordinance from 2020.

Additional measures are currently under consideration for addressing NH_3 emissions in the context of urea-based blended fertilizers. These include options such as substituting urea and ammonium nitrate urea solution with fertilizers with lower specific NH_3 emissions like utilizing urease inhibitors, coating fertilizer granules, adding various substances like zeolite, pyrite, and organic acids, employing irrigation methods or reducing nitrogen excess through lower mineral fertilizer application rates. These measures aim to enhance nitrogen management practices and reduce NH_3 emissions. Overall, adopting efficient fertilization that simultaneously reduces environmentally harmful NH_3 emissions while enhancing plant-available nitrogen can contribute to the goal of reduce nitrogen waste losses.

For this purpose, standardized emission measurement procedures should be developed to analyse the effectiveness of NH_3 mitigation measures. Of particular importance and urgency is the standardization of measurement methods suitable for use at the field level. Such standardized methods would enable the systematic examination of different fertilizer applications and mitigation measures in a replicable manner. Regarding NH_3 emissions from the agricultural sector, quantification of the relative difference between application techniques is relevant for selecting and documenting mitigation technologies. For recording of NH_3 emissions, the calculation of EMEP emission factors, and the evaluation of both mitigation measures and policy actions related to the application of nitrogen fertilizers under practical conditions, suitable measurement methods are required (Umweltbundesamt, 2018).

2.4 Nitrogen transformation processes after urea fertilization

The conversion of urea is defined by hydrolysis, nitrification, and denitrification (Figure 3). During this nitrogen turnover, next to the plant uptake nitrogen is lost in different ways. Nitrogen loss occurs on one hand due to NH_3 , nitrous oxide and molecular nitrogen emissions and on the other hand as a result of being washed out from the root-covered soil layer.

After application, urea is first converted by hydrolysis into ammonium, which is available to plants but can be bound to negatively charged soil particles. Subsequently, it is oxidized by nitrifying bacteria such as *Nitrosomonas* and *Nitrobacter* to nitrate, a form that can be easily absorbed by plants but is also susceptible to leaching losses. Under anaerobic soil conditions, nitrate can be reduced to gaseous nitrogen by denitrifying microorganisms (e.g., *Pseudomonas*), resulting in nitrous oxide emissions and nitrogen losses. On average 0.62% of urea applied is lost in the form of nitrous oxide emissions from managed German agricultural soils (Mathivanan et al., 2021).

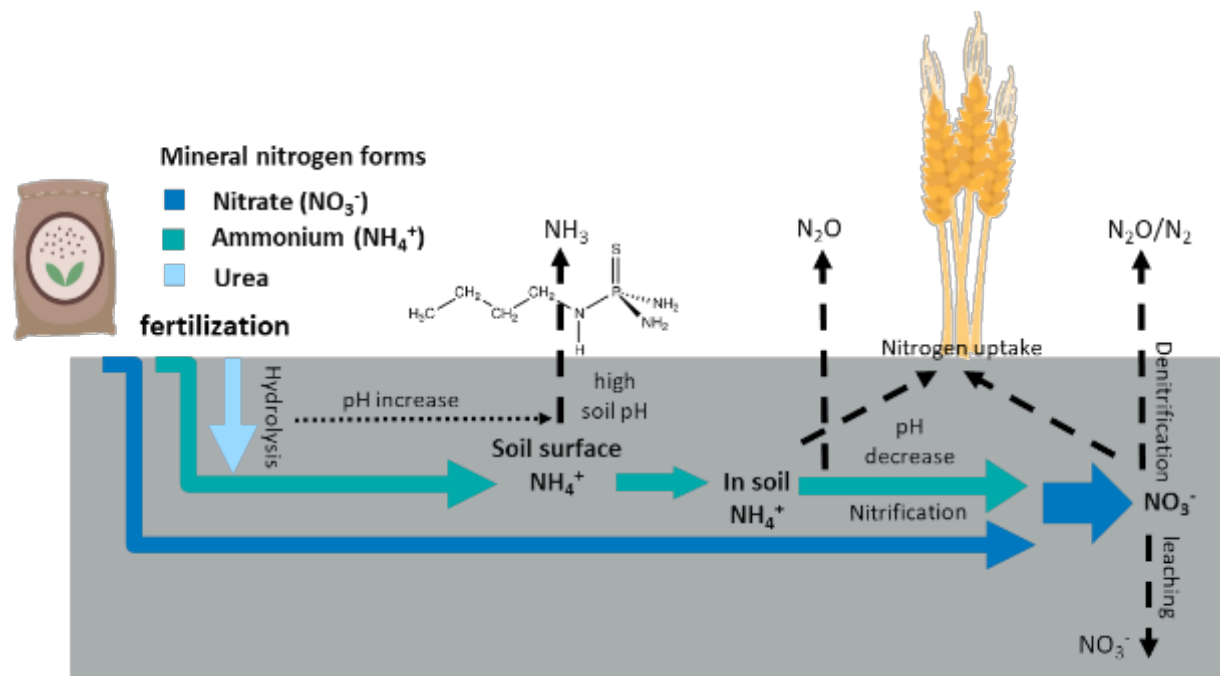


Figure 3 Nitrogen transformation processes after fertilization with different nitrogen forms with losses due to NH_3 and N_2O emissions and leaching next to the plant uptake (adapted from Biewald et al., 2025)

Hydrolysis of urea and NH₃

Ammonia is a colourless gas with a molar mass of 17.031 g mol⁻¹ and a characteristic smell, with a smell detection threshold of 2.6 ppm by humans. NH₃ exhibits a high water solubility, attributed to its Henry's law constant of 67.8 mol kg⁻¹ bar⁻¹ (Liu et al., 2018). It is classified as a base, with a pK_b value of 4.74 (Equation 2).

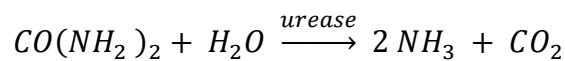
Equation 2 Hydrolysis of NH₃



Due to its high solubility, polarity, and its propensity to form strong hydrogen bonds with water, NH₃ tends to adsorb to most materials exposed to air (Parrish, 2000). This property can pose challenges in NH₃ measurement, as it can lead to memory effects if retained in tubing and on instrument surfaces (Vaitinen et al., 2014).

The hydrolysis of urea with water is catalysed by the enzyme urease which contains a nickel core (Mazzei et al., 2019). The product hydrolysed to ammonium carbamate decomposes into CO₂ and NH₄⁺. Urease is produced by microbes and plants and belongs to the group of amidases, which accelerate the cleavage of amide bonds (Equation 3).

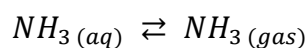
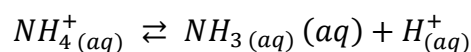
Equation 3 Hydrolysis of urea with urease



Influencing factors on NH₃ emissions

The extent of NH₃ emissions following urea application is significantly influenced by temperature and soil pH levels. NH₄⁺ and the NH₃ gas, exist in an equilibrium within the soil solution and this balance depends on the pH of the aqueous soil solution and temperature. With increasing pH value and temperature, the equilibrium is shifted from dissolved NH₄⁺ towards NH₃ being consequently released into the air due to the constant transport away from the boundary layer (Equation 4).

Equation 4 Equilibrium of NH₃ and NH₄⁺ and transport from liquid to gaseous phase and transport from boundary layer



During the hydrolysis process, the soil pH temporarily rises in the vicinity of the urea fertilizer granule, reaching pH levels >9 at the granule and a pH of 8.4, 1.5–2 cm away which leads to an overall pH increase of 2 pH units (Merl et al., 2024). This causes a shift of the $\text{NH}_4^+/\text{NH}_3$ equilibrium towards NH_3 increasing the risk of NH_3 volatilization. This temporary local increase in pH and the resulting shift towards NH_3 are considered main reasons contributing to NH_3 emissions following urea application (Ni and Pacholski, 2022). NH_3 volatilization losses are more pronounced in soils with higher pH, soils with lower cation exchange capacity and in high temperature and high humidity environments (Connell et al., 2011).

Besides the pH and temperature, the soil water has a strong impact on the $\text{NH}_4^+/\text{NH}_3$ -equilibrium. The soil water content at the time of urea fertilization is decisive for the course of dissolution of the fertilizer granules and for the subsequent hydrolysis. No emissions occur when the soil surface is dry (Sommer et al., 2004), while high losses are to be expected on moist, slowly drying soil (Engel et al., 2011). In addition, precipitation influences the course of the NH_3 losses (Bouwmeester et al., 1985). On the one hand, heavy precipitation can transport urea to deeper soil layers and therefore limit NH_3 emissions. On the other hand, low precipitation can favour granule dissolution and hydrolysis on the soil surface, leading to an increase of NH_3 emissions.

2.5 Emission process from applied fertilizer

Emission processes from the soil surface involve interactions within the soil, primarily driven by adsorption and emissions from soil materials, water as well as metabolic processes involving microbes, fungi and roots. The gaseous transport within the soil pores is influenced by soil composition, compaction and moisture content (Sutton et al., 2001). An essential concept to describe the atmospheric conditions, is the quasi-laminar boundary layer which surrounds exchanging surfaces like soil, water, plants and residues located within a few millimetres of the surface. The exchange in this layer is limited by molecular diffusion (Stull, 1988). Positioned above, is the atmospheric boundary layer which is subject to constant turbulence as a result of ground surface and vegetation. This turbulence is characterized by irregular vortices, known as eddies (Figure 4). These eddies transport heat, water vapor, and gases such as ammonia vertically between different regions of the atmosphere, promoting the homogenization of the air. The eddy covariance method quantifies this transport by simultaneously measuring rapid fluctuations in vertical wind speed (3D sonic anemometer) and NH_3 concentrations (quantum cascade laser), enabling the calculation of the net turbulence flux between the surface and the atmosphere.

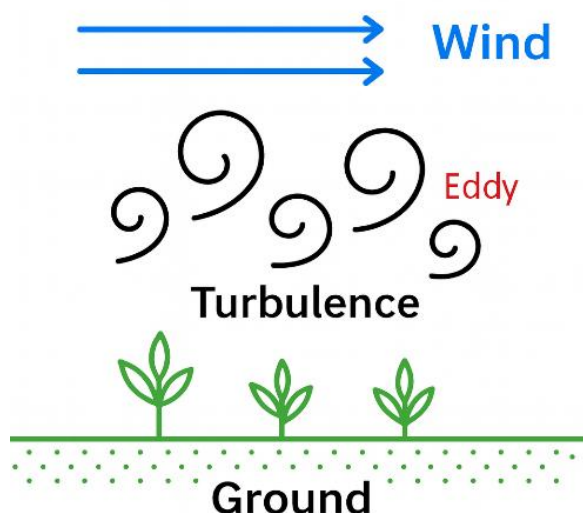


Figure 4 Circular air movements (eddies) caused by turbulence are recorded in order to measure NH_3 flows

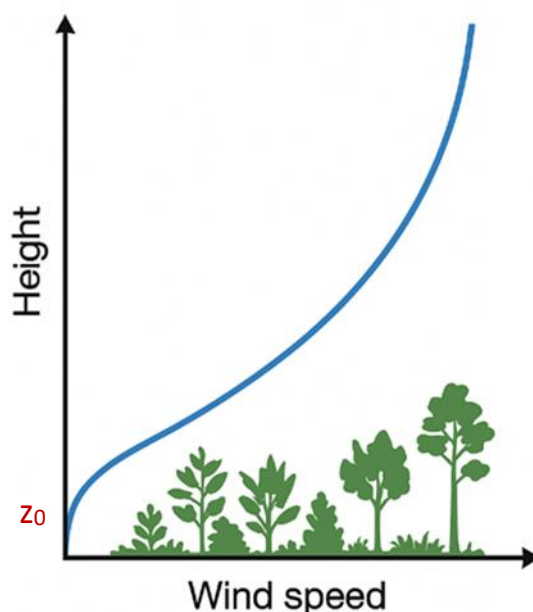


Figure 5 Wind speed profile over atmospheric height and surface roughness length

On the other hand, the horizontal turbulent transport is caused by air currents depending on wind speed and surface roughness length (z_0) (Figure 5). Surface roughness length indicates the height at which the logarithmic wind profile extrapolates to zero. It reflects vertical turbulence caused by horizontal winds over uneven surfaces (Jacobson, 1999). This length varies for different grounds, being about 0.2 mm over smooth surfaces like the sea or paved areas, around 0.25 m above tall crops and over 2 m near large urban centres (Stull, 2017).

The horizontally homogeneous surface layer typically extends to approximately the first 50 meters above the canopy height. Within this layer, the Monin-Obukhov similarity theory characterizes the wind's statistical properties in terms of friction velocity (u^*) and stability. Due to the buoyancy of warm, less dense air, thermal turbulence or free convection occurs, mainly during the day (Stull, 2017). The friction velocity can be described by the momentum flux at the surface according to the Monin-Obukhov similarity theory (Kaimal and Finnigan, 1994), and can be calculated as the square root of the momentum flux. The dynamic stability, the ability of a system to stabilize itself again after a disruption, is measured by the ratio of buoyancy to wind shear effects. To assess stability, often the ratio of measurement height (z) to Obukhov length (L) is used (Equation 5).

Equation 5 The dynamic stability described by the ratio of measurement height to Obukhov length and the ratio of buoyancy to wind shear effects

$$\frac{z}{L} = \frac{-k z g (w'\theta')_0}{u^{*3} \theta}$$

- L = Obukhov length
- z = measurement height
- k = van Karman constant (0.41)
- g = gravitational acceleration $9,81 \text{ m} \cdot \text{s}^{-2}$
- $w'\theta'$ = surface temperature flux
- u^* = friction velocity

Atmospheric stratification is neutral for z/L close to zero, indicating mostly forced convection (Stull, 2017). For stable stratification, z/L is positive, and buoyancy forces return of displaced air parcels to their original position, resulting in laminar flow. Negative z/L values indicate unstable

stratification, where buoyancy moves air parcels further away. Thermal turbulence occurs only during unstable stratification, with very unstable conditions indicating free convection (Stull, 2017). During stable stratification, negative buoyancy forces caused by dense cold air at the surface and warmer layers above can inhibit vertical mixing (Stull, 2017). Turbulence and its vertical extent are crucial for surface gas exchange, controlling the height for gas deposition and atmospheric dilution.

2.6 Measurement methods

In literature, different micrometeorological approaches as well as different chamber measurement principles have been described and evaluated (Table 1) (Sintermann et al., 2012; Umweltbundesamt, 2018). They can be categorized according to the area required for the respective approach. Methods employed in the following studies are highlighted in green and further explained in the following subchapters.

Table 1 Different selected methods and principles for NH₃ measurements with the methods employed in the following studys in green

Method		principle/sensor	area demand
Enclosure methods	Closed static chambers	concentration enrichment e.g. by acid traps with absorption solution	cm ²
	Open dynamic chambers	/ Wind tunnel, Cavity Ring-Down Spectroscopy, Fourier Transform Infrared Spectroscopy, Chemiluminescence, Dräger Tubes	cm ² - m ²
Micrometeorological methods	mass balance, inverse flux modelling	Integrated Horizontal Flux, ZINST height approach (height z, independent of stability), Inverse Dispersion Model	100 m ² - 1 ha
		/	
		with gas concentration measurements by e.g. Leuning and Alpha sampler	
	eddy covariance, Bowen ratio etc.	High Frequency Measurements Laser Fourier Transform Infrared Spectroscopy, Infrar-Red	several ha

Chamber systems (2.6.1) can be used in replicates for treatment comparison as they measure qualitative differences. However, they alter the natural micrometeorological conditions (atmospheric exchange processes, turbulence, temperature, and humidity) on the measurement surface and integrate only over relatively small areas (cm² - m²). The exact real-field scenarios, such as precipitation and wind speed, can be challenging to replicate accurately in chambers, leading to potential inaccuracies. There are a lot of different designs of which chamber- and wind tunnel systems are the most commonly used (Braschkat et al., 1993; Sommer and Misselbrook, 2016).

Micrometeorological methods (2.6.3) measure quantitative losses and have the advantage that the influence of small-scale heterogeneities (e.g., fertilizer distribution, plant growth, soil properties) is low because they integrate over comparatively large areas. However, these approaches are only of limited suitability for evaluating reduction methods. Due to the large amount of space required and, in many cases, electricity demand they are not suitable for agricultural multi-plots comparing different treatment methods, such as different types of fertilizers or application techniques.

Due to the specific application limitations, no internationally accepted standard method of NH_3 emission measurement has been defined yet. The 2019 refinement of the IPCC guidelines notes an uncertainty range for NH_3 emissions from synthetic fertilizers between 2% and 33% (IPCC, 2019) especially when considering absolute nitrogen losses. This large uncertainty is likely to be influenced by the complex environmental processes governing NH_3 emissions and variation induced by measurement methods (Kamp et al., 2024) (Figure 6). In that study of Kamp et al. 2024 measurement methods in field experiments over 7 days were compared. The various concentration measurement methods used with backward Lagrangian stochastic showed differences of 1–13% of the applied total ammoniacal nitrogen. Ammonia emissions measured with wind tunnels were high and depended on the air exchange rate used. Dräger Tube Method emission measurements were lower than those obtained with other methods using backward Lagrangian stochastic. The following subchapters provide a detailed description of the different approaches used to measure NH_3 emissions.

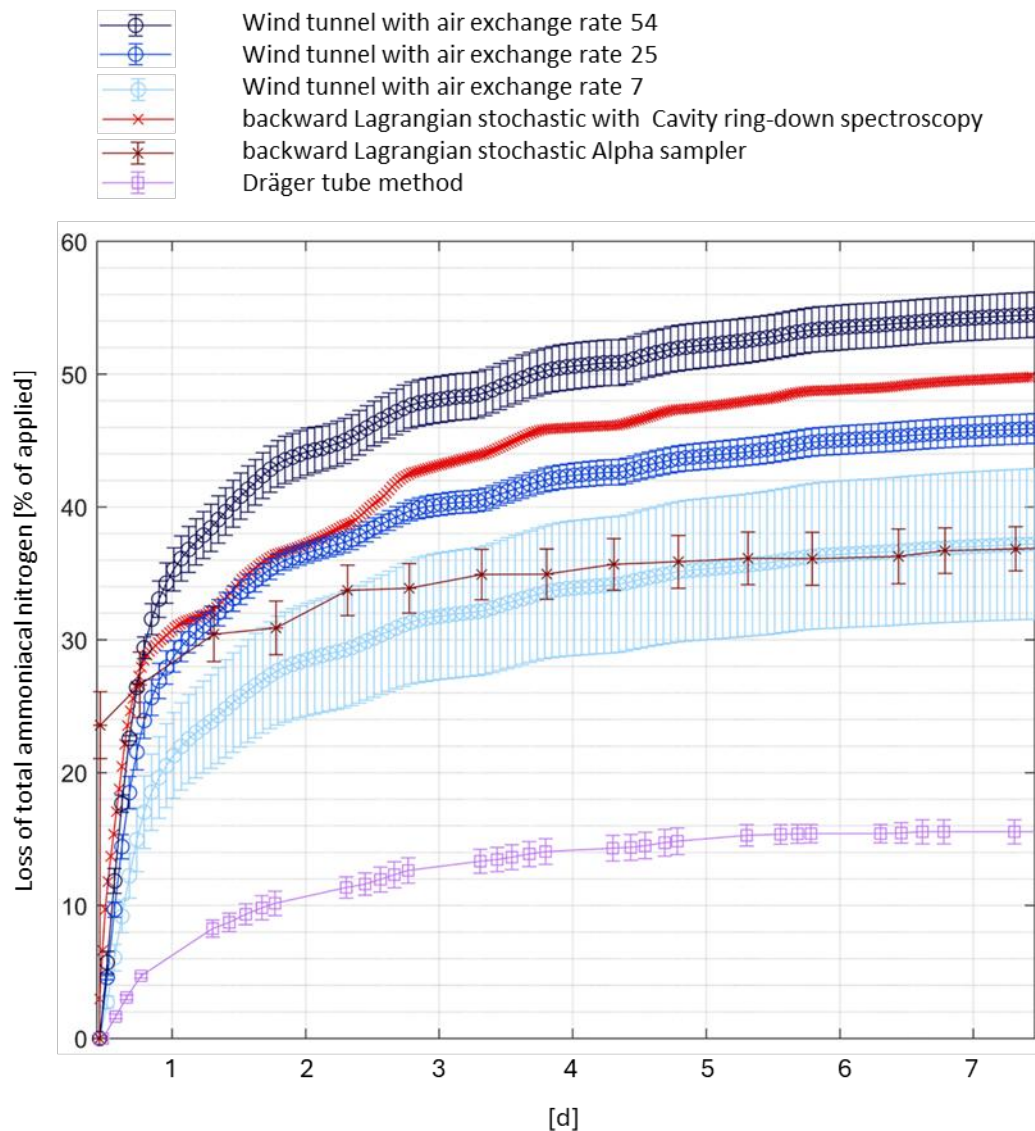


Figure 6 Deviations of cumulative emission as fraction of total applied ammoniacal nitrogen (%) measured with different NH_3 methods (adapted from Kamp et al., 2024)

2.6.1 Enclosure chamber methods

The mass balance principle for determination of the atmosphere-surface exchange can be applied in a simple way by using enclosure methods. Enclosure chamber methods have the advantage of portability and treatment comparisons during process studies that cannot be realised with micrometeorological methods due to their large space requirement and, in many cases, electricity.

Enclosure chamber methods can be divided into closed and open systems (Hutchinson and Livingston, 1993):

Closed static chambers require an enrichment of the measured gas concentration in the headspace. Therefore, they are not feasible for surface-active gases like NH_3 due to the potential of adsorption on surfaces, e.g. chamber walls. Sampling approaches to determine the gas concentration are e.g., acid traps or by syringe sampling.

Dynamic open chambers allow a continuous exchange of air in the headspace. Alteration of the turbulence within the chamber is unavoidable, often affecting temperature, humidity, and radiation. At lower flow rates, the chamber may fail to replicate field conditions, but it can achieve proper mixing at higher flow rates or with the use of a fan (Woodbury et al., 2011).

Wind tunnels, a form of dynamic open chambers, possess a larger surface area and maintain a continuous airflow across the chamber base. The airflow is predominantly laminar. Wind tunnels are an intrusive technique, requiring a matching of microclimatic conditions inside and outside the tunnel when aiming at measuring absolute fluxes representative for ambient conditions (Loubet et al., 1999). A sampling approach to determine the NH_3 concentration with wind tunnels is the cavity ring-down spectroscopy. Dynamic wind tunnels combined with online cavity ring-down spectroscopy measurements show a low variability compared to other concentration sensors (Pedersen et al., 2020), and are therefore advantageous for comparative measurements of application techniques. However, practical challenges make it difficult to fully replicate turbulence and atmospheric conditions e.g., windspeed and rainfall, as well as soil conditions like moisture and temperature which controls the exchange over the study plot. Moreover, the reliability at field scale is low due to soil variability and potential disturbances of natural soil conditions at the measurement site. Consequently, the wind tunnel technique is best suited for comparative measurements and should be used cautiously when estimating absolute fluxes (Misselbrook et al., 2005).

Another dynamic chamber method is the Dräger Tube Method (Pacholski, 2016), which is extremely simple compared to the other chamber methods (no power demand, no laboratory equipment), using indicator tubes for absolute NH_3 emission detection. In addition, this method reduces the disturbance of the plot since only point measurements are carried out. Furthermore, alteration of the environmental conditions is reduced to a minimum, in comparison to wind tunnels that seal the plot for the entire experimental period.

2.6.2 Standard comparison method

One of the first methods for small experimental plots under ambient climatic conditions is the standard comparison method developed by Vandr  and Kaupenjohann in 1998. First NH_3 is collected on fertilized plots and then compared with NH_3 collected on standard plots (Vandr  and Kaupenjohann, 1998). In this open indirect measurement technique sampling is done by means of small passive flux samplers (2.7). Fluxes from treatment sites are corrected for atmospheric background values by subtraction. The plots cover an area of 2 x 2 m. In the standard plots the gas exposure system contains micro-perforated tubes which release known rates of NH_3 as tracer gas, to determine a transfer coefficient. No absolute measurement of NH_3 concentration in the air is needed for the estimation as it is exclusively based on the proportionality between NH_3 release and sampler measurements. Relative values can then be converted to absolute losses using the transfer coefficients. As the passive flux samplers are positioned above the soil surface this measurement method has no effect on wind speed or precipitation and thus does not affect the NH_3 volatilisation process at the soil surface. This technique has proven valuable in several field studies (M ller and Stinner, 2009; Wulf et al., 2002) particularly for the in-situ determination of NH_3 fluxes from treatment sites with bare soil or limited density of vegetation.

2.6.3 Micrometeorological methods

Micrometeorological methods provide non-intrusive approaches to quantify NH_3 emissions at field scale. Atmospheric concentration measurements of a specific gas are linked with turbulent exchange processes at the specific location (Kaimal and Finnigan, 1994). The commonly used micrometeorological techniques are: Eddy covariance, the integrated horizontal flux approach, the flux gradient technique and inverse dispersion. Some of these methods use continuous high frequency measurements with a quantum cascade laser or Fourier-transform infrared spectroscopy. Micrometeorological methods necessitate the assumption of consistent meteorological and field site conditions to simplify the system into a one-dimensional model. This enables the extraction of gas flux data for the entire footprint area from a single measurement point for concentration and turbulence. This approach has the advantage of offering absolute flux measurements. Another advantage is the reduced influence of small-scale heterogeneities (e.g., fertilizer distribution, plant growth, soil properties), as the measurement area is large. The

emission process relies on wind speed and wind direction. Thus, variations in wind direction or low wind speeds can lead to inaccuracies (Kamp et al., 2024).

The integrated horizontal flux method

The integrated horizontal flux method is a micrometeorological method based on a mass balance technique. It is used to assess the horizontal flux based on measurements taken in the middle of a source and upwind from the source to determine background emissions (Denmead et al., 1977; Denmead, 1998). To apply this method, the gas concentration must be measured at multiple heights (usually four or more) and the concentration data is typically averaged over hours to several days.

In contrast, the **ZINST method** (height z , independent of stability) is a simplified integrated horizontal flux mass balance approach. A two-dimensional turbulent dispersion model is used to generate predictions that allow for measurement of the horizontal flux at a single height, reducing the need for extensive experimental data (Wilson et al., 1982). However, the ZINST method requires a minimum circular field size of 2000 m² to ensure that the assumptions of turbulent dispersion and a horizontally uniform gas flux hold (Wilson et al., 1982). The integrated horizontal flux and ZINST method for NH₃ can be realized by application of various NH₃ concentration measurement approaches (e.g. Leuning samplers, impingers, washing bottles, Alpha samplers).

However, these micrometeorological approaches are of limited use for evaluating mitigation measures, as they require large areas or power supply and are often associated with substantially higher costs. **Eddy covariance** measurements for example have the potential to provide a high measurement accuracy and precision through a quantum cascade laser but are high in cost and need electricity in the field. Overall, measurements of fertilizer variants with repetitions for statistical evaluation is a central prerequisite for scientifically validated proof and requires agricultural plot trials.

Dispersion modelling

Dispersion models are employed to represent the dispersion of substances in the atmosphere. These models are valuable for approximating the concentration of pollutants downwind from a source or predicting concentrations at specific locations under varying conditions. Various frameworks can be utilized in dispersion models:

- The Gaussian distribution model assumes that air pollutants conform to a normal probability distribution.
- In the Lagrangian framework, simulations of particle trajectories in a moving reference frame are used to track the movement of particles through the atmosphere.
- The Eulerian analytical approach relies on surface layer similarity theory within a fixed reference system as a framework for analysis (Schmid, 1994).

There are two techniques for modelling emissions from a source, which are defined by the direction of particle trajectory simulation:

- **Forward models** where particles are modelled from the source into the environment or towards the sensor location
- **Backward/Inverse models** where particles are modelled from the measuring point and their path backward in time towards the source is traced

Forward models can be inefficient due to the large number of particles that need to be simulated, as only a small fraction of them reaches the locations of interest. If concentrations at specific measurement points are required, backward models are significantly faster and more flexible due to the resulting significant reduction of computational complexity.

Backward Lagrangian stochastic in Inverse Dispersion Models

Inverse Dispersion Models aim to infer information about emissions from a known source, based on concentration measurements. They are not fundamentally constrained by the size or shape of the emission source, provided that the atmospheric transport simulated by the model is accurately represented (Flesch et al., 2004). Furthermore, the placement of the sensor within the emission plume can be flexible, and any measurable tracer property can be used in the Inverse Dispersion Model as long as it is predicted by the model and exclusively linked to the source emissions. To run an Inverse Dispersion Model effectively, variable spatial and temporal wind fields are required for both average wind speed and turbulence. These can be determined with a limited number of observations and using the Monin-Obukhov similarity theory if measurements are conducted within the horizontally homogeneous surface layer (Flesch et al., 2004)

The backward Lagrangian stochastic model, as introduced by Flesch et al. (1995), offers a fast and flexible approach for calculating short-range dispersion of NH_3 (Flesch et al., 1995). Turbulent dispersion is represented in this model by calculating many random trajectories of fluid elements

or particles, which together reproduce the statistical properties of turbulence. The backward Lagrangian stochastic model as a backward model estimates the concentration to emission rate ratio (C/Q) within a measurement interval based on the measured turbulence and wind field characteristics of that time interval (Equation 6). The model computes trajectories moving upwind in a backward time direction starting from the sensor's location (Figure 7). This process results in the creation of a record of landing positions (touchdowns) where the particles touch the ground. The number of trajectories can be increased, which will increase the number of touchdowns decreasing the model uncertainty.

Equation 6 Emission rate from sampled tracer concentration and modeled dispersion coefficient

$$Q = \frac{C}{(\frac{C}{Q})_{sim}}$$

Q = emission rate within a measurement interval

C = time-average tracer concentration (above background)

$(C/Q)_{sim}$ = dispersion coefficient (D) from model prediction for the measurement interval

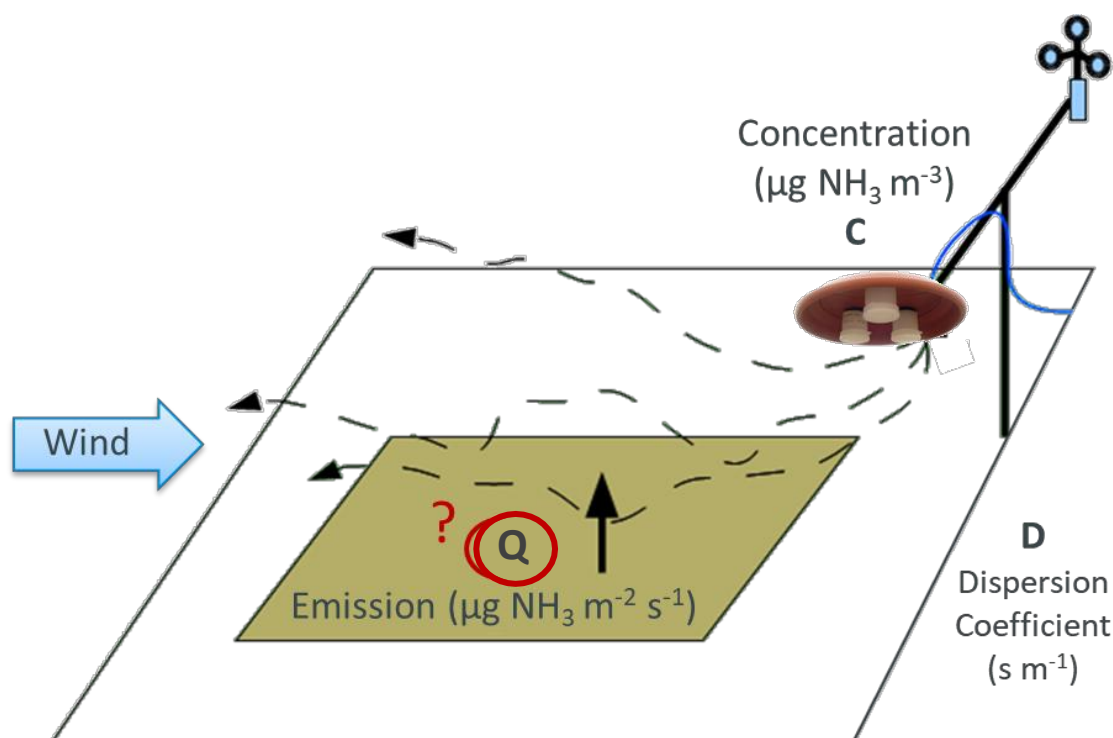


Figure 7 Illustration of the backward Lagrangian stochastic technique for estimating tracer emission rate with the average concentration C measured at point downwind of the source. The dispersion coefficient (D) is the ratio $(C/Q)_{sim}$ which is calculated from upwind trajectory touchdowns inside the source (adapted from Flesch et al., 2004)

For atmospheric concentration NH_3 measurements, needed for modelling, monitors like cavity ring-down spectroscopy or the passive Alpha samplers are used. Carozzi et al. 2013 estimated NH_3 emissions from surface application of dairy slurry by using an Inverse Dispersion Modelling technique associated with the long-term exposure Alpha samplers for NH_3 concentration and the measurement of the atmospheric turbulence by weather measurements (Carozzi et al., 2012; Carozzi et al., 2013; Lavrsen Kure et al., 2018; Loubet et al., 2018).

The backward Lagrangian stochastic model is available as open source software WindTrax (www.thunderbeachscientific.com) (Flesch et al., 2004) with a graphical user interface and as a package (bLSmodelR) in the software R (Häni, 2020).

2.7 Determination of atmospheric NH₃ concentration

All NH₃ flux calculation approaches rely on the combination of atmospheric NH₃ concentration measurements and model/experimental approaches representing the NH₃ transport process in the atmosphere. Only NH₃ leaving the soil-plant continuum can be considered as volatilized. Measurement approaches for atmospheric NH₃ vary with respect to resolution in time, accuracy and precision. The following subchapters provide a detailed description of the different devices used for NH₃ concentration measurements.

2.7.1 NH₃ passive samplers: Alpha, Leuning, Acid Traps

Passive samplers collect chemicals from the environment over a longer period of time without requiring energy or active pumps. They use natural processes such as diffusion to absorb and accumulate pollutants from media such as the air (Figure 8).

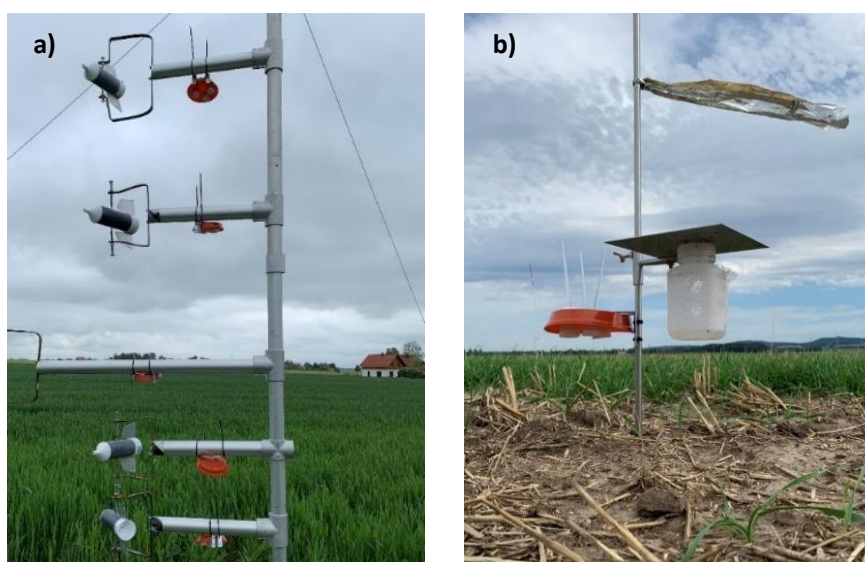


Figure 8 Concentration measurement methods for NH₃ in field trials a) rotating Leuning sampler left and Alpha sampler right and b) Alpha sampler left and sulphuric acid traps right

Alpha samplers (Adapted Low- cost Passive High Absorption diffusive samplers, UKCEH) (Tang et al., 2001) are passive diffusion samplers that are based on the principle of gas diffusion through a polytetrafluoroethylene (PTFE) membrane, where the emitted NH₃ is absorbed on a filter paper coated with citric acid (Figure 8). The concentration measurements have been validated for

atmospheric concentrations up to 25 ppb (Martin et al., 2019). In the field the samplers were changed once a day.

Leuning samplers (Leuning et al., 1985) provide the product of wind speed and NH_3 concentration and thus the NH_3 emission from the surface can be determined as horizontal NH_3 transport without additional wind speed measurement (Figure 8, left). The samplers are mounted on a mast to rotate freely on a circular plot area of minimum 20 m radius. Each Leuning sampler is coated by 3% oxalic acid in acetone solution to absorb the NH_3 emissions and can be extracted after exposition in the field.

Acid Traps (Vandré and Kaupenjohann, 1998) consisted of square HDPE bottles with holes in the sides (Figure 8, right), which are equipped with PE grids for protection against particle contamination (debris, insects etc.). The lid is attached to a stainless-steel roof, which protects against rain and thus against possible dilution of the sampler solution. Immediately after fertilization, the acid traps are set up and filled with 20 ml of collector solution (0.05 M H_2SO_4). The absorbent solution is then changed daily.

2.7.2 **NH_3 monitors: optical/laser-based spectroscopic measurement methods**

Laser- and infrared-based spectroscopic methods are used in environmental monitoring because they enable continuous, sensitive, and reliable determination of NH_3 in the gas phase (Figure 9).



Figure 9 Concentration measurement methods for NH_3 in field trials left wind tunnels used with cavity ring-down spectroscopy and right quantum cascade laser

Cavity ring-down spectroscopy is a highly sensitive optical spectroscopic technique that measures by scatter and absorption of light at a specific wavelength the absolute optical extinction of gaseous samples. **Photoacoustic spectroscopy** involves shining intermittent light on a sample and detecting the resulting periodic temperature fluctuations as pressure changes. A **Quantum cascade laser** is a semiconductor laser that operates at wavelengths in the mid-infrared and far-infrared (terahertz radiation). Unlike traditional semiconductor lasers, which generate light through the radiative recombination of an electron from the conduction band with a hole in the valence band (interband transition), quantum cascade lasers emit light through intersubband transitions of electrons within the conduction band. **Fourier-transform infrared spectroscopy** is a method utilized to capture an infrared spectrum of absorption or emission from the gas samples. A Fourier-transform infrared spectroscopy spectrometer gathers high-resolution spectral data across a broad spectral range simultaneously. This provides a significant advantage over a dispersive spectrometer, which measures intensity within a narrow wavelength range at a time.

2.7.3 NH_3 concentration indicators tubes

Indicator tubes can be used to measure NH_3 through colour reaction (Figure 10) in different concentration ranges and are offered by various manufacturers. An established method in Germany that uses very small chambers and indicator tubes is the Dräger Tube Method (Pacholski et al., 2006). Initially, it was developed for CO_2 measurement (Richter, 1972) and subsequently enhanced for qualitative NH_3 measurement following urea fertilization in China (Roelcke et al., 2002). Subsequently, through calibration in comparison with micrometeorological measurements (Pacholski et al., 2006), quantitative measurements were made possible.



Figure 10 Indicator tubes as concentration measurement method for NH_3 in field trials (Dräger Tubes)

The system of the Dräger Tube Method consists of four small chambers, which are connected with Teflon tubes. A portable sucking pump is used to draw air inside through an indicator tube. The NH_3 concentration (ppm) of the sucked air is displayed immediately by a colour change on the indicator tube. Due to the diurnal flux variations measurements have to be carried out multiple times throughout the day.

These indicator tube measurements can be combined with NH_3 concentration measurements using passive flux samplers (Vandré and Kaupenjohann, 1998) or denuders. By measuring a standard comparison variant using both methods the qualitative losses of the passive samplers can be converted into absolute losses (kg N ha^{-1}). Therefor a transfer quotient (Gericke et al., 2011; Ni et al., 2014; Ni et al., 2015) is calculated. This allows many variants to be covered with less time-consuming passive samplers, making them suitable for multi-plot experiments.

2.7.4 **NH₃ active samplers: impingers, washing bottles**

The impingers or washing bottles are active samplers. As air is sucked through the glass impinger or bottle, NH₃ reacts into an acidic solution inside (e.g., 20 mL of 0.05 M HNO₃) and is captured as NH₄⁺. The sampled air goes through a stainless-steel tube with perforated Teflon cap, using a suction pump and a flowmeter to detect the flow rate. The NH₃ is trapped in the liquid phase. In the field the integrated horizontal flux approach is then often used to calculate the emissions of the fetch from the detected concentrations in different heights (2.6.2) (Goedhart et al., 2020; Huijsmans, 2003).

2.8 Approaches for replicated small-plot trials

In General, micrometeorological methods require large areas, electricity and are high in cost. Additionally, they need a substantial unfertilized buffer zone surrounding the NH_3 source area, making replicate measurements difficult. This is in contrast to the typical agricultural practice of conducting replicated field plot experiments with relatively small plots (Petersen, 1994). Such small plot experiments are crucial for statistical analysis of replicated NH_3 loss measurements.

Methods used for comparative measurements of NH_3 losses are:

- **dynamic chamber methods** like wind tunnels (Loubet et al., 1999). However, most of these techniques tend to overestimate NH_3 losses and determine NH_3 loss potentials rather than actual NH_3 losses under field conditions (Sommer et al., 2005).
- **standard comparison method** during which NH_3 is collected on fertilized small plots under ambient climatic conditions and then compared with NH_3 collected on standard releasing plots (Vandré and Kaupenjohann, 1998).
- **passive samplers** like sulfuric acid traps or denuders offer qualitative NH_3 concentration measurements. In combination with direct emission measurements they can be used to assess quantitative NH_3 emission in plot experiments with different variants (Ni et al., 2014).

Passive Sampling methods which detect qualitative differences of emissions in multi plot experiments have to be scaled to absolute values from parallel reference measurements. Quantitative NH_3 losses can be calculated using for example the measurements of the backward Lagrangian stochastic dispersion modelling (Gericke et al., 2011) or open dynamic chamber method with Dräger Tubes (Ni et al., 2014) as a reference. These **combined approaches** for replicated small-plots were proved to be a suitable approach for determining the quantitative NH_3 losses in field trials. Suitable agricultural trial plots are at least 4 m² in size and have three or four replicates for statistical comparison. Combined approaches thus offer a cost-effective and flexible way to estimate NH_3 emissions using inexpensive, non-powered samplers. Nevertheless, an internationally accepted standard for NH_3 emission measurements is still lacking and the frequently employed Dräger-tube method used as a reference remains laborious and time-consuming.

2.9 Mitigation strategies of NH₃ emissions from field applied fertilizer

Different mitigation strategies for NH₃ volatilization from nitrogen applied in agriculture are described in the following. Generally, they can be divided into four groups, in congruence with the 4R nutrient stewardship concept (Table 2). It was introduced (Bruulsema T. et al., 2009) to achieve cropping system goals with economic, social and environmental benefits.

Table 2 The 4R nutrient stewardship concept

4R	Definition	Example
Right source	matches fertilizer formulation to crop needs	non-urea-based fertilizer enhanced efficiency fertilizers
Right rate	matches amount of fertilizer type to crop needs	specific rates based on nitrate soil tests, yield history and soil types
Right place	keeps nutrients where crops can use them	incorporation after broadcast application direct band application or injection
Right time	makes nutrients available when crops need them	application of nitrate after soil cools in fall or in spring before/at seeding and not on frozen or snow-covered soil

Thus, usage of non-urea-based fertilizer can be chosen, the fertilizer rate can be reduced and the fertilizer can be incorporated to reduce NH₃ emissions. Furthermore, there are different farming practices such as adjusting irrigation amount to mitigate NH₃ volatilization. Incorporation and irrigation after fertilization can transport fertilizer into the soil, consequently reducing NH₃ volatilization by on average 55% and 35%, respectively (Pan et al., 2016). In addition to such farm management practices, there are numerous enhanced efficiency fertilizers investigated e.g., the urease inhibitor N-(n-butyl) thiophosphoric triamide (NBPT). Among these, urease inhibitors and controlled release fertilizers such as polymer sulphur-coated urea and polyolefin-coated urea (Chen et al., 2008) decrease NH₃ volatilization. On the other hand, nitrification inhibitors can increase NH₃ losses while decreasing N₂O emissions (Ni et al., 2014). Recent studies focused on inexpensive amendments to mitigate NH₃ volatilization using natural mineral or industrial by-products or chemicals that have high NH₄⁺ binding capacity e.g. zeolite or acidifying effects e.g. humic acid (Ahmed et al., 2006).

2.9.1 Incorporation techniques for NH₃ emission mitigation

Fertilizer incorporation or injection, such as slit incorporation, increases the contact area between soil and fertilizer, enhancing NH₄⁺ sorption to the soil matrix. These techniques significantly influence NH₃ emissions. A broad overview of studies investigating mitigation of NH₃ emissions by incorporation is displayed in Table 3.

Table 3 Mitigation of NH₃ emissions by incorporation

Technique and fertilizer	Mitigation compared to broadcast application	Reference
Incorporation of urea by surface mixing	20%	(Du Preez and Burger, 1987)
Incorporation of urea by band application	53%	(Du Preez and Burger, 1987)
Incorporated urea	86%	(Prasertsak, 2002)
Incorporated urea with urease inhibitors	47% to 91%	(Fontoura and Bayer, 2010)
Incorporated urea	34%	(Woodley et al., 2020)
Incorporated urea	40%	(Kreuter et al., 2020)
Incorporated urea + nitrification and urease inhibitors	70%	(Kreuter et al., 2020)
Urea ammonium nitrate solution injection	60%	(Drury et al., 2017)
Urea ammonium nitrate solution injection	99%	(Woodley et al., 2020)

In addition to mere incorporation, its depth, weather conditions and soil properties such as cation exchange capacity, pH, water content, and texture (Du Preez and Burger, 1987; Sommer et al., 2004) also affect NH₃ reduction. Thus, incorporating urea 3 to 5 cm deep in moist soil reduced NH₃ losses by 86% (Prasertsak, 2002). Soil clay content and pH buffer capacity influence NH₃ volatilization, with higher clay content correlating to lower NH₃ losses due to better NH₄⁺ binding

(Pelster et al., 2018). Soil water content impacts urea hydrolysis and $\text{NH}_4^+\text{-N}$ turnover (Sommer et al., 2004), and the urease enzyme activity (Engel et al., 2011).

In agricultural practice, plowing, rotary tilling, and cultivating are common soil cultivation methods. While plowing turns soil at 15-25 cm depth, rotary tillers and cultivators mix soil at 5-20 cm depth. All these methods can incorporate mineral fertilizer to reduce NH_3 losses. However, there is limited data on the interaction between incorporation techniques on varying soil conditions and their effect on NH_3 emissions.

The literature indicates that fertilizer incorporation is effective in reducing NH_3 emissions. However, in accordance with the variance stated in Table 3, a review determined the estimated reduction potential for incorporation to range from 50 to 80% (Bittman et al., 2014). In addition, there is insufficient data for reliably estimating emission levels for different incorporation techniques under the same soil conditions. Furthermore, it is essential to understand the risk of increased N_2O due to the incorporation of urea (pollution swapping). All in all, consistent information on the variation in these variables is needed for better evaluation of the mitigation measures.

2.9.2 Urease inhibitors for NH_3 emission mitigation

Urease inhibitors added to urea fertilizer slow down urea hydrolysis (Wang et al., 2020) (Figure 3). This is reducing NH_3 volatilization by attenuating the pH increase of the soil, providing more time for NH_3 to be adsorbed by soil and plants (Wang et al., 2020). The mechanism of inhibition involves reversible complexation of the nickel centres in the urease active site by the inhibitor molecule. This impedes substrate binding and induces temporary deactivation of the enzyme. The effectiveness of inhibition depends on the concentrations of urea and the inhibitor, the active ingredient, and the inhibitor's degradation rate.

Meta-analyses show that urease inhibitors can reduce NH_3 emissions by 30-70% in both laboratory and field experiments, with some studies reporting up to 90% reduction (Klimczyk et al., 2021; Ni et al., 2018; Pan et al., 2016; Pan et al., 2022; Silva et al., 2017). This is also supported by a recent meta-study for which an average NH_3 mitigation potential of 51% across 76 studies was determined (Fan et al., 2022).

However, the applied urease inhibitors primarily affect NH_3 hydrolysis but do not reduce N_2O emissions or nitrate leaching (Sigurdarson et al., 2018). Instead, some studies indicate a risk of "pollution swapping" with reduced NH_3 emissions leading to higher soil nitrate concentrations. Thus, studies reported increased N_2O emissions after use of urease inhibitor (Drury et al., 2017; Hu et al., 2020; Woodley et al., 2020). Although the overall emission-reducing effect of urease inhibitors is promising, further research is needed to understand the conditions and extent of potential N_2O emission increases (Fan et al., 2022).

Combination with nitrification inhibitors

Nitrification inhibitors slow down the microbial oxidation of NH_4^+ to nitrate by suppressing the activity of the ammonium monooxygenase enzyme in nitrifying bacteria (Soares et al., 2012). As a result, nitrogen is preserved in form of NH_4^+ reducing nitrate leaching and N_2O emissions (Ruser and Schulz, 2015) (Figure 3). A recent meta-study across 422 studies showed that nitrification inhibitors reduced N_2O emissions by 49% (Fan et al., 2022). However, nitrification inhibitors do not decrease NH_3 emissions but can lead to an increase instead (Soares et al., 2012; Wang et al., 2020). This effect was shown in 82 studies with an average increase of 9% compared to urea without inhibitors (Fan et al., 2022). The prolonged higher soil pH and NH_4^+ concentration due to nitrification inhibition can increase NH_3 volatilization (Soares et al., 2012).

Combining urease inhibitor and nitrification inhibitors with urea fertilizer extends NH_4^+ availability to plants, reducing NH_3 volatilization, N_2O emissions, and nitrate leaching (Gioacchini et al., 2002). Experiments showed that combining urease inhibitors and nitrification inhibitors can mitigate NH_3 emissions by up to 89% (Hu et al., 2020; Martins et al., 2017), with an average reduction of 38% (Fan et al., 2022). Additionally, the combined use of both inhibitors can reduce N_2O emissions by up to 69%, with an average mitigation of 31% (Fan et al., 2022; Martins et al., 2017; Ni et al., 2018).

Current research has focused only on a few inhibitor products. Thus, further studies on other compounds used in agricultural practice are needed.

3 Methodological approach

3.1 Research Gap

Agricultural NH_3 emissions have become a central policy concern, as tightening emission ceilings increase the pressure to implement effective mitigation strategies. While incorporation of fertilizers and the use of urease inhibitors are widely promoted as key measures, their relative effectiveness under practical field conditions remains insufficiently understood.

There is a lack of detailed investigations on how different, practice-oriented incorporation techniques perform across diverse soil environments, which restricts a reliable evaluation of their mitigation effects. Moreover, existing research has largely focused on a small number of inhibitor products, particularly NBPT, despite the fact that other formulations are widely used in agricultural practice. At the same time, potential pollution-swapping effects, such as increases in N_2O emissions after urea incorporation or inhibitor application, remain insufficiently quantified. Together, these gaps highlight the need for systematic assessments that simultaneously evaluate NH_3 and N_2O responses of mitigation measures (2.9).

To date, NH_3 mitigation measures have rarely been statistically assessed in replicated field trials, and no European or internationally accepted standard for measuring NH_3 emissions in such trials is available. Although combined measurement approaches, such as using low-cost passive samplers together with micrometeorological techniques, offer a flexible and cost-effective alternative, consistent methodological validation is still lacking (2.8).

Research Questions

1. How effective are different practice-oriented fertilizer incorporation techniques in reducing NH_3 emissions across diverse soil conditions, and to what extent do soil properties modulate their mitigation performance? How significant is the risk of pollution swapping due to increased N_2O emissions after incorporation?
2. How effectively do different urea mitigation strategies, including practical incorporation techniques and alternative urease inhibitors used alone or in combination with nitrification inhibitors, reduce NH_3 losses while influencing N_2O emissions and potential pollution-swapping effects under agricultural soil conditions?

3. How accurately can NH_3 emissions from field-applied synthetic fertilizers be quantified using simultaneous measurements from replicated plots needed for evaluation of mitigation measures. How well do different multi-plot measurement approaches perform when validated against micrometeorological reference methods?

3.2 Objectives

Objective 1:

Analysis and evaluation of the effect of different urea incorporation techniques on NH_3 emission reduction depending on soil texture (sandy, loamy, clayey) and moisture content (70% and 30% water holding capacity). → Publication 1

Therefore, three incorporation techniques are mimicked and investigated: surface incorporation by cultivating, deep incorporation by plowing, and the slit application followed by closing the slit. The mesocosm experiment is conducted using open dynamic incubation chambers, during which NH_3 emissions are quantified through acid trap washing bottles while N_2O emissions are measured using gas chromatography.

The following **lead questions** shall be answered in this work:

- Do all reduction measures result in lower NH_3 emissions than standard surface application, and does deep incorporation have the greatest effect?
- Is the reduction effect of incorporation greater with increasing clay content in the soil?
- Does urea incorporation promote N_2O emissions in soils with higher moisture content?

Objective 2:

To evaluate the effectiveness of urea incorporation (slit injection) and the use of the rarely investigated urease inhibitor (N-(2-Nitrophenyl) phosphoric triamide, 2-NPT) alone and in combination with nitrification inhibitor (N-[3(5)-methyl-1H-pyrazol-1-yl methyl] acetamide, MPA) for reducing NH_3 losses, taking into account N_2O emissions and pollution swapping.
→ Publication 2

Thus, as before mesocosm experiments are conducted in open dynamic incubation chambers, with NH_3 emissions being quantified through acid trap washing bottles and N_2O emissions by gas chromatography.

The following **lead questions** shall be answered in this work:

- Which mitigation measure shows the greatest NH_3 reduction effect?
- Does the incorporation of urea and the use of urea + urease inhibitor promote N_2O emissions?
- Is nitrification the most important N_2O production process in the mitigation measures investigated?

Objective 3:

Evaluation of the accuracy of two practical and energy independent small-plot measurement methods needed for statistical analysis of mitigation options as a prerequisite for scientifically validated evidence. → Publication 3

Consequently, the Dynamic Chamber Dräger Tube Method and Inverse Dispersion Modeling with Alpha samplers are compared in replicated field plots against a micrometeorological reference method (Integrated Horizontal Flux with Alpha samplers). The same field trials are carried out in six locations over Germany (1x north, 2x central and 2x south-west) using broadcast application of mineral urea fertilizer in winter wheat in 2021 and 2022. Due to three split applications per year this results in a total of 18 field trials. As reference simultaneous micrometeorological measurements on larger round plots are conducted.

The following **lead questions** shall be answered in this work:

- Is Inverse Dispersion Modeling with Alpha samplers a suitable method for quantifying NH_3 emissions on small plots with acceptable accuracy and precision compared to the reference?
- Is Inverse Dispersion Modeling with Alpha sampler superior to the more time-consuming Dräger Tube Method?
- Does the Integrated Horizontal Flux with Alpha sampler reference show good agreement with the cumulative NH_3 emissions obtained with Leuning Sampler Integrated Horizontal Flux/ZINST method?

The following chapter presents the three publications addressing the objectives outlined above.

4 Publications

This chapter presents the three publications addressing the objectives outlined in the previous chapter.

Publication 1

Götze, H., Saul, M., Jiang, Y., Pacholski, A., 2023. Effect of Incorporation Techniques and Soil Properties on NH_3 and N_2O Emissions after Urea Application. *Agronomy* 13, 2632. <https://doi.org/10.3390/agronomy13102632>

Publication 2

Götze, H., Buchen-Tschiskale, C., Eder, L., Pacholski, A., 2025b. Effects of inhibitors and slit incorporation on NH_3 and N_2O emission processes after urea application. *Agric. Ecosyst. Environ.* 378, 109307. <https://doi.org/10.1016/j.agee.2024.109307>

Publication 3

Götze, H., Brokötter, J., Fröhl, J., Kelsch, A., Kukowski, S., Pacholski, A.S., 2025a. Assessment of Different Methods to Determine NH_3 Emissions from Small Field Plots After Fertilization. *Environments* 12, 255. <https://doi.org/10.3390/environments12080255>

4.1 Effect of incorporation techniques and soil properties on NH₃ and N₂O emissions after urea application

Götze, H., Saul, M., Jiang, Y., Pacholski, A., 2023. Effect of Incorporation Techniques and Soil Properties on NH₃ and N₂O Emissions after Urea Application. *Agronomy* 13, 2632.

DOI: <https://doi.org/10.3390/agronomy13102632>

Keywords: Ammonia volatilization; urea; emission mitigation; fertilizer incorporation; climate-controlled chamber; nitrous oxide; nitrogen

Abstract: Ammonia (NH₃) emissions affect the environment, the climate, and human health and originate mainly from agricultural sources like urea fertilizers. Such losses from urea fertilizer can be avoided by different application techniques like incorporation. However, the knowledge of the effect of these techniques on NH₃ emissions is very limited and ambiguous since incorporation can also promote nitrous oxide (N₂O) emissions. Three different principles of fertilizer incorporation methods were compared in three different soils (sandy, loamy, and clayey) at two moisture levels of 70% and 30% water-holding capacity (WHC), shallow mixing at 2 cm, injection with the slit technique at 5 cm, and deep complete incorporation at 5 cm simulating plow incorporation. The laboratory study was conducted with open dynamic incubation chambers where NH₃ emissions were monitored with washing bottles while N₂O emissions were studied with gas chromatographic (GC) measurements. The highest cumulative NH₃ emissions occurred at low soil moisture levels in sandy soil (34% of the N applied). A maximum reduction in emissions by 87% was achieved with slit injection and 82% with deep injection compared to standard surface application. The reduction effect was positively related to increasing clay content. N₂O emissions were delayed and highest from sandy soil. Overall, all urea incorporation techniques showed great potential for mitigating NH₃ emissions on the clayey soil; for sandy and drier soils, only deeper or closed slit injection were consistently effective. However, connected to the surface incorporation at the higher moisture level, a relevant increase in N₂O emissions compared to surface application was observed. Therefore, an increase in N₂O emissions by urea incorporation may rule out specific incorporation techniques for NH₃ emissions reduction from field-applied urea. In agricultural practice, a lower reduction in NH₃ by fertilizer incorporation can be assumed in sandy soils or under dry soil conditions, as well as a more challenging technical implementation.

Article

Effect of Incorporation Techniques and Soil Properties on NH_3 and N_2O Emissions after Urea Application

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Abstract: Ammonia (NH_3) emissions affect the environment, the climate, and human health and originate mainly from agricultural sources like urea fertilizers. Such losses from urea fertilizer can be avoided by different application techniques like incorporation. However, the knowledge of the effect of these techniques on NH_3 emissions is very limited and ambiguous since incorporation can also promote nitrous oxide (N_2O) emissions. Three different principles of fertilizer incorporation methods were compared in three different soils (sandy, loamy, and clayey) at two moisture levels of 70% and 30% water-holding capacity (WHC), shallow mixing at 2 cm, injection with the slit technique at 5 cm, and deep complete incorporation at 5 cm simulating plow incorporation. The laboratory study was conducted with open dynamic incubation chambers where NH_3 emissions were monitored with washing bottles while N_2O emissions were studied with gas chromatographic (GC) measurements. The highest cumulative NH_3 emissions occurred at low soil moisture levels in sandy soil (34% of the N applied). A maximum reduction in emissions by 87% was achieved with slit injection and 82% with deep injection compared to standard surface application. The reduction effect was positively related to increasing clay content. N_2O emissions were delayed and highest from sandy soil. Overall, all urea incorporation techniques showed great potential for mitigating NH_3 emissions on the clayey soil; for sandy and drier soils, only deeper or closed slot injection were consistently effective. However, connected to the surface incorporation at the higher moisture level, a relevant increase in N_2O emissions compared to surface application was observed. Therefore, an increase in N_2O emissions by urea incorporation may rule out specific incorporation techniques for NH_3 emissions reduction from field-applied urea. In agricultural practice, a lower reduction in NH_3 by fertilizer incorporation can be assumed in sandy soils or under dry soil conditions, as well as a more challenging technical implementation.

Keywords: ammonia volatilization; urea; emission mitigation; fertilizer incorporation; climate-controlled chamber; nitrous oxide; nitrogen



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1. Introduction

Ammonia (NH_3) emissions affect the environment and climate. Thus, the deposition of NH_3 in terrestrial or aquatic ecosystems can contribute to environmental degradation through eutrophication [1,2], acidification, and loss of biodiversity [3]. In addition, it is an important precursor in the formation of fine particulate matter (diameter < 2.5 μm , PM 2.5), which has an adverse effect on the environment and human health [4,5]. Critical levels, defined in the Convention on Long-Range Transboundary Air Pollution (CLRTAP) agreement, were exceeded for a significant number of protected ecosystems in Europe [6]. Currently, 95% (equivalent to 629 kt) of German NH_3 emissions stem from agriculture. With the new National Emission Ceilings Directive (NEC Directive) of Europe 2016/2284, Germany has committed itself to reduce national emissions of NH_3 by 5% by 2020 and

by 29% by 2030 compared to 2005, with a linear reduction path between 2020 and 2030. In the field of synthetic nitrogen fertilizers, urea-containing fertilizers are of particular importance as they cause 80% of the NH_3 emissions. For broadcast urea application, the maximum loss of total applied N through volatilization can be up to 64–68% [7,8]. In conclusion, the NH_3 loss results in significant costs, both for reduced nitrogen use efficiency and for the ecosystem and health system restoration defined in the CLRTAP agreement in 2021. Measures to reduce this emission from the application of synthetic nitrogen fertilizers have been taken in the amendment of the German fertilizer ordinance DüV20 [9]. Since spring 2020, urea fertilizer must only be applied in combination with a urease inhibitor (UI) or, alternatively, has to be incorporated within four hours. Overall, efficient fertilization measures that simultaneously decrease environmentally harmful NH_3 emissions and increase plant available nitrogen can help to achieve the goal of halving N waste losses.

Fertilizer incorporation or injection, like slit incorporation, provides an increase in the contact area between soil and fertilizer, accelerating the sorption of ammonium (NH_4^+) to the soil matrix. Therefore, the emission event is strongly influenced by the application technique of the fertilizer. Incorporation and irrigation after or with fertilization can encourage fertilizer transport into the soil and can significantly decrease NH_3 volatilization by 54.7% and 35% [10]. A laboratory study by Du Preez and Burger [11] shows the mitigation effect of different application techniques on NH_3 emissions from various urea- and ammonium-based fertilizers on five soils adjusted to a pH of 8.8. Urea applied with broad distribution showed the highest losses, while incorporation immediately after application and application in bands reduced NH_3 emissions by one and two-thirds, respectively. In a study over four experimental years by Fontoura and Bayer, NH_3 emissions from incorporated urea were 1.1% and 6.6% with urease inhibitor versus 12.5% of applied nitrogen with surface application [12]. Woodley et al. [13] demonstrated a 34% reduction effect with broadcast-incorporated urea fertilizer compared to the broadcast option in 3-year field trials. Injection of urea ammonium nitrate solution (UAN) even provided a 60% [7] to 99% [13] reduction in emissions. Equally important are the mentioned urease inhibitors that significantly reduced NH_3 volatilization on average around 53.7% [10]. In Germany, Kreuter et al. [14] investigated the mitigation effect of double inhibition with nitrification and urease inhibitor and incorporation of urea versus broad distribution at different sites and crops (rapeseed, wheat, barley). Both inhibitor use and placement resulted in significant mitigation of emissions at two of the three sites studied despite low emission levels due to unusual drought conditions in the experimental years. Inhibitor use reduced NH_3 emissions by 70% over the entire growing season, and incorporation reduced NH_3 emissions by approximately 40%.

Additional factors regarding the reduction potential of NH_3 after incorporation are the depth of incorporation, weather conditions, and soil properties (including cation exchange capacity (CEC), pH, water content, and texture) [11,15]. Incorporation of urea to a depth of 3 to 5 cm below the surface in moist soil reduced NH_3 losses by 86% [16]. Physical and chemical soil characteristics affect NH_3 volatilization. Pelster et al. [17] showed a negative relationship between NH_3 volatilization losses, soil clay content, and soil pH buffer capacity. A 90% reduction in NH_3 losses occurred when clay content increased from 10 to 20%. This indicates that NH_4^+ bound to clay does not contribute to rapid NH_3 volatilization. The soil water content has a great influence on both processes: hydrolysis of urea and turnover of NH_4^+ -N in the soil [15] and the urease enzyme activity [18,19]. Nevertheless, studies demonstrate that only qualitative effects but not quantitative effect size [15] are essential for policy.

Drury et al. [7] found “pollution swapping”, where lower NH_3 volatilization losses due to UI caused greater concentrations of soil nitrate (NO_3^-)-N, which then caused increased nitrous oxide (N_2O) emissions. However, the combination of UI with nitrification inhibitors (NI) resulted in N_2O losses comparable to untreated urea while reducing NH_3

volatilization losses. Overall, it is necessary to know the magnitude of the risk that the incorporation of urea can lead to an increase in N_2O under certain conditions.

In agricultural practice, there are three main techniques for soil cultivation. Plowing turns the soil, usually at a depth of 15–25 cm. The rotary tiller and cultivator are used after plowing to loosen the soil, prepare the seedbed, control weeds, and apply fertilizer and compost. These machines do not turn over the soil as plowing does but rather mix soil at a depth of 5–20 cm. Mineral fertilizer can be incorporated by all of these methods to avoid NH_3 losses. However, there is still a lack of experimental data on the incorporation techniques of agricultural practice in interaction with varying soil conditions and their effect on NH_3 emissions. Regarding N_2O emissions, no significant differences were found between different incorporation depths [20], but there is still a lack of understanding. Altogether, there is a high demand for studies that quantify trace gas emissions after these different incorporation techniques and quantitatively evaluate the mitigation measures.

The presented literature survey highlighted many existing studies on the effects of fertilizer incorporation on NH_3 emissions. Since the incorporation of synthetic nitrogen fertilizers is assumed to be a very efficient measure, the state of knowledge and the published data for the evaluation of the different incorporation techniques site-specifically are insufficient for a reliable estimation of the emission level. However, there is a lack of consistent information on the variation in these variables depending on specific incorporation measures under the same soil conditions. This study shall serve as a novel approach for generating deeper knowledge under controlled conditions and an orthogonal study design for an optimized use of synthetic nitrogen fertilizers.

Therefore, a laboratory experiment was conducted to analyze and evaluate the effect of urea incorporation techniques on NH_3 emission reduction in three different soils and at two moisture levels. Three methods were mimicked and investigated: surface incorporation by cultivating, deep incorporation by plowing, and the slit application followed by closing the slit. The main objective was the quantification of the effects on NH_3 emissions reductions, considering pollution swapping by N_2O emissions after incorporation. We hypothesized that (a) all mitigation measures have lower NH_3 emissions than the standard surface broadcast application of urea, with deep incorporation showing the greatest effect, and (b) the higher the clay content and thus the cation exchange capacity of the soil, the greater this mitigation effect. Furthermore, we hypothesized that (c) a higher soil moisture content increases the rate and the absolute NH_3 loss, and (d) in contrast, incorporation of urea fertilizer can also promote N_2O emissions in soils with higher moisture levels.

2. Materials and Methods

Two incubation studies were carried out in the microcosm laboratory at Thünen Institute of Climate–Smart Agriculture from November 2022 to January 2023 to measure NH_3 and N_2O emission after urea application with the varying application techniques: one setup for NH_3 and one for N_2O measurements. Three variables, their influence, and interactions were studied: application technique, soil texture, and soil moisture. Two approaches were chosen since air exchange rates need to be adjusted for the measurement of the different gas species.

2.1. Experimental Design and Tested Treatments

In both incubation experiments, different application techniques were compared with a dosage of 174 kg N ha^{-1} for NH_3 quantification and 260 kg N ha^{-1} for N_2O quantification from urea fertilizer. For the second test, a higher fertilizer amount was selected in order to achieve a sufficiently high measuring signal at a constant flow rate in the chambers. In addition to an unfertilized control, four techniques were investigated: standard surface application, surface incorporation by mixing with soil at 2 cm depth, slit injection, and deep incorporation (fertilizer completely covered by 5 cm soil layer). In order to simulate closed slot injection of fertilizer, a DEEPOT 32.1 deep deposit fertilizer machine (Rauch, Sinzheim, Germany) was used, placing urea fertilizer in a 5 cm deep slit produced with a

plastic spatula. Afterward, the fertilizer was covered with soil and compacted by a cork rolled over the soil surface (Figure 1c). The same number and size of granules were applied in each replicate container. The incorporation techniques were recorded in a standard protocol to ensure uniform performance. Nevertheless, small differences remain that can be attributed to different people. Three soils strongly differing in soil texture (Table 1) were selected to study NH_3 emissions under two different soil moisture levels, 70% (F1) and 30% (F2) water-holding capacity (WHC). The first soil is SI2 soil with 68.16% sand. The loamy soil has a silt proportion of 69.44% (Ut3), and the clayey soil (Lu) has a clay content of 21.51% and, therefore, has the highest CEC of 14.31%.

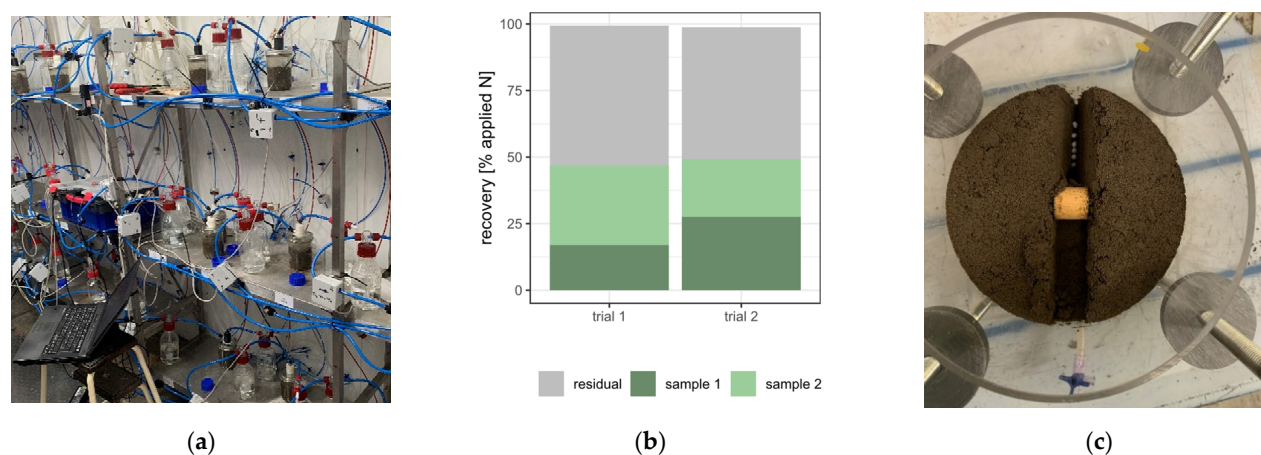


Figure 1. (a) Setup of flow chambers for NH_3 quantification, (b) recovery of the setup, and (c) application of urea with slit injection technique.

The soil for both experiments was sampled in 0–20 cm depth (Ap horizon) of three different agricultural fields in Germany 2022: Meine (sandy loam), Sickte (silty loam), and Dürnast (clay loam). These soils originated from field trial sites of the research project network and were selected for the broadest possible diversity. In preparation for both experiments, the soil was sieved (<2 mm). Furthermore, the water content was determined before each experiment by drying the soil at 105 °C until its weight remained constant. The mass of soil packed into the respective vessels was calculated depending on the individual water content and soil type. The amount of water required to achieve the soil moisture content was added to the soil by gradual mixing (Equation (1)) calculated with θ_1 the water-holding capacity [Vol.%]. A guideline value from the manual of soil mapping [21] for soil type SI3 (27 Vol.%) with an addition of 5 Vol.% for medium-humic soils was used to estimate the water-holding capacity (θ_1). This results in 22.4 Vol.% for 70% moisture content and 9.6 Vol.% for 30%. In addition, the storage density (ρ_b) was determined gravimetrically, and after drying at 105 °C, the residual water content (θ_0) was determined.

$$\Delta\theta = (\theta_1 - \theta_0) \times (\rho_{\text{water}} / \rho_b) \quad (1)$$

The column was compacted with a punch to reach the typical field bulk density (1.4 g cm⁻³). This is considered a typical bulk density for sandy soils. However, the topsoil was disturbed by incorporation, so this has no influence, and the same bulk density was used for all soils. To prevent nitrification, other biomineralization processes, and evaporation of water, the soil was continuously covered and stored at 4 °C after sampling.

Table 1. Three different soils used in the experiments—locations, composition, total carbon (TN), total nitrogen (TN), and pH.

Soil	Region of Location	Coordinates	Sand	Silt	Clay	Texture	TC	TN	CEC	pH (CaCl ₂)
		North/East	[mass%]			[21]	[mass%]		[cmol kg ⁻¹]	[mol L ⁻¹]
1 Sandy	Central Germany Meine	52.387309/10.562801	68.61	24.24	7.15	Sl2	1.39	0.11	7.53	6.59
2 Loamy	Central Germany Sickte	52.111943/10.411358	17.61	69.44	12.96	Ut3	1.44	0.13	12.51	6.02
3 Clayey	South Germany Dürmast	48.407058/11.694203	13.75	64.74	21.51	Lu	1.26	0.13	14.31	6.75

2.2. Flow Chambers for NH₃ Loss Quantification

The experiments were conducted with flow chambers in a temperature-controlled chamber environment to quantify the NH₃ losses from N fertilizers (Figure S1). Frequent acid trap sampling also enabled comparisons of different incorporation techniques. The chamber airflow ran constantly between sampling periods (to simulate windy conditions) and was humidified with washing bottles. The temperature was set to 20 °C, providing supportive conditions for NH₃ volatilization.

Soils with and without urea application were incubated in a climatic chamber (HVST 705 EP, Roller, Gerlingen, Germany) at 20 °C. A system was designed to quantify NH₃ losses from the different treatments. The design of the experiment was based on findings from previous studies on NH₃ volatilization [22,23]. The basic idea is that the head space of an incubation container is continuously flushed with air, and the resulting NH₃ emissions are absorbed in an acid solution and subsequently analyzed.

The dimensions of the round incubation jars were 12 cm in height with a diameter of 7.5 cm (Figure 1a). A deflector plate was attached to the jar lid, creating a uniform laminar flow while ensuring sweeping of the entire soil surface [24]. The volume of the soil column was 300 mL with 150 mL headspace volume and the deflector protruding 3.5 cm into the jar. One gas wash bottle (114452972, Rettberg GmbH, Göttingen, Germany) was filled with water to produce almost complete water saturation of the incoming air stream and one behind the vessel. The exhaust air passed through another wash bottle filled with a sulfuric acid solution (100 mL, 0.005 M H₂SO₄), absorbing emitted NH₃. A fritted glass diffuser was used to obtain complete absorption of NH₃ into the solution.

The constant flow of humidified air was led over the soil column surface. The required airflow was supplied by an air compressor with a water separator and controlled by pressure regulators. The airflow of each incubation vessel was monitored and controlled by flow sensors (IDT FS200, Renesas, Tokyo, Japan). The flow rate was set to 8 headspace volumes min⁻¹. The tightness of all incubation tubes was checked using pressure difference measurement. Preparatory experiments proved a second downstream acid trap and repetitive daily trap changing unnecessary, as the capacities of the 100 mL of H₂SO₄ were sufficient to capture emissions completely. Furthermore, it was found that emissions after urea application ceased after two weeks, as they showed no difference from emissions from untreated soil.

The tightness and NH₃ recovery efficiency of the system was evaluated in a separate trial with emissions from a 9.5 pH-controlled NH₄⁺ bicarbonate solution (200 ppm, 5.5456 mM (NH₄)₂SO₄) in the same flow chamber facility (Figure 1b). Emitted NH₃ was captured with acid trap sampling in two separate trials subsequently. Sampled NH₃ and residual NH₄⁺ in solution added up to a nitrogen recovery of 99% within the measurement uncertainty of the NH₄⁺ concentration measurement for both trials.

2.3. NH₃ Analysis Flux Calculation

The NH₄⁺ concentration in sulfuric acid was measured using an NH₃ selective electrode (Thermo Scientific Orion Versa Star Pro Electrochemistry Meters, Waltham, MA, USA, range (ISE) 0.0001 to 19,990 ppm, accuracy (ISE) ±0.2 mV or ±0.05% of reading). Samples were stored at 4 °C until measurement.

For the calculation of NH_3 loss, the daily concentrations (C_{NH_3}) in the acid solution were multiplied by the volume of acid (V_{acid}) and summed up to the total amount of NH_3 ($M_{\text{NH}_3 \text{ cum}}$) (Equation (2)).

$$M_{\text{NH}_3 \text{ cum}} = \sum_{i=1}^{ti} C_{\text{NH}_3} \times V_{\text{acid}} \quad (2)$$

The emissions (kg N ha^{-1}) were determined by multiplying the mass loss (M) with the fertilized surface area (A) in the flask (Equation (3)).

$$F = M \times A \quad (3)$$

2.4. Flow Chambers for N_2O Loss Quantification

The microcosm system allows for automated incubation of soil columns (microcosms) under controlled conditions in order to study the formation of greenhouse gases in agricultural soils [25,26]. The used cylindrical chambers were 18 cm high and 14.3 cm in diameter. The headspace volume was 1230 mL, and the soil volume was 1600 mL. The additional amount of water needed to achieve the target soil moisture content was determined using Equation (1). The calculated mass of soil, depending on the water content and soil type, was filled into the chambers and compacted once to a final bulk density of 1.4 g cm^{-3} . For statistical analysis of the factors incorporation technique and soil moisture, only sandy and loamy soil was used since, for capacity reasons, the clayey soil was only investigated at one moisture level.

2.5. N_2O Flux Calculations

Artificial air (21% O_2 , 79% N_2) was pumped at a flow rate of approximately 15 mL min^{-1} through a chamber containing distilled water with a bubbler into the chambers containing the soil and fertilizer treatments in the chamber at 20°C . Every incubation vessel was measured every 6 h. Blanks for measuring background concentrations of the gas mixture and five standards for calibrations were regularly integrated into the measurement sequence. Gas samples and standards were determined using a gas chromatograph (GC-2014, SHIMADZU, Kyoto, Japan) equipped with an electron capture detector. The analytical precision was determined by repeated measurements of standards (0.33, 0.55, 2.01, 6.94, 40.4, and 130 ppm N_2O). For flux calculations, the mass concentrations (C) were calculated in Equation (5) via the mass volume (V_m) according to the ideal gas law (Equation (4)) from the mole mass in g mol^{-1} (M) of CO_2 and N_2O provided from the GC measurement.

$$V_m = \frac{R \times T}{p} \quad (4)$$

The temperature in the microcosm system was 20°C (288.15 K), the pressure was 101.325 kPa (22.41396954 L/mol), and the general gas constant was $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

$$C = \frac{(c - c_{\text{blank}}) \times M}{V_m} \quad (5)$$

M is the molar mass (N_2O 44 g mol^{-1} , CO_2 44 g mol^{-1}), and T is the temperature (K). Mass flow (F), therefore, was calculated by C and the flow rate (Q) provided from the flow meter (Equation (6)).

$$F = \frac{(C \times Q)}{A} \quad (6)$$

A denotes the soil surface of the column in m^2 , and Q is the flow rate in mL min^{-1} . Cumulated fluxes were obtained by integrating the emissions from the whole observation period after linear interpolation. Treatments were evaluated based on their cumulated emissions.

2.6. Soil Analysis

For determination of mineral nitrogen content (NO_3^- and NH_4^+), all soil samples were stored at -20°C until preparation. Mineral nitrogen sample preparation and extraction were performed for all samples according to German laboratory standards [27]. Water content (24 h at 105°C) and pH were determined for each sample. An amount of 50 g of homogenized soil was extracted with 200 mL of 0.0125 M CaCl_2 (1:4) and shaken in an overhead shaker for one hour. The mixture was then filtered through nitrogen-free filter paper (MN 6141/4) and stored at -20°C until analysis by a continuous flow analyzer.

2.7. Soil Recovery

Soil samples were analyzed at the beginning of the experiment and after the incubation period to evaluate recovery (r). For the calculation, the final $N_{\min}$ value (mineral N- NH_4 and NO_3) was divided by the initial value, which consisted of the $N_{\min}$ content at the beginning of the experiment and the fertilized N amount (Equation (7)). The differences that occurred were based, among other things (e.g., biological processes), on the loss due to NH_3 emissions.

$$r = \frac{N_{\min, \text{end}}}{(N_{\min, \text{start}} + N_{\text{fertilizer}})} \quad (7)$$

2.8. Data and Statistics

All the statistical analyses were carried out in R Studio (R Studio, Version 2023.6.0.421, R Studio Inc., Boston, MA, USA) with the free statistical software R 4.2.2 (R Core Team, 2022). All graphical representations were created using the appropriate R packages, including [ggplot2]. A generalized linear model approach was used to test for the effects of treatment soil texture and moisture on cumulative NH_3 -N losses using the analysis of variance (ANOVA) analysis. The factors influencing cumulative NH_3 emissions analyzed were fertilizer treatment, soil texture, and soil moisture level. Differences between fertilizer treatments were determined using the Sidak post hoc test at the 95% confidence level. The residual distribution was tested, and the Shapiro–Wilk test for normal distribution was performed. Compact letter displays [multcomp, emmeans] were used to report the results of all pairwise comparisons among treatment means. Means not sharing any letter are significantly different by the Sidak test at the 5% level of significance.

3. Results

3.1. NH_3 Emissions

Over all soil textures and moisture levels, all three investigated factors, incorporation system, soil texture, and soil moisture, had a highly significant main effect on cumulative NH_3 losses (Table 2). There were also interactions between the factors of application and soil texture, as well as application, soil texture, and moisture. Lower significant effects were determined for the interactions between application and moisture as well as soil texture and moisture.

Table 2. Results of ANOVA analysis with the variables of application, soil texture, and moisture on NH_3 losses. Residual standard error: 1.28. Signif. codes: * for $p < 0.05$, *** for $p < 0.001$.

	Degrees of Freedom	Sum Square	Mean Square	F-Value	Pr(>F)	
Application	3	829.7	276.56	167.846	2×10^{-16}	***
Soil texture	2	421.8	206.41	125.271	$<2 \times 10^{-16}$	***
Moisture	1	64.7	64.73	39.286	9.76×10^{-8}	***
Application-soil texture	6	69.5	11.58	7.030	2.08×10^{-5}	***
Application-moisture	3	17.1	5.69	3.450	0.0237	*
Soil texture-moisture	2	12.5	6.27	3.807	0.0292	*
Application-soil texture-moisture	6	113.2	18.86	11.445	6.58×10^{-8}	***
Residuals	48	79.1	1.65			

As an example, the maximum cumulative NH_3 loss from the sandy soil detected was 54 and 59 kg N ha^{-1} at soil moistures of 70 and 30%, respectively (Figure 2). A different conversion kinetic for the two different soil moisture levels could be determined, with a slower increase in emissions at the beginning at 30% soil moisture.

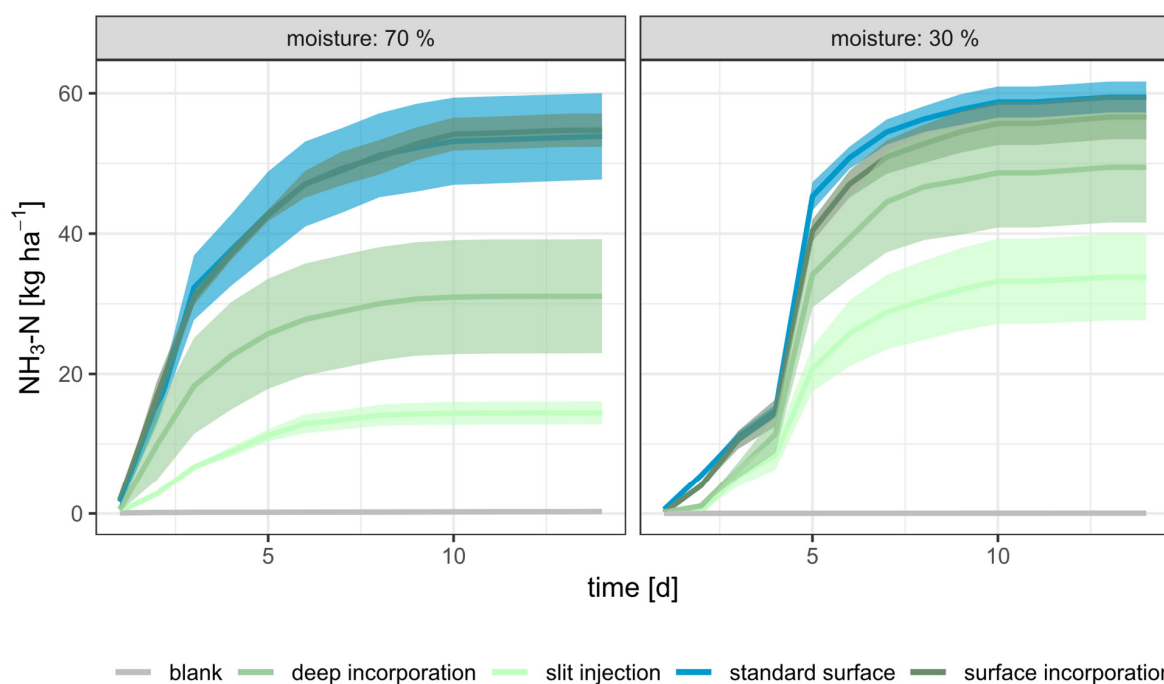


Figure 2. Cumulative NH_3 -N losses from urea applied to the sandy soil of the investigated soils from different application techniques, including standard surface application, surface incorporation, deep incorporation, and slit injection, from sandy soil at two moisture levels (70 and 30 % WHC); lines depict mean values ($n = 3$) while shaded bands indicate standard deviation.

The sandy soil displayed the highest sand content, with 69%. Urea applied with surface incorporation showed no difference from the standard surface application. Slit injection and deep incorporation showed lower emissions than standard surface application, but the mitigation effect was much greater at a soil moisture of 70%. There, the minimum losses were 31 and 14 kg N ha^{-1} for deep incorporation and slit injection. Differences were also observed in the kinetics of NH_3 formation: The higher soil moisture led to faster volatilization, but 14 days after the start of the experiment, the same final level was reached. Across the three soils studied, urea standard surface application on sandy soil had 25% higher emissions than the same treatment on the other two soil textures. Urea standard surface application and surface incorporation had significantly higher emissions than slit injection and deep incorporation. Surface incorporation had no significant mitigation effect for sandy and loamy soil at either soil moisture compared to standard surface application. With slit injection and deep incorporation, mitigation effects were obtained. Slit injection has the lowest losses down to less than 5%, and in six of the eight treatments, less than 10% loss of the applied N amount (Figure 3). Slit injection performed significantly differently from standard surface application at all moisture levels and all soil textures. This was the case for deep incorporation as well, except for the sandy soil at 70% soil moisture. Surface incorporation differed significantly only for clayey soil.

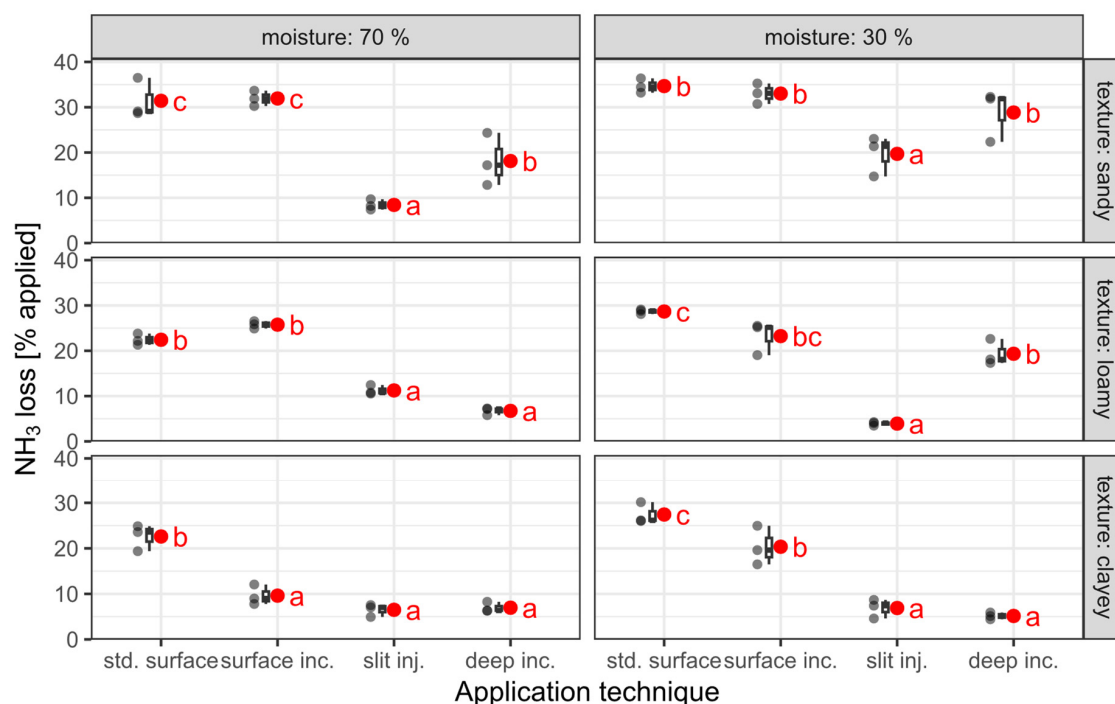


Figure 3. NH_3 losses [% of N applied] from urea fertilizer applied with standard (std.) surface, surface incorporation (inc.), slit injection (inj.), and deep incorporation (inc.) technique on three different soils (loamy, sandy, clayey) at two different moisture levels (70 and 30% WHC); replicates and boxplots are in black, and red indicates the mean values and compact letter display. (Means not sharing any letter are significantly different by the Sidak test at the 5% level of significance with 95% confidence).

At 70% soil moisture, NH_3 mitigation potentials were significantly higher than for the drier soil. At 70% soil moisture, 43% mitigation was achieved with deep incorporation and 74% with slit injection (Figure 4). The slit technique had the greatest mitigation potential compared to deep incorporation at both soil moisture levels. The fertilized loamy soils showed lower NH_3 emissions. Similarly, no significant reduction in losses could be achieved with surface incorporation. Both variants show losses in the range of 10–13%. At a soil moisture of 70%, emissions can be reduced by 50% with slit injection and 71% with deep incorporation. At a soil moisture of 30%, the maximum reduction potential was 87% with slit injection. The clayey soil showed the lowest losses and the greatest reduction effects after incorporation. Surface incorporation reduced losses from 8 to 12% on the moist variant. Slit injection and deep incorporation showed a significant effect, with losses ranging from 5 to 8%. This corresponds to a reduction in emissions compared to the standard surface application of urea with 72–82%. Overall, higher emissions were observed on sandier soil. Lower soil moisture resulted in higher emissions but with a much smaller influence compared to soil texture.

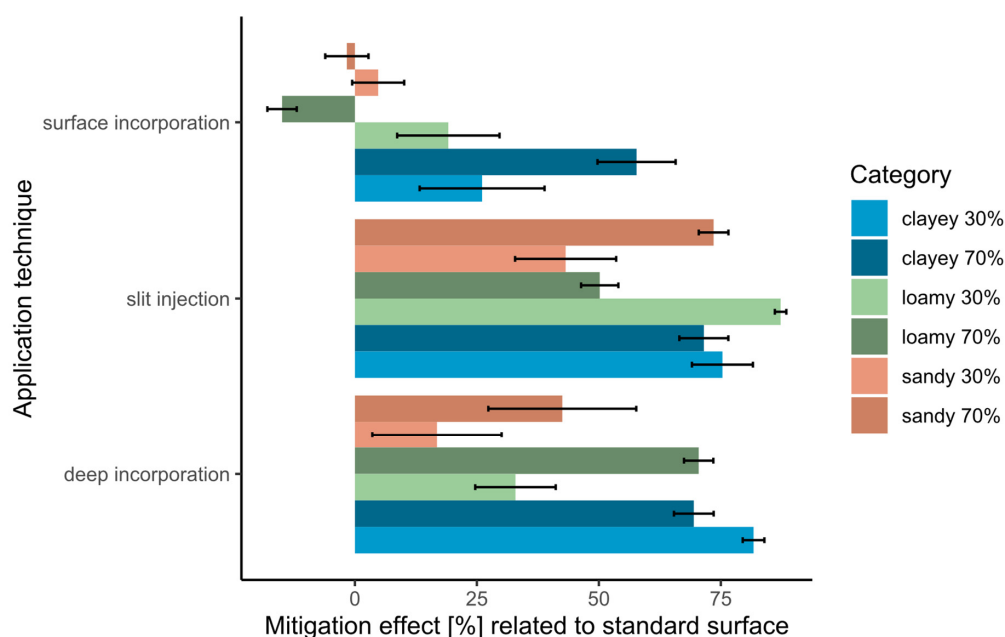


Figure 4. NH₃ mitigation effect [%] related to the cumulative loss of standard surface treatment with losses of surface incorporation, slit injection, and deep incorporation technique on three different soils (loamy, sandy, clayey) at two different moisture levels (70 and 30% WHC) each.

3.2. N Recovery NH₃ Experiment

The recovery relates the values measured in the soil after incubation to the N_{min} values at the experimental start and the fertilized N amount. The investigated factors of application technique and soil texture had a highly significant effect on the recovered fertilizer N in the soil (Table 3). Low significant interactions were determined between application and moisture. Overall, the highest recovery was observed under the application technique of slit injection (Figure 5).

Table 3. Results of ANOVA analysis with the variables of application, soil texture, and moisture on recovery. Residual standard error: 15.84. Signif. codes: *** for $p < 0.001$, . for $p < 0.1$.

	Degrees of Freedom	Sum Square	Mean Square	F-Value	Pr(>F)	
Application	3	5145	1715	6.833	0.0006	***
Soil texture	2	7478	3739	14.898	9.27×10^{-6}	***
Moisture	1	282	282	1.122	0.2948	
Application-soil texture	6	1503	250	0.998	0.4377	
Application-moisture	3	1807	602	2.4	0.0794	.
Soil texture-moisture	2	14,994	7497	29.87	3.74×10^{-9}	***
Application-soil texture-moisture	6	1915	319	1.271	0.2883	
Residuals	48	12,047	251			

There were also interactions between the variables of soil texture and moisture (Table 3). The highest recovery occurred for the clayey soil at 70% soil moisture (Figure S2). For the clayey soil, the recovery was higher at higher soil moisture (16–46%); for the sandy soil, this relation was reversed (Figure 5).

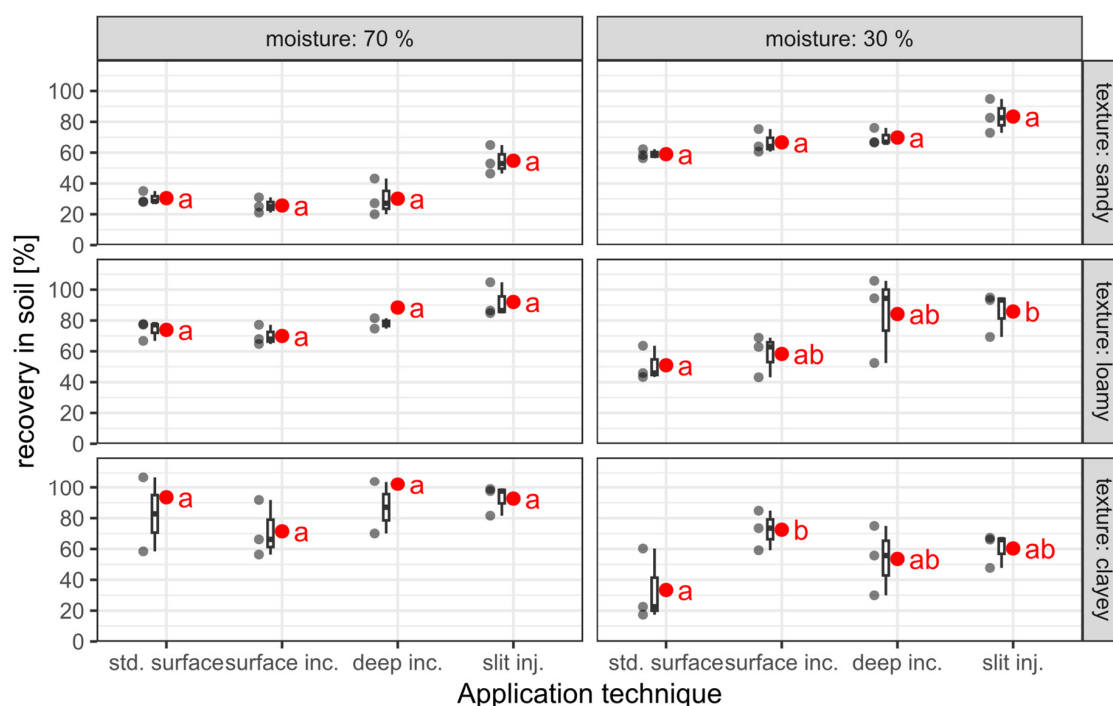


Figure 5. Recovery of mineral N content in three different soils (sandy, loamy, clayey) at two different moisture levels (70 and 30% WHC) with standard (std.) surface, surface incorporation (inc.), slit injection (inj.), and deep incorporation (inc.) technique after incubation for two weeks with start NO_3 and total N from fertilizer and $N_{\min}$ after two weeks; replicates and boxplots are in black, and red indicates the mean values and compact letter display. (Means not sharing any letter are significantly different by the Sidak test at the 5% level of significance with 95% confidence).

3.3. N_2O Emissions

The level of N_2O emissions depends primarily on soil texture (Figure 6), while the application technique and soil moisture had a significant effect too (Table 4). There were also interactions between soil texture and moisture variables. Less significant interactions were determined between application and moisture, as well as application and soil texture. In addition, incorporation was technically almost unfeasible in clayey soils at low soil moisture levels.

Table 4. Results of ANOVA analysis with the variables of application, soil texture, and moisture on N_2O losses. Residual standard error: 0.22. Signif. codes: * for $p < 0.05$, ** for $p < 0.01$, *** for $p < 0.001$.

	Degrees of Freedom	Sum Square	Mean Square	F-Value	Pr(>F)	
Application	1	2.91	2.91	61.89	0.0158	*
Soil texture	1	157.32	157.32	3351.30	0.0003	***
Moisture	1	27.93	27.93	594.95	0.0017	**
Application-soil_texture	1	1.24	1.24	26.38	0.0359	*
Application-moisture	1	4.12	4.12	87.76	0.0112	*
Soil texture-moisture	1	13.42	13.42	285.90	0.0035	**
Application-soil_texture-moisture	1	1.23	1.23	26.19	0.0361	*
Residuals	2	0.09	0.05			

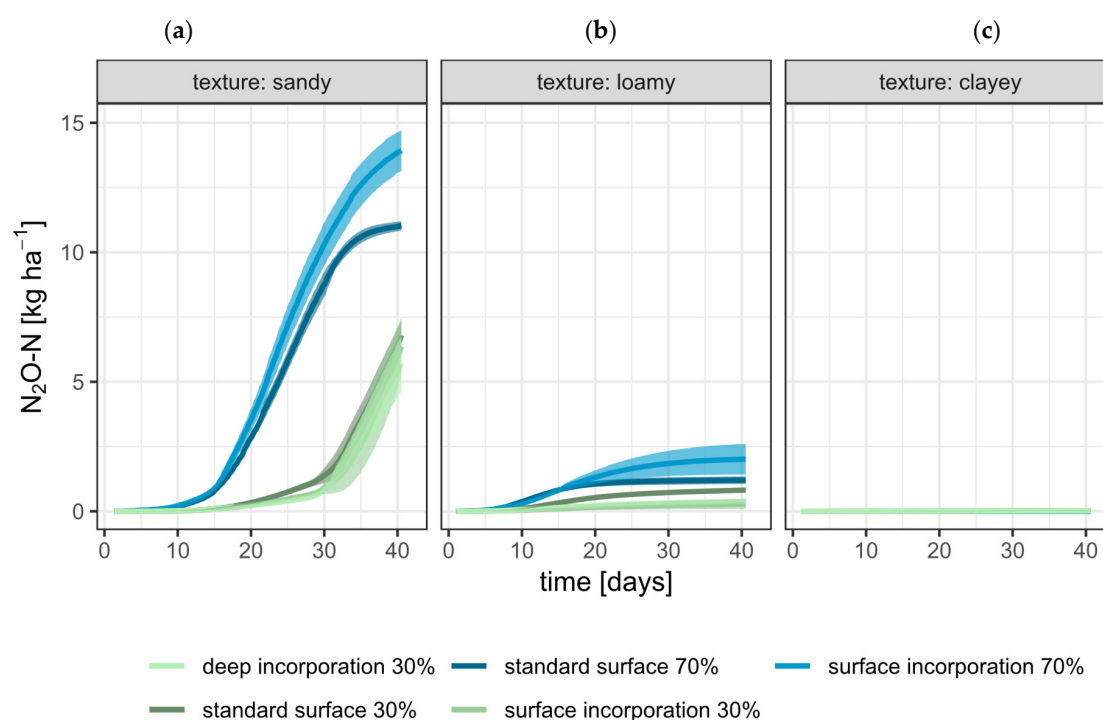


Figure 6. Cumulative losses of $\text{N}_2\text{O-N}$ from urea applied with different application techniques, including standard surface, surface incorporation, and deep incorporation, on sandy (a), loamy (b), and clayey soil (c) at two moisture levels of 70% and 30% WHC; lines depict mean values ($n = 3$) while shaded bands indicate standard deviation.

Nitrous oxide emissions varied significantly depending on soil texture. The highest losses were found in the treatments on sandy soil. Thus, higher soil moisture resulted in earlier N_2O loss (Figure S3), but emissions in the variants with 30% soil moisture increased to a similar level with a time lag. Minor differences occurred between the incorporation treatments (5.81 to 6.97 kgN ha^{-1}), while at 70% soil moisture, surface incorporation had higher emissions compared to standard surface application, 13.97 and 11.04 kgN ha^{-1} . For the sandy soil treatments, there was a lag time in the increase in N_2O emissions at 30% soil moisture, but losses were significantly lower compared to 70% soil moisture. The highest loss was 2.01 kgN ha^{-1} at surface incorporation and 1.20 kgN ha^{-1} at standard surface application. In contrast, at the lower soil moisture, the standard surface application had the highest emissions of 0.82, while the surface and deep incorporation variants were 0.28 and 0.38 kgN ha^{-1} , respectively. By far, the lowest losses of less than 0.03 kgN ha^{-1} occurred in the treatments on clayey soil.

4. Discussion

The data on NH_3 emissions in the literature shows a high variability due to different experimental conditions. Variables such as the type of urea incorporation, soil properties (e.g., pH, pH buffer capacity, CEC, water content), and climatic conditions vary over different experiments, which is why the impact of these effects cannot be quantified. Overall, observed emission rates (3–36% NH_3 and 0.1–5% N_2O of N applied) were within the range of emissions reported from field studies.

4.1. Effect of Application Technique on NH_3

The results show that incorporation depth and intensity had a significant impact on NH_3 emissions and that the reduction potential, depending on the type of incorporation, can be high. According to Rochette et al. [28], for each centimeter of incorporation depth,

NH₃ emissions decreased by 12.5%. They showed that incorporation depth explains 75% of the overall variability between different studies in the literature.

In this study, mitigation by closed slit injection was highest since the furrow was sealed by rolling over, reducing macropores. Across all soil textures and moisture contents, mitigation potential ranged from 43 to 87% emission reduction compared to standard surface application in our study. The field experiments of Drury et al. [7] showed that injection of liquid UAN reduced NH₃ volatilization by 60% compared to broadcast urea.

In this study, deep incorporation also showed great potential but with much higher variability. While on the clayey soil, a reduction of 82% was achieved by deep incorporation, the reduction potential on the other textured soil and at low soil moisture was significantly lower by 17 and 32% for sandy and loamy soils, respectively.

Surface incorporation led to the lowest mitigation. Clayey soil, especially for the high moisture level, and the other two textured soils showed a very low reduction potential. This led to a non-significant increase in emissions compared to surface broadcast application at higher soil moisture, with 2 to 15% higher emissions on the sandy and loamy soils compared to the standard surface application. Overall, the first hypothesis (a) can only be partially confirmed. The mitigation measures showed lower NH₃ emissions than the standard surface application of urea, except for surface incorporation in some cases. Moreover, the strongest reduction was achieved with slit injection instead of deep incorporation.

4.2. Effect of Soil Texture

The sandy soil is a brown earth podsol composed of nutrient-poor glacial sands with low WHC. Due to higher sand content, these soils have a lower potential to retain NH₄⁺ ions, as sand does not have many functional groups that can adsorb NH₄⁺ ions [29]. The resulting increased risk of NH₃ loss was also clearly reflected in the present experimental results; the sandy soil showed the highest losses with 29–36% loss of the applied N with surface-applied urea. The coarse structure and porosity of the soil also complicate the implementation of incorporation. In contrast to sand, clay and silt particles have a much larger surface area and more functional groups with a greater ability to adsorb NH₄⁺ ions, and NH₃ emission rates tended to be lower in fine-textured soils [30]. This relationship was equally clear from these experiments.

The loamy soil consists of deep-humic Chernosem parabraunerde consisting of loess or loess loam, and the clay soil was a brown earth podsol from base-poor sandstones and quartzites. With increasing clay content and CEC, emissions of NH₃ also decrease [31]. Losses with standard surface application were 19–30% of the applied N on the loamy and clayey soils. According to Pelster [17], increasing the clay content from 10 to 20% led to a 90% reduction in NH₃ emissions for urea incorporated with slit injection in 5 cm depth since NH₄⁺ bound to cation exchange sites does not contribute to rapid NH₃ volatilization. Such a strong reduction in the emissions could not be proven with the used clayey soil, which, with a clay content of 21.5%, had an even 14.3% higher proportion than the sandy soil. The losses of surface applied urea were 19–25% from the clayey soil with a soil moisture content of 70% and 26–30% loss of the applied N amount at 30% soil moisture content. Zhenghu et al. [32] also showed that clay content was negatively correlated with NH₃ volatilization, but cation exchange capacity was correlated even more. Overall, it should be emphasized that in clayey soil, all three incorporation methods showed a significant reduction in NH₃ emissions compared to loamy and sandy soil. Surface incorporation showed a significant mitigation compared to the standard surface application in clayey soil only. Deep incorporation and injection showed losses of only 6% of N applied. In addition, there were no N₂O emissions that differed from the control. Altogether, hypothesis (b) on the stronger mitigation effect of higher clay content was supported by the data.

4.3. Effect of Soil Moisture

The soil water content has a great influence on the processes of urea hydrolysis and turnover of NH₄⁺-N in the soil. Very dry soils can inhibit urea hydrolysis, while increased

water contents can increase the rate [15]. Moreover, due to the hygroscopic of urea granules, NH_3 emissions can be higher from urea also on dry soil at high air humidity [15].

In all investigated soil textures, a faster conversion of urea could be observed at a higher soil moisture, especially in sandy soil (Figure 2). At 30% soil moisture, a lag phase occurs before the exponential phase. In addition, the exponential phase is much more extended before reaching the stationary phase with almost the same final loss compared to the standard surface applied urea, 25 and 27 mg at 70 and 30%, respectively. Literature reports that the risk of volatilization is increased after surface application of urea at higher soil moisture [33], but recent studies have shown that at low water contents, emissions can be higher too when a higher temperature predominates [34]. In addition, a study by Engel et al. [19] found that losses were greatest when surface application of urea at high water content was followed by a period of slow drying with little or no precipitation. This is also consistent with Forrestal et al. [35], who found that the main factor for maximum volatilization of urea was initial soil moisture and low-rainfall events. This is not consistent with the observations made here. The highest losses were measured on soils with the lower moisture level.

In the end, the humidity of the air was decisive as it caused the granules to dissolve and thus emit NH_3 . After sufficient test duration, the same loss level is reached. Future studies should investigate how the results differ after one week with dry soil and dry airflow. Hypothesis (c), stating that higher soil moisture content increases the velocity, can be verified, but the absolute NH_3 losses are not affected as long as humidified air is used. In the field, the current weather conditions affect NH_3 emission rates. Air temperature increases the NH_3 concentration in solution, while precipitation has a diluting effect and promotes rapid infiltration of the fertilizer into the porous soil medium [36].

4.4. N Recovery

The recovery was highest in loamy and clayey soils under soil moisture of 70%, averaging 81.1 and 90.0% of start N_{min} (Figure 5). This is also reflected in the NH_3 losses since the highest emissions occurred in sandy soil. Due to the high clay content of the clayey soil of 21.51 mass%, more NH_4^+ was probably bound to the adsorbing surfaces and, therefore, unavailable for microorganisms [17]. Nitrification can be inhibited by low moisture content. In terms of incorporation, the recovery rates matched the observed emissions; the highest recovery for slit injection was 78.2%, and the lowest for standard surface and similarly low for surface incorporation (56.9 and 60.8%). In clayey soils, the recovery was lower at 30% soil moisture, which is reflected in higher NH_3 losses. In sandy soils, a reverse relation was observed with respect to recovery. However, the NH_3 losses in sandy soil were higher at 30% than at 70%. This lower recovery at high soil moisture in sandy soil can be attributed to strong denitrification resulting in high N_2O losses, which were higher at 70% moisture content than at 30% (Figure 6). At the higher soil moisture level, almost no NO_3^- was recovered, hypothetically indicating a strong denitrification process (Figure S2). Overall, the gaps in the recovery can be explained well by the measured emissions.

4.5. Pollution Swapping by Increased N_2O Emissions Due to Urea Incorporation

Primarily, the soil texture had a great influence on the N_2O losses. While the emissions from clayey soil at the low water level were in the range of the background signal, losses of up to 14 kg N ha^{-1} were detected from the sandy soil. Second, N_2O losses were also increased by higher soil moisture in the sandy and loamy soils, as observed in other studies [34,37]. In the sandy soil, this effect was very pronounced, and in addition, the N_2O losses occurred much earlier than at the drier level. Under consideration of practical farming, this could be problematic, especially in humid spring conditions. Generally, seasonal variations in precipitation have a major influence on the occurrence and magnitude of the mitigation effect due to incorporation.

Significant differences in N_2O emissions due to incorporation were only noticeable at the higher moisture level. Surface incorporation increased emissions of N_2O by 27% in sandy soil and 67% in loamy soil. However, absolute N_2O losses from the sandy soil were much higher than those from the loamy soil and were emitted in addition to the likewise high NH_3 emissions. Overall, N_2O emissions began to increase only after 10 days.

The processes underlying the observed N_2O emission pattern were not measured directly by, e.g., isotopic labeling. However, based on the mineral N recovery at the end of the experiment, it can be speculated that—in contrast to the sandy soil with the very high N_2O emissions—emissions from the loamy soil mainly stemmed from the nitrification process, indicated by a high share of a nitrate N in the soils. In contrast, almost no fertilizer-derived nitrate was observed in the sandy soil at the end of the experimentation. This may indicate a strong denitrification activity on that soil, in particular under high soil moisture conditions [38,39].

In particular, the very low N_2O emissions in the clayey soil at both soil moisture levels call for an explanation. Nitrification may have been hampered under low moisture conditions indicated by very low nitrate concentrations (Figure S2), resulting in a source limitation for N_2O emissions by both nitrification and denitrification. This was not the case for the higher soil moisture content where increased fertilizer-derived nitrate concentration but no increase in fertilizer-derived N_2O emissions were observed, calling for other explanatory processes [39]. However, other processes explaining unaccounted fertilizer N, such as ammonium fixation in clay particles, microbial uptake, or changed $\text{N}_2\text{O}/(\text{N}_2\text{O} + \text{N}_2)$ product ratios [40], are potential explanatory variables that are not accounted for by the study data.

Under the conditions prevailing in this study, the emission process in the sandy soil was not yet finalized. It must be emphasized that, under practical conditions, this scenario would be unrealistic since nutrient uptake by plants and rainfall could have already occurred and changed the emission process. Moreover, the effect of incorporation occurs rather late, which can be held against high pollution swapping in practice and needs to be confirmed by field tests.

4.6. Transfer to Agricultural Practice

This study was conducted under controlled environmental conditions and, therefore, does not account for differences in weather, such as temperature, time of day, or season. In the experiments of Wenzhu et al., low soil moisture and higher temperatures led to the highest NH_3 emissions [41]. However, the nitrogen application rate had a greater effect on NH_3 emissions compared with temperature, moisture, and their combined effect and should also be investigated in further experiments. The experiment of this study included only one application rate and one N fertilizer form and, as the experiments of Krichler also pointed out, the importance of available $\text{NH}_4\text{+N}$ content as a reinforcing factor [42]. The use of ammonium nitrate as a fertilizer source could reduce the NH_3 emissions by 88.3% [43]. Knowledge of interactions between these factors and other soil properties, like pH in the topsoil, that can increase NH_3 losses and adsorption on soil particles [28,42] is needed. The experiments were conducted on disturbed soil columns without plant cover. For these reasons, this trial should be supplemented by further laboratory tests and confirmed by field trials.

Increasing nitrogen efficiency by minimizing nitrogen losses is of great importance to farmers, especially in times of sharply rising fertilizer prices. One successful option, as shown here, is incorporation. Loose incorporation at the soil surface can be achieved by mechanical mixing by a cultivator. There are also forms of band application in which fertilizer is applied in a furrow slit, which is subsequently closed. This technique is equivalent to an injection, where the fertilizer is injected into the soil directly next to the plant. This allows a targeted placement of the fertilizer and reduces losses by leaching or evaporation. However, incorporating split applications during plant growth is often not possible. Also, the injection technique for granulated urea is not yet commercially available. Under con-

trolled conditions, NH_3 emissions were successfully reduced compared to surface-applied urea in the present trial as long as the incorporation is deep enough or soil pores are closed afterward. The 50–80% reduction potential of surface incorporation used in policy mitigation measures [44] cannot be confirmed by these tests. For sandy soils or dry conditions, a significantly lower reduction must be assumed. Adopted and carefully planned strategies suited for local weather and soil conditions are most promising for minimizing NH_3 emissions. Furthermore, technical implementation can lead to different results. Final trials are needed to evaluate under field conditions that consider N uptake and real weather conditions such as precipitation and temperature at the time of fertilization.

5. Conclusions

Experiments designed to quantify the NH_3 losses from N fertilizers applied with different incorporation techniques were conducted in a temperature- and light-controlled chamber environment using an open, dynamic system. The emissions show a typical urea NH_3 emissions profile with a single peak. The highest measured NH_3 emissions occurred at the lower soil moisture level of 30% on the sandy soil, 34% of the N applied. A maximum reduction in emissions of 87% could be achieved with slit injection instead of deep injection with 82% compared to urea standard surface application. Furthermore, the reduction effect increased with increasing clay content of the soil. Contrary to the hypothesis that higher soil moisture content increased velocity and absolute NH_3 losses, lower losses were observed compared to the lower moisture content of 30%. Overall, in controlled conditions, urea incorporation shows great potential for mitigating NH_3 , especially in clayey soils; for sandy, loamy, and drier soils, deeper incorporation or injection should be selected, while surface incorporation was not sufficient or even ineffective under these conditions.

N_2O emissions were delayed and highest on the sandy soil. Due to the surface incorporation, pollution swapping was observed at the higher moisture levels. The results of this study highlight the risk that under specific soil conditions, in particular high soil moisture, incorporation of urea, or other synthetic fertilizers, can increase N_2O emission, calling eventually for other reduction measures, e.g., coating or inhibition of fertilizers to reduce NH_3 emissions. Further field assessments of the NH_3 and N_2O emissions from urea applied with surface incorporation, deep incorporation, and slit injection compared to urea applied with standard surface technique are therefore recommended.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/agronomy13102632/s1>, Figure S1: Setup flow chambers for NH_3 loss quantification; Figure S2: Mineral N content in three different soils (sandy, loamy, clayey) and two different moisture levels (70 and 30% WHC) of NH_3 experiment after incubation for two weeks with start NO_3 (grey line) and total N from fertilizer and start NO_3 (yellow line); Figure S3: Fluxes of N_2O -N from urea applied with different application techniques, including standard surface, surface incorporation, and deep incorporation, on sandy and loamy soil at two moisture levels, 70% and 30% WHC.

Author Contributions: H.G.: conceptualization, methodology, software, validation, formal analysis, investigation, resources, data curation, writing—original draft preparation, writing—review and editing, visualization, and project administration. M.S.: methodology, validation, investigation, data curation, and writing—review and editing. Y.J.: validation, formal analysis, and writing—review and editing. A.P.: conceptualization, methodology, writing—original draft preparation, writing—review and editing, supervision, project administration, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

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4.2 Effects of inhibitors and slit incorporation on NH_3 and N_2O emission processes after urea application

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Abstract: The use of urea fertilizers in agriculture is associated with many negative environmental impacts and is a source of ammonia (NH_3) and nitrous oxide (N_2O) emissions. Such losses from urea fertilizer can be avoided by different mitigation techniques. Three different mitigation principles, urease inhibitor (N-(2-Nitrophenyl) phosphoric triamide, 2-NPT) (UI) alone and urease inhibitor in combination with nitrification inhibitors (N-[3(5)-methyl-1 H-pyrazol-1-yl] methyl] acetamide, MPA) (NI) and closed slit incorporation of urea fertilizer into the soil, were compared on a sandy loam soil at a soil water level of 70 % water-holding capacity. An in vitro microcosm approach with open dynamic incubation chambers was used to monitor NH_3 emissions over two weeks with NH_3 sampling by washing bottles. N_2O emissions were studied over ten weeks in slow throughflow mesocosms with continuous gas chromatographic (GC) measurements. To get insights into N_2O production and consumption processes, gas samples were taken after six weeks and N_2O isotopocules were analyzed by isotope ratio mass spectrometry (IRMS). Slit injection showed the greatest effect on NH_3 emission reduction by 79.6 % (40.6 % by UI, and 46.7 % by UINI) compared to surface applied urea. Minor pollution swapping to N_2O was observed at the beginning of the trial due to incorporation but not in the cumulative emissions over the entire incubation time. The reduction effect of UINI on N_2O emissions decreased over time with no cumulative emission reduction at the end of experimentation. N_2O isotopocules confirmed the high contribution of nitrification to N_2O production. In contrast and bacterial denitrification, nitrifier denitrification and fungal denitrification were involved on a much lower level and N_2O reduction to N_2 was not pronounced. All NH_3 mitigation measurements were effective to decrease NH_3 emissions while their effects on N_2O emission varied over time. Factors as crop N uptake and rainfall would further modify the overall effect on N_2O emissions and need to be considered for final pollution swapping assessment. Further research on the impact of NI on non-target microbial communities is warranted to elucidate potential environmental consequences and long-term efficacy of inhibitor compounds.



Effects of inhibitors and slit incorporation on NH_3 and N_2O emission processes after urea application

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ABSTRACT

The use of urea fertilizers in agriculture is associated with many negative environmental impacts and is a source of ammonia (NH_3) and nitrous oxide (N_2O) emissions. Such losses from urea fertilizer can be avoided by different mitigation techniques. Three different mitigation principles, urease inhibitor (N-(2-Nitrophenyl) phosphoric triamide, 2-NPT) (UI) alone and urease inhibitor in combination with nitrification inhibitors (N-[3(5)-methyl-1 H-pyrazol-1-yl] methyl] acetamide, MPA) (NI) and closed slit incorporation of urea fertilizer into the soil, were compared on a sandy loam soil at a soil water level of 70 % water-holding capacity. An in vitro microcosm approach with open dynamic incubation chambers was used to monitor NH_3 emissions over two weeks with NH_3 sampling by washing bottles. N_2O emissions were studied over ten weeks in slow throughflow mesocosms with continuous gas chromatographic (GC) measurements. To get insights into N_2O production and consumption processes, gas samples were taken after six weeks and N_2O isotopocules were analyzed by isotope ratio mass spectrometry (IRMS). Slit injection showed the greatest effect on NH_3 emission reduction by 79.6 % (40.6 % by UI, and 46.7 % by UINI) compared to surface applied urea. Minor pollution swapping to N_2O was observed at the beginning of the trial due to incorporation but not in the cumulative emissions over the entire incubation time. The reduction effect of UINI on N_2O emissions decreased over time with no cumulative emission reduction at the end of experimentation. N_2O isotopocules confirmed the high contribution of nitrification to N_2O production. In contrast and bacterial denitrification, nitrifier denitrification and fungal denitrification were involved on a much lower level and N_2O reduction to N_2 was not pronounced. All NH_3 mitigation measurements were effective to decrease NH_3 emissions while their effects on N_2O emission varied over time. Factors as crop N uptake and rainfall would further modify the overall effect on N_2O emissions and need to be considered for final pollution swapping assessment. Further research on the impact of NI on non-target microbial communities is warranted to elucidate potential environmental consequences and long-term efficacy of inhibitor compounds.

1. Introduction

Due to the increased availability of nitrogen (N) mainly through urea fertilizer production based on the Haber-Bosch process, agricultural productivity increased globally particularly within the decades following the second world war. Compared to other commonly available mineral N fertilizers, urea has the advantages of a high N content of 46 %, a low cost per unit of N due to lower production costs, availability in most markets, low corrosion, compatibility with most fertilizers, and provides prompt N availability to plants (Silva et al., 2017). However, for broadcast urea application, the loss of total applied N through

ammonia (NH_3) volatilization can reach up to 68 % (Drury et al., 2017; Rochette et al., 2009). Ammonia emissions exert a profound impact on the environment and climate. The deposition of NH_3 in terrestrial or aquatic ecosystems can contribute to environmental degradation through processes such as eutrophication (Bergström et al., 2008; Bergström and Jansson, 2006), acidification, and biodiversity loss (Clark and Tilman, 2008). Additionally, NH_3 serves as a crucial precursor in the formation of fine particulate matter, characterized by a diameter less than 2.5 μm , which has detrimental effects on both the environment and human health (Griffith et al., 2015; Wang et al., 2016).

In addition, on average 0.62 % (0.43–0.85 %) of urea application is

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lost in the form of nitrous oxide (N₂O) emissions from managed European agricultural soils (Mathivanan et al., 2021). Nitrous oxide is one of the three important atmospheric greenhouse gases (GHGs) with about 265 times the global warming potential of carbon dioxide (IPPC, 2014). In alignment with the new National Emission Ceilings Directive (NEC Directive) of Europe 2016/2284, Germany has pledged to reduce national NH₃ emissions by 5 % by 2020 and by 29 % by 2030 compared to 2005. This mitigation is mandated to follow a linear path between 2020 and 2030. Since spring 2020 measures have been implemented in the amendment of the German fertilizer ordinance DüV20 [9]. Urea fertilizer must be applied in combination with a urease inhibitor (UI) or, alternatively, has to be incorporated within four hours, aiming to mitigate NH₃ emissions associated with the use of mineral N fertilizers.

Fertilizer incorporation or injection, like slit incorporation, provides an increase in the contact area between soil and fertilizer, accelerating the sorption of ammonium (NH₄⁺) to the soil matrix. Studies demonstrated a mitigation potential in NH₃ emissions by up to 91.2 % by incorporation compared to surface application, even lower emissions than a urease inhibitor treatment (Fontoura and Bayer, 2010; Pan et al., 2016; Woodley et al., 2020). Different soil properties e.g. cation exchange capacity (CEC), pH, water content, and texture, can limit the efficiency of incorporation as a mitigation strategy for NH₃ emissions (Du Preez and Burger, 1987; Sommer et al., 2004). Additionally, incorporating the urea fertilizer in the soil may increase the N₂O emissions by up to 67 % (Götze et al., 2023) since it immediately creates anaerobic conditions favourable for denitrification (Venterea and Coulter, 2015).

Urease inhibitors (UI) added to the fertilizer mitigate NH₃ volatilization through the slowdown of urea hydrolysis by binding to the urease enzyme. The delayed hydrolysis of urea results in a lower soil pH increase which allows more time for the adsorption of ammonia by the soil and plants, preventing volatilization (Wang et al., 2020). The efficacy and duration of UI are contingent upon the concentrations of urea and the inhibitor, chemical structure of the inhibitor, as well as the degradation rate of the inhibitor. Presently, only a few urease-inhibiting compounds are applied in commercial agriculture due to cost and toxicity concerns, in particular N-(n-Butyl) thiophosphoric triamide (NBPT). Meta-analyses show that UIs can reduce NH₃ emissions by 30–90 % in both laboratory and field experiments compared to surface-applied urea (Klimczyk et al., 2021; Pan et al., 2016; 2018). Although several meta-studies on efficacies of inhibitor compounds exist, actually only NPBT, was studied in great detail. In several agricultural regions other inhibitor compounds are used more widely, in Germany in particular the UI compound 2-NPT (N-(2-Nitrophenyl) phosphoric triamide, 2-NPT) and the nitrification inhibitor (NI) N-[3 (5)-methyl-1 H-pyrazol-1-yl] methyl] acetamide (MPA). There is a strong need to close the research gaps for these compounds. However, since UI primarily affects urea hydrolysis, its use does not directly result in a reduction of N₂O emissions and/or other N losses, such as nitrate (NO₃) leaching (Sigurdarson et al., 2018). Several studies have shown the risk of “pollution swapping” when UI was used to reduce NH₃ losses, because higher soil NO₃ concentrations resulted in an increase of N₂O emissions by up to 36 % (Hu et al., 2020; Drury et al., 2017; Woodley et al., 2020). Nevertheless, on average there appears to be an emission-reducing effect, although this is still uncertain in terms of the conditions and the extent of its occurrence (Fan et al., 2022). The highlighted risk that under specific soil conditions, incorporation of urea in combination with the addition of UI can increase N₂O emission, is calling for other reduction measures to reduce NH₃ emissions in these situations.

Nitrification inhibitors curtail NO₃- losses by impeding the production of NO₃- through the deceleration of NH₄⁺-oxidation to NO₂ by ammonia oxidising bacteria and archaea (Soares et al., 2012). Although several NI compounds have proven to be effective, the risk of higher NH₃ emissions, due to the addition of NI should not be neglected in the environmental and economic assessment. The inhibition of nitrification, while reducing N loss through NO₃ leaching and N₂O emissions,

maintained higher soil pH and NH₄⁺ concentration for an extended period, creating favourable conditions for an increase in NH₃ volatilization (Soares et al., 2012).

The combined application of UI and NI (UINI) with urea fertilizer extends the availability of NH₄⁺ to plants by reducing NH₃ volatilization, N₂O emissions, and NO₃-leaching losses (Gioacchini et al., 2002). Experiments demonstrated a mitigation potential in NH₃ emissions through a combined treatment with UINI by up to 89 % (Hu et al., 2020; Martins et al., 2017) with Fan et al., 2022 showing an average of 38 % (n=77). On the other hand, the combined use of both inhibitors showed the a N₂O emission mitigation potential up to 69 % (Martins et al., 2017; Ni et al., 2018) with an average of 31 % (n=118) (Fan et al., 2022).

In order to better assess the N₂O mitigation potential, it is important to know something about the prevailing N₂O production and consumption processes, because this is the only way the inhibitors can be used in a targeted manner. While a reduction of the nitrification rate can be considered a direct effect of NI on mitigating N₂O emissions, the reduced availability to the former process can also reduce N₂O emissions as an indirect effect of NI application. However, the effect of UI or a combined UINI use on the prevailing N₂O production processes is to our knowledge currently largely unclear. Therefore, site-specific nitrogen isotope ratios of N₂O may be useful, as they provide a more nuanced constraint on biogeochemical cycling in soil than its bulk composition alone (Kelly et al., 2023). Up to now, isotopic analysis of the four most abundant isotopocules of N₂O (¹⁴N¹⁴N¹⁶O, ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N¹⁴N¹⁸O) (Toyoda et al., 2017) have been widely used to quantify N₂O production and consumption processes in soils (Buchen et al., 2018; Di Wu et al., 2019; Lewicka-Szczepak et al., 2020). This approach allows to study the contributions from the four main N₂O production processes, such as bacterial denitrification (bD), nitrifier denitrification (nD), nitrification (Ni) or fungal denitrification (fD) to the total N₂O emissions (Yu et al., 2020) of different mitigation measures.

This study specifically focused on the effectiveness of incorporation of the rarely investigated UI 2-NPT to mitigate NH₃ losses, while taking N₂O emissions and their production and consumption production processes into account. Furthermore, the effectiveness of the combination of UI “2-NPT” and the also rarely studied NI MPA is evaluated considering the mitigation of potential “pollution swapping”. Therefore, a laboratory experiment was conducted for optimal understanding of the processes under controlled conditions, investigating the effect of broadcast urea application, urea application with urease inhibitor (urea + UI), urea application combined with urease and nitrification inhibitor (urea + UINI), incorporation of urea by slit injection into the soil (urea - INC), and an untreated control. We hypothesized that (a) all mitigation measures lower NH₃ emissions compared to the standard surface broadcast application of urea, with UI showing the greatest effect. Furthermore, we hypothesized that (b) incorporation of urea and urea + UI promote N₂O emissions and (c) urea + UINI has the greatest mitigation effect on N₂O emissions. We further hypothesized that (d) nitrification is the most important N₂O production process with respect to the investigated mitigation measures examined.

2. Materials and methods

Two incubation experiments were carried out in the microcosm laboratory at Thünen Institute of Climate–Smart Agriculture from April to June 2022 to investigate NH₃ and N₂O emissions following urea application with the varying mitigation techniques: one setup for NH₃ (Exp. NH₃) and one for N₂O measurements (Exp. N₂O) (Fig. 1). Two approaches were necessary, since the two gas species require different air exchange rates.

2.1. Experimental design and tested treatments

In both incubation experiments, three different NH₃ emission mitigation techniques for urea fertilization were compared with an



Fig. 1. Set-up of flow chambers for N_2O quantification.

application rate equivalent to $174 \text{ kg urea N ha}^{-1}$ ($0.167 \text{ g fertilizer, 6 granules}$) for the Exp. NH_3 and to 260 kg N ha^{-1} ($0.907 \text{ g fertilizer, 19 granules}$) for the Exp. N_2O according to the soil surface. For the Exp. N_2O , a higher fertilizer amount was selected to achieve a sufficiently high measuring signal at a constant flow rate in the chambers. In addition to an unfertilized control, four fertilizer treatments were investigated: standard surface urea application (urea), slit injection (urea - INC), urea with urease inhibitor 2-NPT (urea + UI) and urea with urease inhibitor 2-NPT plus nitrification inhibitor MPA (urea + UINI), with $n=3$ for the Exp. NH_3 and $n=4$ for the Exp. N_2O . In order to simulate closed slit injection of fertilizer, slit injection was mimicked to a DEEPOT 32.1 deep deposit fertilizer machine (Rauch Sinzheim, Germany), placing urea fertilizer in a 5 cm deep slit produced with a plastic spatula. Afterwards, the fertilizer was covered with soil and compacted by a cork rolled over the soil surface. The same number and size of granules (diameter of 3.5 mm) were applied in each replicate container.

The soil for both experiments was sampled in 0–20 cm depth (Ap horizon) from a sandy loam agricultural field in Meine (Germany 2022) (Table 1). In preparation for both experiments, the soil was sieved ($<2 \text{ mm}$). Furthermore, the soil water content was determined before each experiment by drying the soil at 105°C until its weight remained constant. The amount of water required to achieve the soil moisture content was added to the soil by gradual mixing calculated with θ_1 the water-holding capacity [vol%]. A guideline value from the manual of soil mapping (Sponagel, 2005) for soil type Sl3 (27 vol%) with an addition of 5 vol% for medium-humic soils was used to estimate the water-holding capacity (θ_1). This results in 22.4 vol% for 70 % plant available moisture content and 47.49 % water filled pore space (WFPS).

The column was compacted to reach the typical field bulk density of 1.4 g cm^{-3} , which is considered as a typical bulk density for sandy soils like Meine. This resulted to 479 g soil per chamber for the Exp. NH_3 and 2587 g for the Exp. N_2O . To prevent enhanced N transformation and evaporation of water, the soil was continuously covered and stored at 4

$^\circ\text{C}$ after sampling.

2.2. Flow chambers for NH_3 loss quantification

The experiments were conducted with flow chambers in a temperature-controlled chamber environment to quantify the NH_3 losses from N fertilizers (Götze et al., 2023). Frequent acid trap sampling also enabled comparisons of different incorporation techniques. The chamber airflow ran constantly between sampling periods (to simulate windy conditions) and was humidified with washing bottles. The temperature was set to 15°C , providing supportive conditions for NH_3 volatilization.

Soils with and without urea application were incubated in a climatic chamber (HVST 705 EP, Roller Gerlingen, Germany) at 15°C . This system was designed to quantify NH_3 losses from the different treatments. The design of the experiment was based on findings from previous studies on NH_3 volatilization (Gronwald et al., 2018; Roelcke et al., 1996). The basic idea is, that the head space of an incubation container is continuously flushed with air, and the resulting NH_3 emissions are absorbed in an acid solution and subsequently analysed.

The dimensions of the round incubation jars were 12 cm in height with a diameter of 7.5 cm deflector plate attached to the jar lid, creating a uniform laminar flow while ensuring sweeping of the entire soil surface (Flura et al., 2013). The volume of the soil column was 300 mL with 150 mL headspace volume and with the deflector protruding 3.5 cm into the jar. One gas wash bottle (114452972, Rettberg GmbH Göttingen, Germany) was filled with water to produce almost complete water saturation of the incoming air stream and one behind the vessel. The exhaust air passed through another wash bottle filled with a sulfuric acid solution (100 mL, 5 mM H_2SO_4), absorbing emitted NH_3 . A fritted glass diffuser was used to obtain complete absorption of NH_3 into the solution.

The constant flow of humidified air was led over the soil column surface. The required airflow was supplied by an air compressor with a

Table 1

Soil used in the experiments—locations, soil texture, total carbon content (TN), total nitrogen content (TN), cation exchange capacity (CEC) and soil pH.

Soil	Region of Location	Coordinates North/East	Sand [mass%]	Silt	Clay	Texture (Sponagel, 2005)	TC [mass%]	TN	CEC [cmol kg ⁻¹]	pH (CaCl ₂) [mol L ⁻¹]
Sandy	Central Germany Meine	52.387309/10.562801	68.61	24.24	7.15	Sl2	1.39	0.11	7.53	6.59

water separator and controlled by pressure regulators. The airflow of each incubation vessel was monitored and controlled by flow sensors (IDT FS200, Renesas Tokyo, Japan). The flow rate was set to 8 headspace volumes min^{-1} . The tightness of all incubation tubes was checked using pressure difference measurement. Preparatory experiments proved a second downstream acid trap and repetitive daily trap changing unnecessary, as the capacities of the 100 mL of 5 mM H_2SO_4 were sufficient to capture emissions completely. Furthermore, it was found that emissions after urea application ceased after two weeks, as they showed no difference from emissions from untreated soil.

2.3. NH_3 analysis flux calculation

The NH_4^+ concentration in acid traps was measured using an NH_3 selective electrode (Thermo Scientific Orion Versa Star Pro Electrochemistry Meters, Waltham USA, range (ISE) 0.0001–19990 ppm, accuracy (ISE) ± 0.2 mV or ± 0.05 % of reading). Samples were stored at 4 °C until measurement.

For the calculation of NH_3 loss, the daily concentrations (C_{NH_3}) in the acid solution were multiplied by the volume of acid (V_{acid}) and summed up to the total amount of NH_3 ($M_{\text{NH}_3\text{cum}}$) (Eq. 1).

$$M_{\text{NH}_3\text{cum}} = \sum_{t=1}^n C_{\text{NH}_3} \times V_{\text{acid}} \quad (1)$$

The emissions (kg N ha^{-1}) were determined by multiplying the mass loss (M) with the fertilized surface area (A) in the flask (Eq. 2).

$$F = M \times A \quad (2)$$

2.4. Flow chambers for N_2O loss quantification

The microcosm system allows an automated incubation of soil columns (microcosms) under controlled conditions in order to study the formation of greenhouse gases in agricultural soils (Hantschel et al., 1994; Säurich et al., 2019). The used cylindrical acryl glass chambers were 18 cm high and 14.4 cm inner diameter. The headspace volume was 1230 mL, and the soil volume was 1600 mL. The additional amount of water needed to achieve the target soil moisture content was determined. Similar to Exp. NH_3 , the sieved soil was compacted once to a bulk density of 1.4 g cm^{-3} .

2.5. N_2O flux calculations

Synthetic air (21 % O_2 , 78 % N_2) was pumped continuously at a flow rate of approximately 15 mL min^{-1} through a chamber containing distilled water with a bubbler into the chambers containing the soil and fertilizer treatments in the chamber at 20 °C. Headspace gas from every incubation chamber was sampled directly every 6 h using steel cannulas connected to a gas chromatograph. Blanks for measuring background concentrations of the synthetic air gas mixture and five standards for calibrations were regularly integrated into the measurement sequence. Gas samples and standards were determined using a gas chromatograph (GC-2014, SHIMADZU Kyōto, Japan) equipped with an electron capture detector. The analytical precision was <1.5 % CV and determined by repeated measurements of standards (0.33, 0.55, 2.01, 6.94, 40.4, and 130 ppm N_2O). For flux calculations, the mass concentrations (C) were calculated in Eq. 5 via the mass volume (V_m) according to the ideal gas law (Eq. 3) from the mole mass in g mol^{-1} (M) of CO_2 and N_2O provided from the GC measurement.

$$V_m = \frac{R \times T}{p} \quad (3)$$

Taking into the temperature in the microcosm system of 20 °C (288.15 K), the pressure of 101.325 kPa (22.41396954 L/mol), and the general gas constant of $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ into account, the concentration was corrected according to Eq. 4:

$$C = \frac{(c - c_{\text{blank}}) \times M}{V_m} \quad (4)$$

M is the molar mass (N_2O 44 g mol^{-1} , CO_2 44 g mol^{-1}) and T is the temperature (K). Mass flow (F , $\mu\text{g N m}^{-2} \text{ h}^{-1}$) therefore, was calculated by the mass concentration C and the flow rate (Q) provided from the flow meter (Eq. 5).

$$F = \frac{(C \times Q)}{A} \quad (5)$$

A denotes the soil surface of the column in m^2 , and Q is the flow rate in mL min^{-1} . Cumulated fluxes were obtained by integrating the emissions from the whole observation period by linear interpolation.

2.6. Soil analysis

For determination of mineral nitrogen content (N_{min} = sum of NO_3^- -N and NH_4^+ -N), all soil samples were frozen at -20 °C until preparation. N_{min} extraction was performed for all samples according to German laboratory standards (VDLUF, 2002). Mineral N was extracted from 50 g of homogenized soil with 200 mL of 0.0125 M CaCl_2 (1:4) and shaken in an overhead shaker for one hour. The mixture was then filtered through nitrogen-free filter paper (MN 614/4) and stored at -20 °C until analysis by a continuous flow analyser (CFA-Analyser San++, Skalar Analytical B.V.). Soil water content was determined by drying the sample for 24 h at 105 °C.

2.7. Recovery of fertilizer N in soil

Soil samples were analysed at the beginning of the experiment and after a period of incubation to evaluate N recovery (r). For the calculation, the final N_{min} value was divided by the initial value, which consisted of the N_{min} content at the beginning of the experiment and the fertilized N amount (Eq. 6). The differences that occurred were based, among other things (e.g., N transformation processes), on the loss due to NH_3 and N_2O emissions. The mineralization, detected in incubated control chambers without fertilization, was very low and was therefore later neglected.

$$r = \frac{(N_{\text{min, end}} - N_{\text{Mineralisation}}) + N_{\text{NH}_3} + N_{\text{N}_2\text{O}}}{(N_{\text{min, start}} + N_{\text{fertilizer}})} \quad (6)$$

2.8. Isotopocule analyses and calculations

In addition to automatic gas sampling and close to the mid-term N recovery sampling, a manual headspace gas sampling was done six weeks after the beginning (day 43) of the Exp. N_2O in order to get insights into N_2O production and consumption processes during a high emitting period. Thus, one crimped 100 mL vial was connected for 24 h hours to the vents of the soil chamber.

Gas samples were analysed for N_2O isotopocules using a Delta V isotope ratio mass spectrometer (Thermo Scientific, Bremen, Germany), which was coupled to an automatic preparation system with PreCon plus Trace GC IsoLink (Thermo Scientific, Bremen, Germany). Briefly, N_2O was pre-concentrated, separated, and purified, and m/z 44, 45, and 46 of the intact N_2O^+ ions as well as m/z 30 and 31 of NO^+ fragment ions were determined, as described in Lewicka-Szczepak et al. (Lewicka-Szczepak et al., 2014). Results were calculated according to Röckmann et al. (Röckmann et al., 2003) and Toyoda and Yoshida (Toyoda and Yoshida, 1999). The ^{15}N site preference ($\delta^{15}\text{N}_{\text{N}_2\text{O}}^{\text{SP}}$) was defined as the difference between $\delta^{15}\text{N}_{\alpha\text{N}_2\text{O}}$ and $\delta^{15}\text{N}_{\beta\text{N}_2\text{O}}$ values. All isotopic values are given as delta values (δ), expressed in per mille (‰) deviation from the $\delta^{15}\text{N}/^{14}\text{N}$ and $\delta^{18}\text{O}/^{16}\text{O}$ ratios of the reference materials (i.e., atmospheric N_2 and Vienna Standard Mean Ocean Water (VSMOW), respectively). The analytical precision determined as standard deviation (1σ) of the internal standards for measurements of $\delta^{18}\text{O}_{\text{N}_2\text{O}}$ and $\delta^{15}\text{N}_{\text{N}_2\text{O}}^{\text{SP}}$ were

typically 0.1 ‰ and 0.5 ‰, respectively.

During headspace sampling, the collected N_2O was a mixture of atmospheric and soil-emitted N_2O . Thus, δ values of soil-emitted N_2O were calculated using a basic isotopic mixing model (Well et al., 2006). To calculate the contribution of nitrification (Ni), fungal denitrification (fD), nitrifier denitrification (nD) and bacterial denitrification (bD) to N_2O production and the degree of N_2O reduction to N_2 (consumption), a dual isotope plot – a so called SP/O MAP based on $\delta^{15}N_{N_2O}^{SP}$ and $\delta^{18}O_{N_2O}$ values – was applied. A detailed calculation strategy can be found in the supplement (Di Wu et al., 2019). Two possible scenarios in case of N_2O source mixing and reduction were evaluated:

– Case 1 – N_2O produced from bacterial denitrification is first partially reduced to N_2 , followed by mixing of the residual N_2O with N_2O from other pathways.

– Case 2 – N_2O produced by various pathways is first mixed and afterwards reduced.

For further processing, evaluation of distribution and uncertainty parameters for the contribution of the different N_2O pathways and the residual unreduced fraction of N_2O (r) with respect to the differences scenarios, the recent Monte Carlo modelling tool FRAME for 2D application (Lewicki et al., 2022) was used. Isotopic ranges for each process (endmember areas) and isotopic fractionation factors (ϵ values) for N_2O reduction processes were derived from literature values (Table S1).

2.9. Data and statistics

All the statistical analyses were carried out in R Studio (R Studio, Version 2023.6.0.421, R Studio Inc., Boston, MA USA) with the free statistical software R 4.2.2 (R Core Team, 2022). All graphical representations were created using the appropriate R packages, including [ggplot2]. An ANOVA analysis was used to test for fertilizer treatment effects on cumulative NH_3 -N losses. Differences between fertilizer treatments were determined using the Sidak post hoc test at the 95 % confidence level. The residual distribution was tested, and the Shapiro–Wilk test for normal distribution was performed. Compact letter displays [multcomp, emmeans] were used to report the results of all pairwise comparisons among treatment means. Means not sharing any letter are significantly different by the Sidak test at the 5 % level of significance.

3. Results

3.1. NH_3 emissions

Overall, all three mitigation measures (urea - INC, urea + UI and urea + UINI), reduced cumulative NH_3 losses. The maximum cumulative NH_3

loss was $80.37 \text{ kg N ha}^{-1}$ (45.98 % of applied N) with urea standard surface broadcast application (Fig. 2a). For the latter treatments, an NH_3 emission kinetic for the application techniques could be determined, with a faster increase in emissions at the beginning when urea was applied with standard broadcast application. Urea + UINI had lower emissions in the beginning than urea + UI, but 14 days after the start of the experiment, the same final level was reached.

Slit injection and the two inhibitor treatments showed significantly lower NH_3 emissions compared to standard surface application, but the emissions were significantly lowest and the mitigation effect greatest with urea - INC ($16.38 \text{ kg N ha}^{-1}$, 79.62 %). Slit injection had the lowest losses down to less than 9.41 % loss of the applied N amount. The NH_3 losses were 47.72 and $42.82 \text{ kg N ha}^{-1}$ for urea + UI and urea + UINI, respectively and in the range of 20.81–31.14 % of applied N (Fig. 2b). There was no significant difference in between the two inhibitor variants urea + UI and urea + UINI. The mitigation effect was 40.62 % and 46.72 % respectively (Fig. 2c). The cumulated NH_3 emissions of the experiment are given in Table 2.

3.2. N_2O emissions

Nitrous oxide fluxes varied significantly depending on the chosen mitigation strategy (Fig. 3a). The urea incorporated in the soil urea - INC produced one peak with significantly higher hourly N_2O emissions than the other treatments in the first 10 days after fertilization. Emission from urea + UI and urea peaked at day 18 after fertilization at 1.7 and $1.25 \text{ g N}_2O\text{-N ha}^{-1} \text{ h}^{-1}$ with slow decline afterwards. Urea + UINI showed a slow increase to the highest hourly N_2O of $2.1 \text{ g N}_2O\text{-N ha}^{-1} \text{ h}^{-1}$ after 71 days.

Elevated cumulative emissions were observed with urea application via standard surface broadcast application or with the addition of a UI, 0.88 and $0.89 \text{ kg N ha}^{-1}$, respectively (Fig. 3b). Notably, urea - INC demonstrated significantly pronounced lower fluxes from day 40 of incubation, with cumulative losses of $0.56 \text{ kg N ha}^{-1}$ at the end of the trial after 77 days, corresponding to a 64.31 % reduction in N_2O emissions. The utilization of double-inhibited fertilizer (urea + UINI) initially displayed the most substantial mitigation effect on N_2O losses; however, emissions began to rise after 20 days, increasing exponentially from day 50 until reaching levels similar to those of standard spread fertilizer (Fig. 3b). The emission events prevailed even at the end of the measuring period. The cumulated N_2O emissions of the experiment are shown Table 2.

3.3. N balances and recovery of applied fertilizer N

Soil mineral N was determined after 14 days in the NH_3 Exp. and

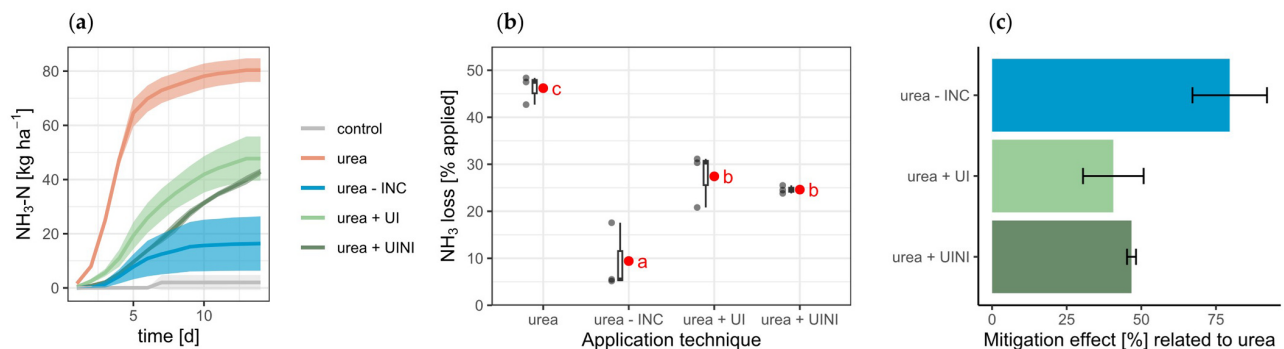


Fig. 2. a) Cumulative NH_3 -N losses from urea applied to the sandy soil from different application techniques, including standard surface application, slit injection, urea + UI and urea + UINI; lines depict mean values ($n = 3$) while shaded bands indicate standard deviation (left diagram), b) NH_3 losses (% of N applied) from urea fertilizer applied with standard surface application (urea), slit injection technique (urea - INC), urea + UI and urea + UINI; replicates and boxplots are in black, and red indicates the mean values and compact letter display (Means not sharing any letter are significantly different by the Sidak test at the 5 % level of significance with 95 % confidence) (middle diagram) and c) and the mitigation effect compared to standard surface application of the mitigation measures (right diagram). $n=3$.

Table 2

N balance in the two experimental setups (NH₃ Exp. and N₂O Exp.) with the treatments standard surface urea (urea), urea applied with slit injection technique (urea – INC), urea with urease inhibitor (urea + UI) and urea with urease and nitrification inhibitor (urea + UINI) with start N_{min} and End N_{min} after incubation, N from fertilizer and the emitted N; * are estimated values from the parallel experiment.

	Treatment	Incubation [d]	Start N _{min} [kg N ha ⁻¹]	Fertilizer N	End N _{min}	cum. NH ₃ -N	cum. N ₂ O-N	N balance %
set-up	urea	14	6	174	81±21	80±4	*0.5±0.001	90±14
	urea - INC	14	6	174	161±17	16±10	*0.5±0.06	99±15
	urea + UI	14	6	174	95±13	48±8	*0.5±0.06	79±12
	urea + UINI	14	6	174	127±11	43±1	*0.1±0.001	94±7
N ₂ O Exp.	urea	37	14	260	208±20	*80±4	0.5±0.001	105±9
	urea - INC	37	14	260	208±10	*16±10	0.5±0.06	82±7
	urea + UI	37	14	260	221±15	*48±8	0.5±0.06	98±8
	urea + UINI	37	14	260	187±16	*43±1	0.1±0.001	84±6

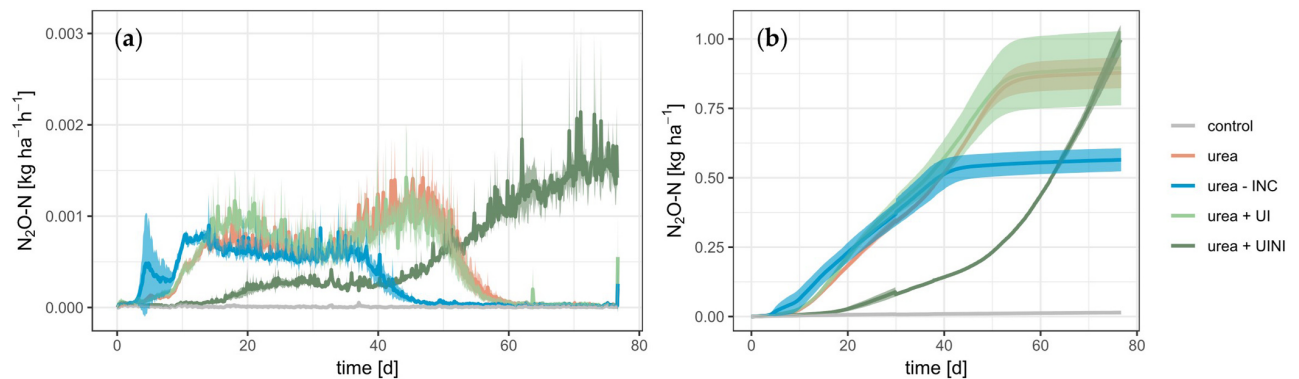


Fig. 3. Cumulative losses (left) and fluxes (right) of N₂O-N from urea applied with different application techniques including standard surface(urea), slit injection technique (urea – INC), urea + UI and urea + UINI; lines depict mean values (n=3) while shaded bands indicate standard deviation.

after 37 days in the N₂O Exp. (Table 2) details on NH₄⁺ and NO₃⁻ composition and dynamics is presented in the supplements (Figure S1). After two weeks of incubation, the NH₃ Exp. showed that the NH₄-N contents were highest when urea was applied with UINI with 88 kg N ha⁻¹. The total mineral N content was highest in the urea - INC treatment with 161 kg N ha⁻¹. In the N₂O Exp., the N_{min} values were more similar between the different treatments. After 37 days of incubation, the NH₄-N value was also highest when applied urea with UINI, 115 kg N ha⁻¹ as in the NH₃ Exp. and the highest N_{min} showed urea + UI. The emissions of the respective other experimental design were used for the balances. In the case of NH₃ emissions, these measurements are probably erroneous due to the low air exchange rate in the N₂O incubation setup, which can result in very low cumulative NH₃ emissions. On the other hand, the soil samples in this experiment were not taken after 14 days but rather 37 days, in contrast to the NH₃ Exp., so that the emission process had run longer. The recovery of applied N was high in both experimental set-ups, between 90 % and 99 % in the NH₃ Exp.

3.4. N₂O isotopocule values

The majority of isotopocule values of soil-emitted N₂O, presented in the dual isotope plot (SP/O MAP, Fig. 4) is situated within the area limited by the different N₂O source mixing and the reduction line, which allows the calculation of the two different scenarios and application of the FRAME model. Values clearly scatter between the mixing lines of the three different N₂O production processes, while clustering in the end-member areas of Ni and fd. Graphical evaluation shows nearly no contribution of N₂O reduction to N₂ under the prevailing conditions at the sampling day. δ¹⁵N_{N2O} values of the urea and urea + UI treatment were with > 28 ‰ slightly higher, when compared to values from the urea - INC and the urea + UINI treatment, while δ¹⁸O_{N2O} ranges were rather similar for all treatments.

3.5. N₂O production and consumption processes

Apart from the graphical evaluation, analysis by the FRAME model indicated that N₂O during the high emitting phase (six weeks after beginning the incubation) was mainly produced by nitrification in both scenarios. Modelled (blue dots) and measured data (black dots) were in good agreement (Figure S3-S6, see panel a and d) for both scenarios. The fractional contribution of nitrification (range of the mean value over all treatments) to the total N₂O production was 42–48 % for Case 1 (Red-Mix) and 40–57 % for Case 2 (Mix-Red). The contribution from bd/nD source was rather low in both cases, while a significant contribution of fungal denitrification could not be neglected. The residual unreduced fraction of N₂O (r) was estimated to be 47–70 % in Case 1 and 73–83 % in Case 2 (Table 3), however histograms of model runs were not always optimal for this fraction (Figs. S1–4, panel b and e). When comparing the different treatments, only the urea + UINI treatment was somewhat different, with a higher estimated contribution of bd/nD (> 39 %), as well as a higher residual unreduced fraction (Table 3).

4. Discussion

4.1. Effect of mitigation technique on NH₃

The results of our experiment showed NH₃ losses similar to many earlier laboratory and field studies (Rochette et al., 2009; Soares et al., 2012; Wang et al., 2020), but higher than in some experiments (Gioacchini et al., 2002; Hu et al., 2020; Ni et al., 2018). Similar efficacies of the mitigation measures were observed in different studies (Abalos et al., 2012; Soares et al., 2012; Wang et al., 2020), nonetheless also higher NH₃ mitigation potential of up to 89 % compared to surface applied urea have been reported for UI and UINI treatments (Gioacchini et al., 2002; Hu et al., 2020; Ni et al., 2018). In comparison, the

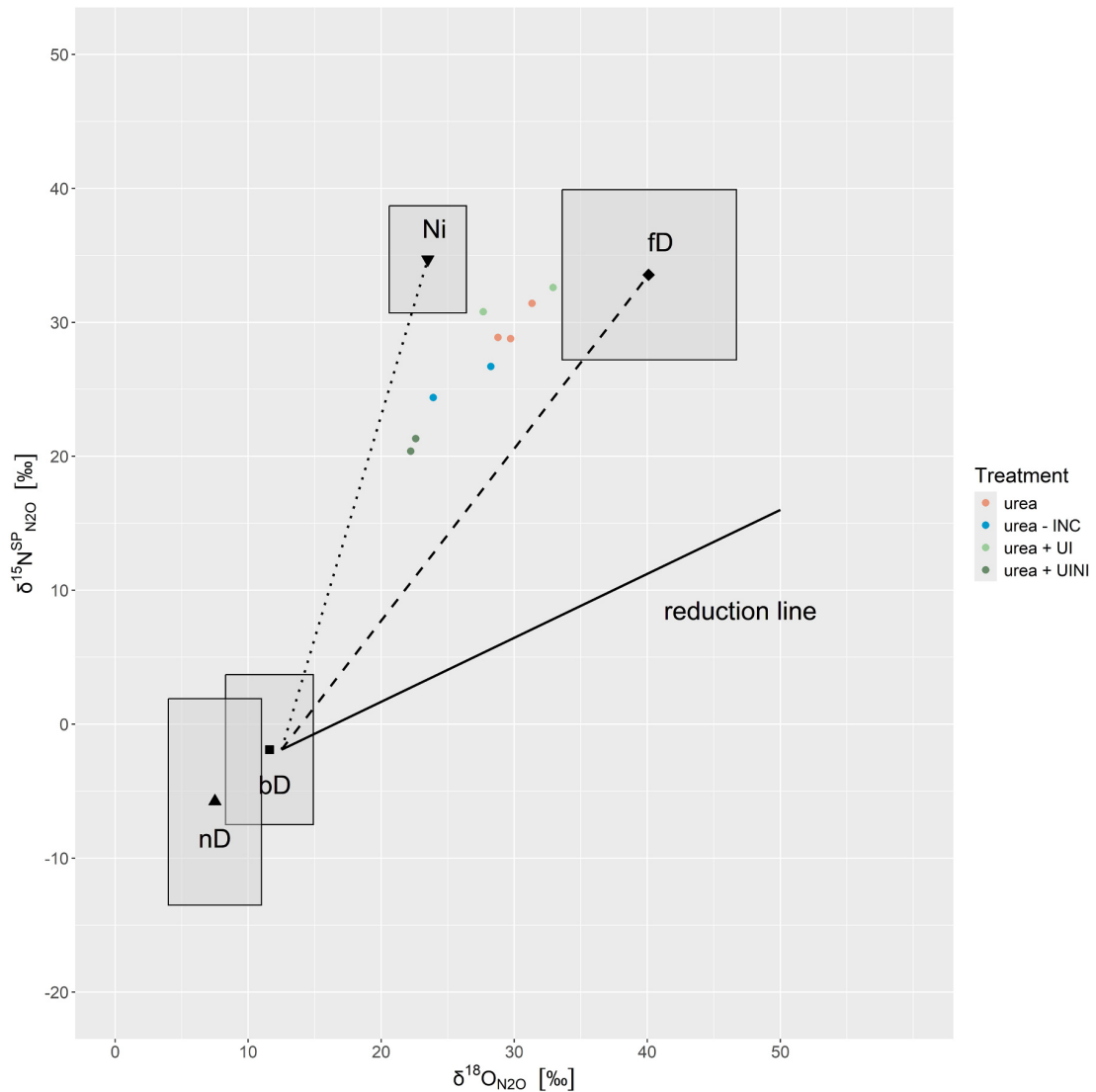


Fig. 4. Isotopocule values of soil-emitted N_2O plotted per treatment at day 43 after start of the experiment. The SP/O map is based on $\delta^{15}N_{N_2O}^{SP}$ and $\delta^{18}O_{N_2O}$ values presented with literature endmember values and theoretical mixing (dotted lines) and reduction (solid line) lines. Mixing lines were drawn between mean values for both $\delta^{15}N_{N_2O}^{SP}$ and $\delta^{18}O_{N_2O}$ of the respective processes. The reduction line represents the mean route based on $\eta_{red}^{15}N_{N_2O}/\eta_{red}^{18}O_{N_2O}$ ratios. $\delta^{18}O_{N_2O}$ values of mixing endmember bacterial denitrification (bD), nitrifier denitrification (nD), and fungal denitrification (fD) are presented in relation to the mean ambient water of -8.4‰ (hence present the expected $\delta^{18}O_{N_2O}$ originating from a particular pathway under these study conditions). For nitrification (Ni) $\delta^{18}O$ correction was not necessary.

Table 3

Simulation results of fractions for N_2O production processes: bacterial denitrification (bD) nitrifier denitrification (nD), fungal denitrification (fD) and nitrification (Ni) and the remaining fraction (r) of N_2O after its reduction by denitrification obtained from FRAME model results (see also Figure S3-S6, panel c and f). Mean values $\pm$ standard deviation. n =2, except urea with n=3.

Treatment	Case 1: Red-Mix				Case 2: Mix-Red			
	bd/nD	fD	Ni	r	bd/nD	fD	Ni	r
urea	0.13 $\pm$ 0.08	0.39 $\pm$ 0.17	0.48 $\pm$ 0.16	0.47 $\pm$ 0.28	0.16 $\pm$ 0.07	0.29 $\pm$ 0.17	0.54 $\pm$ 0.17	0.77 $\pm$ 0.14
urea - INC	0.27 $\pm$ 0.08	0.25 $\pm$ 0.14	0.48 $\pm$ 0.15	0.57 $\pm$ 0.24	0.30 $\pm$ 0.08	0.22 $\pm$ 0.13	0.49 $\pm$ 0.15	0.77 $\pm$ 0.15
urea + UI	0.11 $\pm$ 0.07	0.41 $\pm$ 0.13	0.47 $\pm$ 0.14	0.48 $\pm$ 0.29	0.15 $\pm$ 0.08	0.28 $\pm$ 0.17	0.57 $\pm$ 0.17	0.73 $\pm$ 0.16
urea + UINI	0.39 $\pm$ 0.09	0.19 $\pm$ 0.13	0.42 $\pm$ 0.16	0.70 $\pm$ 0.19	0.42 $\pm$ 0.09	0.18 $\pm$ 0.13	0.40 $\pm$ 0.15	0.83 $\pm$ 0.12

meta-study of Fan et al., (2022) across various UI compounds showed a NH_3 mitigation by 51 % (n=76) compared to only 40.62 % in this trial using 2-NPT which, nevertheless, is probably still in the prediction interval of the Fan et al., (2022) analysis. In the group of UINI with various inhibitor components a reduction of 38 % (n=77) was shown in the

same meta-study and in this trial using 2-NPT and MPA as inhibitors 46.72 %. Even though NH_3 emissions can increase through the addition of NI, depending on the soil properties (Soares et al., 2012; Wang et al., 2020), the meta-analysis of Kim et al. and others reported a decrease when combined with UI (Kim et al., 2012). However, since the

measurement period in this experiment was with 14 days not long enough to capture the plateau of the cumulated NH_3 emissions of the UINI treatment, the cumulated emissions could have increased significantly to or above the level of the UI treatment. For further experiments on the impact of UINI on NH_3 volatilization, we therefore recommend an experimental duration until the end of the emission process. Due to the measurement period, the NH_3 emissions of the UINI treatment did not decline as much as the other treatments, with significantly higher emissions of up to $0.002 \text{ kg N ha}^{-1} \text{ h}^{-1}$ at the end of the experiment.

The incorporation of urea into the soil (urea - INC), which simulated the deep depot fertilizer applicator, reduced the cumulated NH_3 emissions to $16.38 \text{ kg N ha}^{-1}$. This 79.62 % reduction compared to the urea treatment is in line with previously published work. For example Rochette et al. found that urea incorporation reduced cumulated NH_3 emissions by 52 % and up to 70 % at a similar depth (Rochette et al., 2009, 2013). Furthermore, an average reduction of NH_3 emissions of 63 % at the depth of 5 cm was reported (Rochette et al., 2013). In a recent study from 2023, in which various incorporation techniques were examined on different soil textures and moisture levels, the mitigation potential for urea - INC ranged between 43 % and 87 % (Götze et al., 2023). With a NH_3 mitigation of 79.62 % measured in this experiment, results are well in line with 74 % reported for sandy soils and a similar soil moisture (Götze et al., 2023).

The low emissions and the resulting high $N_{\min}$ values in urea - INC treatment are reflected in the high recovery rate. This is similar in other treatments where, however, also higher NH_3 emissions accounted for the high N recovery. In the urea + UI treatment the N recovery was only 79 % however, did not differ significantly (Figure S2). Causes for the low recovery in the urea + UI treatment could be higher denitrification and N_2O production or NO loss.

However, minimal NH_3 emissions were measured at a greater incorporation depth than 7.5 cm (Rochette et al., 2013). Overall incorporation was the most effective option in case of NH_3 emission mitigation and this trial shows that UINI can achieve the same level of reduction potential as the single-inhibited variant UI. Nevertheless, the implementation of slit injection technique has several limitations in the field, which were investigated in another research project (Mallast et al., 2022). In soils that are too moist and have a high clay content, as well as in higher crops, like wheat and rape, the fertilizer cannot be incorporated using this technology and a traditional spreading method must be used (Mallast et al., 2022). The hypothesis put forward can only be partially accepted, as all mitigation measures showed an effect, but the strongest effect was achieved by incorporation instead of UI.

4.2. Effect of NH_3 mitigation technique on N_2O emissions

All three mitigation measures (INC, UI and UINI) did not lead to a significant increase in cumulative N_2O emissions compared to the reference treatment of surface broadcast urea at the end of the trial. However, the N_2O emission kinetics differ between the urea - INC and urea + UINI treatments. While the emission curve of broadcast urea and urea with UI show a very similar course, the N_2O emissions initially increase with urea addition, while the double-inhibited fertilizer shows almost no emissions for the first 10 days. This is in line, with the well-known dependency of N_2O losses on soil texture and soil moisture, since higher soil moisture in the sandy and clay soils can enhance the denitrification potential, as observed in other studies (Drame et al., 2023; Liu et al., 2022). In previous studies, surface incorporation has shown that pollution swapping from NH_3 to N_2O might occur (Mallast et al., 2022), especially on moist sandy soils (Götze et al., 2023). However, in our case the deep incorporation by closed slit injection did not increase cumulative N_2O emissions after 20 days, with a strong decline of emissions after 40 days. The addition of the combined UI and NI (2-NPT and MPA) to urea led to a significant reduction of N_2O emissions by up to 70 % compared to surface applied urea in the measurement period of 50 days. But, reflecting longer dry periods without

precipitation or other environmental impacts, N_2O emissions were later increased to the same level as in the single inhibited and broadcast urea treatments. It must be emphasized that the investigated scenario without N uptake by plants and rainfall, which are known to impact N_2O emission kinetics, are not directly transferable to practical conditions in the field. Nevertheless, the application of NI alone without plant N uptake may not be sufficient to reduce N_2O emissions over time and would require further measures.

In this incubation experiment, the recovery was at least 82 %. In contrast to the NH_3 Exp., the lowest recovery was detected in the treatment urea - INC, which can be attributed to the more difficult sampling procedure in this trial due to the slit injection and the sampling with soil corer in the soil columns.

Although NI could reduce N_2O emissions and thus significantly reduce the atmospheric concentration of a very climate-damaging greenhouse gas, further research on the non-target microbial communities needs to be conducted to compare the benefits of N_2O emissions reduction with the long-term environmental impacts. Overall, the hypothesis put forward can be partially rejected, since UINI did not show the greatest reduction potential over the whole incubation time. The use of UI did not promote the N_2O emissions and so incorporation except for the first trial days.

4.3. N_2O production and consumption processes

Even if the N_2O emissions of the different NH_3 mitigation measures tested did not lead to an increase in N_2O emissions compared to conventional surface urea application, the isotope analyses of soil-emitted N_2O provided short-term insights into the ongoing production and consumption processes. Results of the SP/O MAP and the FRAME model confirm a high contribution of N_2O production from nitrification for all treatments. A high contribution of nitrification was not surprising, since NH_4^+ -based fertilizers, like urea provide available NH_4^+ immediately. However, a such long lasting effect after six weeks of application was unexpected. After this time, most of the NH_4^+ applied with the fertilizer in the soil should have already been converted to NO_3^- (Figure S1) and thus likely promote the process of denitrification. However, in general the contribution of bacterial denitrification or nitrifier denitrification was rather low (Table 3), and the residual unreduced N_2O fraction (r) also showed that the most was emitted as N_2O and that the N_2O reduction played a more minor role under the prevailing soil conditions at the sampling day.

The urea and urea + UI treatments have a very similar N_2O course over time. This can also be confirmed in the proportions of the individual processes, which differed only very slightly for the two treatments. However, over time, the N_2O emissions of the urea + UINI treatment were in the opposite direction and the emissions increase continuously over the experimental period, although they were very low at the beginning. Overall, the urea + UINI emissions were only about half as high as the emissions from the urea and urea + UI treatment, but showed a higher proportion from the bD/nD fraction. This might be due to the delay of urea hydrolysis by the use of UI, which promoted NH_4^+ formation. In combination with NI, which might have reduced or delayed the oxidation of NH_4^+ to NO_3^- in soil, the NH_4^+ was probably more stable and N_2O production was somewhat delayed (Thapa et al., 2016). This assumption can be confirmed by the $N_{\min}$ sampling in the N_2O Exp., where 62 % of the mineral nitrogen in the UINI treatment was in the form of NH_4^+ (Figure S1). Moreover, available NH_4^+ potentially can be rapidly nitrified and then followed by denitrification compared to the use of urea alone (Akiyama, H., Yan, X., and Yagi, K., 2010), which might explain the increased bD/nD fractions.

Surface incorporation (urea - INC) can stimulate N_2O production in sandy soils up to 27 % (Götze et al., 2023). Moreover, fertilizer incorporation is known to stimulate the process of denitrification by the creation of anaerobic hot spots in soils, if soil moisture exceeds 70 % WFPS (Davidson, 1993), N_2O consumption, i.e. reduction to N_2 might

also occur and might explain a missing N losses in the N recovery (Table 2). However, soil moisture levels were with about 47 % WFPS in our experiment not ideal for complete denitrification, which was further underlined by findings of the SP/O MAP (Fig. 4) and the FRAME model.

4.4. Relevance for in situ conditions

One advantage of combined UI and NI is the reduced use of fertilizer due to the reduced emissions and higher nutrient use efficiency. Thus, saving costs on labour and fertilizer by reducing the frequency of fertilizer application (Abalos et al., 2014; Sanz-Cobena et al., 2012). Currently, however, the price of double-inhibited fertilizers is still higher than that of the single-inhibited variants, motivating a choice for economic over environmental aspects for farmers. To make a full cost-benefit assessment, yield effects also need to be taken into consideration. Additionally, use of nitrification inhibitors may also allow a reduction of the amount and frequency of fertilizer application, therefore saving costs (machine passes, fuel, hourly wages) and allowing more flexible timing of fertilization due to only two fertilizer applications (Abalos et al., 2014). Nonetheless, comparable effects could be attained by adapting the crop irrigation management or applying recommended amounts of fertilizer without the additional costs of the inhibited fertilizers. Reduced N application rates through the use of inhibited fertilizers without yield losses, making the inhibited product more economical. A holistic assessment should also consider the additional benefits of lower N application rates, such as the reduction in soil acidification caused by NO_3 leaching, which is associated with longer-term management costs (Rose et al., 2018). Moreover, since the emission reduction of inhibitors depends on the physicochemical soil properties and climatic conditions, the economic viability must be evaluated for each situation (Abalos et al., 2014; Klimczyk et al., 2021). Incorporation of urea into the soil is the most economic fertilization option. However, the simulated deep depot fertilizer machine by Rauch is hardly used by farmers, due to the purchase costs of an additional device. More research is required to optimize the combination of UI and NI and to develop practical machines for the incorporation of urea, especially under difficult conditions (wet, clayey or hardened soil) (Mallast et al., 2022), to increase environmental but also economic benefits (Thapa et al., 2016).

This study was conducted under controlled environmental conditions and, therefore, does not account for differences in weather, such as temperature, precipitation, time of day, or season. The experiments were conducted on disturbed soil columns without plant cover and N uptake. For these reasons, this trial should be supplemented by further laboratory tests and confirmed by field trials

5. Conclusions

All NH_3 mitigation options significantly reduced emissions, with closed-slit incorporation achieving the highest reduction compared to surface-applied urea. However, the NH_3 reduction from UI (2-NPT) and UINI (2-NPT+MPA) was lower than expected compared to meta-studies involving mainly the UI NBPT, highlighting the need for individual studies on various inhibitors to better understand their efficacy. In contrast to controlled environment studies, practical implementation of incorporation technology is challenging for many soil properties and conditions and due to limited machinery availability. The study showed that while urea + UINI treatment initially reduced N_2O emissions, N_2O release later on increased over a prolonged dry period without precipitation. Incorporation on the other hand reduced cumulative N_2O emissions in particular considering longer time periods. This highlights the need to differentiate the effect of UI and NI on emissions with and without canopy and crop N uptake. In situations with crops, effects of NI on short term cumulative N_2O emissions are more relevant than from soil without crops. The SP/O MAP approach with the FRAME model was useful for estimating N_2O production and consumption processes,

showing nitrification as the main source six weeks post-fertilizer application, with minor contributions from other processes as fungal denitrification. N_2O consumption occurred under experimental conditions, and further isotope sampling is recommended to study N_2O kinetics of UI and UINI in more detail. The presented data contribute to a conclusive assessment of inhibitor substances for which more laboratory and field studies under varying environmental and management conditions are required.

The interest in alternative fertilization methods with innovative injection and placement technologies to reduce the nitrogen problem is steadily increasing. However, many farmers are uncertain as to which regulations and rules will be introduced in the future, which is an obstacle to the willingness to invest. But next to the potential of inhibitor use to greatly improve the sustainability of N-fertilization and achieving globally accepted climate change targets, little is known about their potential to enter the food chain. Further studies with accurate and robust analytical methods for inhibitor detection are required to ensure that these additives do not pose any substantial threat to the environment, food safety and human health.

Supplementary Materials: The following supporting information can be downloaded at www.mdpi.com/xxx/s1, Figure S1: Mineral N content in the NH_3 Exp. (a) after two weeks and the N_2O Exp. after 37 days (b) of incubation with start N_{min} of the soil (grey line) and applied fertilizer N (orange line). Red letters indicate the compact letter display (Means not sharing any letter are significantly different by the Sidak test at the 5 % level of significance with 95 % confidence). Figure S2: Nitrogen balance (%) from urea fertilizer applied with standard surface application (urea), slit injection technique (urea – INC), urea + UI and urea + UINI; replicates and boxplots are in black, and red indicates the mean values and compact letter display (Means not sharing any letter are significantly different by the Sidak test at the 5 % level of significance with 95 % confidence). n=3. Table S1: Summary of mixing endmember isotopic signatures of particular pathways (bD – bacterial denitrification, nD – nitrifier denitrification, fD – fungal denitrification, Ni – nitrification) and reduction fractionation factors (reduction) with respective references. For the model input, each value is corrected with the respective mean isotopic signature of the substrate: for $\delta^{18}\text{O}_{\text{N}_2\text{O}}$ – soil water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) for bD, nD, and fD. The respective substrate-corrected values were applied as a model input for $\delta^{18}\text{O}_{\text{N}_2\text{O}}$. For $\delta^{15}\text{N}_{\text{N}_2\text{O}}^{\text{SP}}$ no substrate correction is needed. As the isotopic endmember ranges of nD and bD overlap considerably, a mean value was used for the 2D model. Figure S3: FRAME results of N_2O production/consumption process analyses of the urea treatment. Panels (a) and (d) show the observed N_2O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N_2O reduction by denitrification, along which the isotopocule ratios of the remaining N_2O are expected to increase if N_2O is reduced. Values are based on Table S1. Panel (b) and (e) show variable correlations based on model runs, using Histograms (on the diagonal) calculated from the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients (bottom-left). Panel (c) and (f) summarizes statistics on the simulation results of fractions of the different N_2O production processes and the residual unreduced N_2O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively. The box encloses the 68 % confidence interval (CI), and the whiskers show 95 % CI. Figure S4: FRAME results of N_2O production/consumption process analyses of the urea - INC treatment. Panels (a) and (d) show the observed N_2O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N_2O reduction by

denitrification, along which the isotopocule ratios of the remaining N_2O are expected to increase if N_2O is reduced. Values are based on Table S1. Panel (b) and (e) show variable correlations based on model runs, using Histograms (on the diagonal) calculated from the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients (bottom-left). Panel (c) and (f) summarizes statistics on the simulation results of fractions of the different N_2O production processes and the residual unreduced N_2O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively. The box encloses the 68 % confidence interval (CI), and the whiskers show 95 % CI. **Figure S5:** FRAME results of N_2O production/consumption process analyses of the urea + UI treatment. Panels (a) and (d) show the observed N_2O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N_2O reduction by denitrification, along which the isotopocule ratios of the remaining N_2O are expected to increase if N_2O is reduced. Values are based on Table S1. Panel (b) and (e) show variable correlations based on model runs, using Histograms (on the diagonal) calculated from the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients (bottom-left). Panel (c) and (f) summarizes statistics on the simulation results of fractions of the different N_2O production processes and the residual unreduced N_2O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively. The box encloses the 68 % confidence interval (CI), and the whiskers show 95 % CI. **Figure S6:** FRAME results of N_2O production/consumption process analyses of the urea + UINI treatment. Panels (a) and (d) show the observed N_2O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N_2O reduction by denitrification, along which the isotopocule ratios of the remaining N_2O are expected to increase if N_2O is reduced. Values are based on Table S1. Panel (b) and (e) show variable correlations based on model runs, using Histograms (on the diagonal) calculated from the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients (bottom-left). Panel (c) and (f) summarizes statistics on the simulation results of fractions of the different N_2O production processes and the residual unreduced N_2O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively. The box encloses the 68 % confidence interval (CI), and the whiskers show 95 % CI.

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CRediT authorship contribution statement

Lea Eder: Writing – review & editing, Validation, Methodology, Investigation, Data curation. **Caroline Buchen-Tschiskale:** Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis. **Hannah Götze:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Andreas Pacholski:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.agee.2024.109307](https://doi.org/10.1016/j.agee.2024.109307).

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4.3 Comparison and evaluation of different methods to determine NH₃ emission after urea fertilization small plot field experiments

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Keywords: Urea fertilization; replicated field plot; inverse dispersion model; integrated horizontal flux method; Dräger tube method; Alpha sampler

Abstract: Ammonia (NH₃) emissions affect the environment, climate and human health and originate mainly from agricultural sources like synthetic nitrogen fertilizers. Accurate and replicable measurements of NH₃ emissions are crucial for research, inventories and evaluation of mitigation measures. There exist specific application limitations of NH₃ emission measurement techniques and a high variability in method performance between studies, in particular from small plots. Therefore, the aim of this study was the assessment of measurement methods for ammonia emissions from replicated small plots. Methods were evaluated in 18 trials on six sites in Germany (2021–2022). Urea was applied to winter wheat as an emission source. Two small-plot methods were employed: inverse dispersion modelling (IDM) with atmospheric concentrations obtained from Alpha samplers and the dynamic chamber Dräger tube method (DTM). Cumulative NH₃ losses assessed by each method were compared to the results of the integrated horizontal flux (IHF) method using Alpha samplers (Alpha IHF) as a micrometeorological reference method applied in parallel large-plot trials. For validation, Alpha IHF was also compared to IHF/ZINST with Leuning passive samplers. Cumulative NH₃ emissions assessed using Alpha IHF and DTM showed good agreement, with a relative root mean square error (rRMSE) of 11%. Cumulative emissions assessed by Leuning IHF/ZINST deviated from Alpha IHF, with an rRMSE of 21%. For low-wind-speed and high-temperature conditions, NH₃ losses detected with Alpha IDM had to be corrected to give acceptable agreement (rRMSE 20%, MBE+2kgNha⁻¹). The study shows that quantification of NH₃ emissions from small plots is feasible. Since DTM is constrained to specific conditions, we recommend Alpha IDM, but the approach needs further development.

Article

Assessment of Different Methods to Determine NH₃ Emissions from Small Field Plots After Fertilization

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Abstract

Ammonia (NH₃) emissions affect the environment, climate and human health and originate mainly from agricultural sources like synthetic nitrogen fertilizers. Accurate and replicable measurements of NH₃ emissions are crucial for research, inventories and evaluation of mitigation measures. There exist specific application limitations of NH₃ emission measurement techniques and a high variability in method performance between studies, in particular from small plots. Therefore, the aim of this study was the assessment of measurement methods for ammonia emissions from replicated small plots. Methods were evaluated in 18 trials on six sites in Germany (2021–2022). Urea was applied to winter wheat as an emission source. Two small-plot methods were employed: inverse dispersion modelling (IDM) with atmospheric concentrations obtained from Alpha samplers and the dynamic chamber Dräger tube method (DTM). Cumulative NH₃ losses assessed by each method were compared to the results of the integrated horizontal flux (IHF) method using Alpha samplers (Alpha IHF) as a micrometeorological reference method applied in parallel large-plot trials. For validation, Alpha IHF was also compared to IHF/ZINST with Leuning passive samplers. Cumulative NH₃ emissions assessed using Alpha IHF and DTM showed good agreement, with a relative root mean square error (rRMSE) of 11%. Cumulative emissions assessed by Leuning IHF/ZINST deviated from Alpha IHF, with an rRMSE of 21%. For low-wind-speed and high-temperature conditions, NH₃ losses detected with Alpha IDM had to be corrected to give acceptable agreement (rRMSE 20%, MBE +2 kg N ha^{−1}). The study shows that quantification of NH₃ emissions from small plots is feasible. Since DTM is constrained to specific conditions, we recommend Alpha IDM, but the approach needs further development.

Keywords: urea fertilization; replicated field plot; inverse dispersion model; integrated horizontal flux method; Dräger tube method; Alpha sampler



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1. Introduction

Ammonia (NH₃) is a globally important air pollutant mainly emitted from agricultural sources. These emissions have negative effects on human health and on the environment

by contributing to the formation of fine particulate matter (PM_{2.5}) [1], eutrophication [2], acidification and loss of biodiversity [3]. With the new National Emission Ceilings Directive (NEC Directive) of the European Union 2016/2284, Germany has committed itself to reducing national emissions of NH₃ by 29% in 2030 compared to 2005. Emissions from synthetic nitrogen fertilizers, with a high share of emissions connected to urea fertilization, contributed about 7% of total German emissions in the year 2021 [4]. Since the year 2020, urea fertilizer may only be applied in combination with a urease inhibitor or, alternatively, has to be incorporated within four hours after application.

Nevertheless, knowledge about NH₃ losses from synthetic fertilizers (e.g., emission factors) and about the effectiveness of emission mitigation measures under field conditions (e.g., fertilizer form, application methods) is still limited for many agro-ecological conditions [5]. In order to relate emission measurements to fertilizer types and mitigation options, replicated plot trials (multi-plot) are a key prerequisite for statistical evaluation and scientific validation. This is particularly needed if the agronomic efficacy of mitigation measures, often considered an additional beneficial effect of emission mitigation, is to be concomitantly assessed.

Common approaches include micrometeorological methods, static and dynamic chambers (enclosures) and sampling methods (e.g., passive samplers) [6,7]. Due to the large area required, micrometeorological methods are limited to the assessment of mitigation measures with repeated field plot trials. This disadvantage is overcome by enclosure methods like chamber systems and wind tunnels, among which a wide range of different designs exists. These can be applied on small plots in multi-plot experiments. However, they alter the ambient micrometeorological conditions of the NH₃ emission process and integrate only over small areas [8,9]. In general, due to specific application limitations, no internationally accepted standard method for NH₃ emission measurement which is more sensitive, selective, robust, low-cost and user-friendly [10,11] has been defined yet for replicated small-plot field trials.

Studies comparing different methods of NH₃ concentration measurement and NH₃ emission flux calculation for fertilized agricultural sites showed that results of similar flux levels can be obtained with different micrometeorological measurement methods, as well as with chamber methods [9]. The most important micrometeorological measurement techniques comprise the integrated horizontal flux method (IHF) [12], the backward Lagrangian stochastic dispersion technique (bLS) [13–15], the aerodynamic flux gradient method [16], the ZINST (height *z*, independent of stability) method [17] and the eddy covariance method [18,19]. These methods share the advantage of a low influence of small-scale heterogeneities (e.g., fertilizer distribution, plant growth, soil properties) as they integrate over larger areas. Since the IHF method is well established, robust and widely applied, it is often used as a reference basis for the evaluation of new measurement methods in comparative studies [9,20]; alternatively, its simplification, ZINST, is used [21].

The aim of this study was therefore to compare and evaluate the accuracy of two practically suitable small-plot methods against a micrometeorological reference method at sites with different soil and climate conditions across Germany. As a reference, the IHF approach with Alpha samplers, employed for the measurement of atmospheric NH₃ concentration profiles (Alpha IHF), was chosen [22]. Additionally, Alpha IHF reference being in an early stage of application, was tested against a second micrometeorological approach, the IHF and ZINST employing Leuning samplers [15,23,24].

The first tested method for small-scale measurements was the enclosure Dräger tube method (DTM) [25], which is considered and discussed as a quantitative dynamic chamber measurement method. Quantitative emissions under field conditions are obtained when raw flux data is corrected by an empirical calibration considering environmental factors

on chamber measurements [26]. The calibration approach was tested and validated in various studies by comparison with simple micrometeorological measurements [21,27]. However, recent studies showed deviations of this method from micrometeorological measurements after slurry application [28]. Furthermore, some studies reported critical aspects of this method in small-plot field trials [29–31], particularly highlighting the risk of cross-contamination of measurement chambers used sequentially on various plots and the detection limit.

As the second method, ammonia concentration measurement with passive Alpha samplers [32] in combination with inverse dispersion modelling (IDM) was chosen [33,34]. Ammonia concentration measurements with passive Alpha samplers have been validated for atmospheric concentrations up to 25 ppb [35]. Carozzi et al. [36,37] estimated NH_3 emissions from the surface application of dairy slurry using a micrometeorological approach. They used an inverse dispersion modelling technique associated with the sequential exposure of Alpha samplers (sampling time 12 h) and measurements of atmospheric turbulence. This combination of Alpha samplers with IDM can be considered superior to the dynamic chamber DTM due to being less intrusive, employing larger plot sizes and being closer to emission process. In addition, this approach is user-friendly and low-cost, and much larger number of plots can be simultaneously handled by one person. However, questions remain with respect to the sensitivity and quantitative validity compared to a reference method of Alpha samplers for this application [38].

During the studies in 2021 and 2022, urea was applied as emission source to winter wheat fields at multiple sites with simultaneous measurements on small and large plots. The experiments were carried out in six locations over Germany (north, $3 \times$ central and $2 \times$ south-west) with broadcast application of mineral urea fertilizer in winter wheat involving three split applications of the fertilizer, resulting in a total of eighteen field trials for this study. We hypothesized, based on a comparison with the reference IHF method, that (a) Alpha IDM is a suitable method to quantify NH_3 emissions in small plots, offering acceptable accuracy and precision, that it is (b) superior to the more time-intensive DTM and (c) that Alpha IHF shows good agreement with cumulative NH_3 emissions obtained with Leuning sampler IHF/ZINST.

2. Materials and Methods

2.1. Site Description and Experimental Design

Experiments following urea application in winter wheat (*Triticum aestivum* L., var. RGT Reform) were conducted in three regions in Germany. The following emission measurement methods were used: on large plots, (1) the IHF method with wind profile measurements and NH_3 concentration measurements with Alpha samplers and (2) the IHF and ZINST with Leuning sampler; on small plots, (3) a calibrated open dynamic chamber method with Dräger tubes and (4) the IDM method with Alpha samplers. For the first time, Alpha samplers in combination with inverse dispersion modelling and bLS were tested for this specific small-plot experimental design [5]. The small-plot experimental design was a randomized complete block design containing 32 small plots in four blocks with 8 plots each. This allowed for a comparison of eight different fertilizer treatments in quadruplicate (Figure S1 and Graphical Abstract); this study focuses on the urea and non-fertilized quadruplicates only. In the space between the small plots, non-emitting nitrate fertilizer was applied. At every location, min. 100 m downwind of the small-plot experiment, a large circular plot experiment was set up. The set up of this study is unique as it includes the same emission measurement methods and samplers simultaneously in one field site, as well as synchronized trials by different research groups (Kiel university (North), University of Hohenheim (South-West), Thünen-Institute (Central)) applying the same experimental

field design with various soil and weather conditions. The measurements methods used in the experiments and the conditions at the six sites are shown in Table 1.

All sites followed local best crop management practices. Urea was applied by broadcast application at optimum N fertilization levels, in three split applications, with total N application rates ranging from 145 to 206 kg N ha⁻¹. This resulted in 18 measurement campaigns lasting between 7 and 19 days. All experimental plots were placed in one homogenous experimental field at each study site. Measurement plots were surrounded by a wide area (2–4 ha) managed with non-emitting fertilizer to establish an even canopy surface. Therefore, the surrounding area and the guard area in the small multi-plot trials were supplied with Ca(NO₃)₂ fertilizer at the same N rate as inside the trial plots. All fertilizers were surface-applied by machinery (pneumatic spreader, drop spreader). The weather conditions, mean air temperature, wind speed at 2 m height, standardized rain and relative humidity during the measurement campaigns for each year and location are shown in Table S1.

As a micrometeorological reference method, IHF was applied with Alpha samplers [22] in one fertilized circular plot (20 m diameter, 1257 m²; central 170 m diameter, 15,394 m²) per site and experiment. A second measurement mast was placed upwind to sample background NH₃ emissions. The atmospheric NH₃ concentration profile was detected by a triplicate of Alpha samplers per measurement height with a time step of one day. The IHF and ZINST methods were also employed, using Leuning samplers for comparison due to their establishment in fertilizer emission measurements. Both sampler types were placed at five heights (0.25, 0.55, 0.95, 1.7 and 2.7 m) in the centre of the circular fertilized plot and at three heights (0.25, 0.95 and 2.7 m) in the background mast (heights measured from the canopy surface).

In the small-plot experiment, triplicates of Alpha samplers were placed at 0.25 m [33] above the canopy in the centre of the small plots (side length 9 m, 81 m²) that either received no synthetic fertilizer ($n = 3$) or were fertilized with urea ($n = 4$). Samplers were exchanged in daily intervals. Higher sampling frequencies were not applied due to low emission levels and associated low atmospheric NH₃ concentrations requiring long exposure times for sensitive passive sampling. Each small plot was completely surrounded by a guard area of the same dimension [21]. In addition, the DTM was also used on urea ($n = 4$) and the control plots ($n = 3$).

Table 1. Overview of the study sites.

		Central		North		South-West	
Location	Hachum Central 1	Sicke Central 1	Meine Central 2	Hohenschulen North	Hohenheim South-West1	Eckartsweiler South-West 2	
Experiments	I-SI, II-SI, III-SI	I-SI, II-SI, III-SI	I-ME, II-ME, III-ME	I-HS, II-HS, III-HS	I-HO, II-HO, III-HO	I-EW, II-EW, III-EW	
Year	2021			2022			
Application date	23 March 27 April and 25 May	15 March, 20 April and 19 May	17 March, 21 April and 17 May	15 March, 27 April and 8 June	28 March, 9 May and 10 June	08 March, 22 April and 24 May	
Duration of experiment [d]	16, 8, 13	16, 14, 11	14, 14, 14	18, 13, 13	7, 11, 17	19, 7, 15	
Measurement methods	Leuning IHF, Alpha IHF, Alpha IDM, DTM, passive sampler	Alpha IHF, Alpha IDM, DTM	Leuning ZINST, Alpha IHF, Alpha IDM, DTM	Leuning ZINST, Alpha IHF, Alpha IDM, DTM	Leuning ZINST, Alpha IHF, Alpha IDM, DTM	Leuning ZINST, Alpha IHF, Alpha IDM, DTM	
Application rate [kg N ha ^{−1}]	40, 70, 60	60, 60, 50	50, 50, 45	60, 70, 60	50, 50, 50	68.5, 68.5, 68.5	
BBCH	22, 30, 39	24, 30, 37	23, 32, 38	23, 31, 51	23, 32, 65	22, 32, 55	
Crop height [m]	0.05, 0.25, 0.65	0.05, 0.2, 0.55	0.05, 0.2, 0.65	0.05, 0.25, 0.70	0.05, 0.45, 0.9	0.05, 0.3, 0.9	
Coordinates North/East	52.111943/10.411358	52.20258681/10.63550590	52.38728164/10.56251223	54.314768/9.998371	48.716286/9.18853	48.518299/7.869955	
Sand [mass-%]	36.78	48.6	68.61	52.54	7.87	33.73	
Silt [mass-%]	37.3	37.3	24.24	31.98	69.3	49.97	
Clay [mass-%]	10.7	14.1	7.15	15.49	22.83	16.3	
TOC [mass-%]	1.64	1.57	1.35	1.22	1.36	1.02	
TC [mass-%]	1.66	1.62	1.39	1.24	1.42	1.02	
CEC [cmol kg ^{−1}]	12.51	13.05	7.52	12.29	14.42	9.08	
pH (CaCl ₂) [mol L ^{−1}]	6.02	6.36	6.59	6.84	6.78	5.97	

2.2. NH_3 Sampling for Atmospheric Concentrations

Micrometeorological measurements with Alpha sampler (IHF) and Leuning sampler (IHF and ZINST) were conducted on large circular plots. In the small plots, IDM with concentration measurement from Alpha samplers and the DTM with Dräger tubes (Table 2) were applied.

Table 2. Overview of applied methods and measurement scales.

Scale	Plot Size	Sampler/Sampling Height	Flux Calculation	References
Small multi-plot	$9 \times 9 \text{ m} = 81 \text{ m}^2$	Dräger tubes (Exhaust air from dynamic chamber)	DTM	[25,26]
		Alpha sampler 0.25 m above canopy	IDM	[13–15,32]
Large circular plots	r = 20 m/1257 m ² location Central 1: r = 70 m/15,394 m ²	Alpha sampler 0.25, 0.55, 0.95, 1.7 and 2.7 m above canopy	IHF	[22]
		Leuning sampler 0.25, 0.55, 0.95, 1.7 and 2.7 m above canopy	IHF ZINST	[12,17,39,40]

2.2.1. Alpha Sampler

Alpha samplers (Adapted Low-cost Passive High Absorption diffusive samplers, UKCEH) [32] were used to measure atmospheric NH_3 concentrations. These passive samplers are based on the principle of gas diffusion through a polytetrafluoroethylene (PTFE) membrane, where the emitted NH_3 is absorbed on a filter paper coated with 12% citric acid. In the field, samplers were exposed in triplicates and changed approximately once a day. The concentration measurements have been validated for atmospheric concentrations up to 25 ppm [35] and against online instruments in situ [41]. For analysis, the coated filters were extracted with 3 mL deionized water for at least one hour. The measurement of the extracts was carried out with an ammonia selective electrode (Thermo Scientific Orion Versa Star Pro Electrochemistry Meters, Waltham, MA, USA) or a U-3210 Spectrometer (Hitachi High-Tech Europe GmbH, Krefeld, Germany). In a round-robin test, the accuracy of the NH_3 measurements of all participating labs was checked and validated. The air concentration of NH_3 was calculated from the amount of NH_3 absorbed from the extracts and the effective volume of air sampled [32].

2.2.2. Leuning Sampler

Leuning samplers capture the emitted NH_3 by the horizontal flow through the sampler's large inner surface, which is coated with oxalic acid and rotates in the direction of the wind. The sampling provides the product of wind speed and NH_3 concentration, and thus the NH_3 emission from the surface can be determined as horizontal NH_3 transport without additional wind speed measurement [40]. The mean horizontal flux at each sampler height is determined from the concentrations of the extracts measured with an ammonia-selective electrode (Thermo Scientific Orion Versa Star Pro Electrochemistry Meters, Waltham, MA, USA).

2.2.3. Dräger Tubes

The quantitative dynamic chamber method [25] employs Dräger tubes to obtain chamber head space ammonia concentrations for the estimation of NH_3 emissions under field conditions. In the field, air is pumped into the Dräger tubes using the Dräger X-

act 5000 Basic electric pump from Drägerwerk AG & Co. KGaA (Lübeck, Germany). Dräger tubes cover concentration ranges between 0.25 and 30 ppm; concentrations below 0.25 ppm are detected by enlarging the volume of air passed through the tubes compared to standard volume.

2.3. Flux Calculations for NH_3 Losses

2.3.1. Integrated Horizontal Flux

The integrated horizontal flux (IHF) method is a micrometeorological mass balance technique used to assess the horizontal flux based on measurements taken upwind and in the middle of a source [12,39]. To apply this method, the concentration is measured at multiple heights (usually four or more), and the concentration data is typically averaged over hours to several days. For larger measurement areas, extrapolation above the maximum height is necessary [42]. From the individual horizontal fluxes, the vertical flow of the entire fertilized round plot is determined by integration and summation [40]. Each horizontal flux is calculated using Equation (1) from the product of wind speed (u) and ammonia concentration (ρ_A) minus background flux ($u\rho_{AB}$) over a radius of the circular fetch (X) and z the height of the sampler over the circular area. Samplers were exchanged daily in this study.

Vertical NH_3 flux from the fertilized area with IHF:

$$F = \frac{1}{X} \int_0^z (u\rho_{AC} - u\rho_{AB}) dz \quad (1)$$

IHF with Alpha samplers

The logarithmic wind profile $u(z)$ was determined through linear regression of measured wind speeds as a function of height (z) with the roughness length (z_0) and the estimated parameter B . By implementing the canopy-specific zero-plane displacement height (d), Equation (2) can be derived.

Logarithmic wind profile:

$$u(z) = B * \log\left(\frac{z-d}{z_0}\right) \quad (2)$$

The NH_3 concentration profile $c(z)$ is described by an exponential function, with decreasing NH_3 concentration (c) with increasing z . The reason for using an exponential function is that the decrease in c is directly related to the concentration below [43] Equation (3).

NH_3 concentration profile with Alpha IHF:

$$c(z) = \alpha + \beta * \exp(-\delta z) \quad (3)$$

The integration of both the NH_3 concentration profile and the wind profile represents the NH_3 emission (F) with the fetch (X) from the source area to the sample mast, as shown in Equation (4).

Vertical NH_3 flux from the fertilized area with Alpha IHF:

$$F = \frac{1}{X} \int_{d+z_0}^{z_p} [c(z) - \alpha] u(z) dz \quad (4)$$

IHF with Leuning sampler

To calculate the vertical flux from the different horizontal fluxes, first, each interval is integrated by the average of the fluxes $u_i\rho_i$ (corrected for background concentrations)

in the fertilized area (Equation (1)) at two heights ($\text{mg NH}_3\text{-N m}^{-2} \text{ h}^{-1}$). Subsequently, it is summed up and multiplied by the height increment (Δh_i) between sampler i and sampler $i - 1$ (m) (Equation (5)) [23]. The horizontal flux of the lowest measuring height was assumed for the lowest horizontal flux increment. The sum of the increments over the five IHF heights is divided by the fetch (X).

Vertical NH_3 flux from the fertilized area with IHF Leuning sampler:

$$F_S = \frac{1}{X} \sum_{i=1}^5 \frac{(u_{i-1}\rho_{i-1} + u_i\rho_i)}{2} * \Delta h_i \quad (5)$$

2.3.2. ZINST Method

As a simplification of the integrated horizontal flux method, the measurement at ZINST height (height z , independent of stability) was published [17]. Using the predictions of a trajectory simulation model of turbulent dispersion, it is shown that the emission from a circular source surface can be calculated from measurements of a single height, the ZINST height. This requires the mean wind speed and the mean concentration at that height (i.e., horizontal NH_3 flux). From the dependence of a function of the roughness length z_0 and the source surface radius R , a stable representative measurement height is obtained, independent of turbulence conditions (Equation (6)). The corrected horizontal flux (F_{ZINST}) over the surface is given by the quotient of the measured flux in ZINST height ($u\rho_{ZINST}^{measured}$) and the correction factor ($c \times wd \times F^{-1}$) [17].

Vertical NH_3 flux from the fertilized area with ZINST Leuning sampler:

$$\frac{u\rho_{ZINST}^{measured}}{F_{ZINST}} = \left(\frac{c * wd}{F} \right)^{given \ on \ graph} \quad (6)$$

2.3.3. Inverse Dispersion Modelling (IDM) with the Backward Lagrangian Stochastic Dispersion Model

The emission flux from small plots was estimated using the backward Lagrangian stochastic dispersion technique (bLS) [13–15]. The bLS approach enables estimation of the emission rate from a downwind concentration measurement. The emission rate (F , $\text{mg m}^{-2} \text{ s}^{-1}$) is derived according to Equation (1).

The bLS model operates backwards in time by modelling the transport of air based on the atmospheric conditions. The model [13] was used with the software “WindTrax” (Thunder Beach Scientific, Halifax, NS, Canada), a freeware tool which combines an interface of mapped sources and sensors with the bLS model for simulating short-range atmospheric dispersion to estimate the NH_3 flux in half-hour intervals. The output of the bLS model is the concentration-to-emission ratio from a specific source ($C \times F^{-1}$), which is calculated based on the exact location of the source and of the sensors (Equation (7)).

Derivation of the emission from measured concentrations using an inverse dispersion model:

$$F = \frac{C}{\left(\frac{C}{F}\right)_{sim}} \quad (7)$$

where C is the time average gas concentration ($\mu\text{g NH}_3 \text{ m}^{-3}$), and $(C \times F^{-1})_{sim}$ ($\text{mg s}^{-1} \text{ m}^{-2}$) is simulated by means of the inverse dispersion model [44]. The flux was calculated for each averaging interval by simulating the backward air motion from the sensor. $(C \times F^{-1})_{sim}$ is averaged over the exposition time of the corresponding sampler; therefore, the emission rate F ($\mu\text{g NH}_3 \text{ s}^{-1} \text{ m}^2$) applies for the whole exposition time. To calculate the total losses, F is cumulated over the sampling time intervals while subtracting the mean of the unfertilized background plots.

The input data used for WindTrax was half-hourly wind speed (u) derived from sonic or cup anemometers. Friction velocity (u^*) [m s^{-1}] was determined by using the converted wind profile equation (Equation (6)) [45] with von Kármán constant ($k = 0.41$), the windspeed from a sonic anemometer at 2 m height (z_u) and the displacement height (d) (Equations (8) and (9)). The surface roughness length (z_0) is obtained directly by wind profile measurements (height where $u = 0$) [45] if windspeed measurements were conducted in at least three different heights. Otherwise, z_0 is set to 15% canopy height (z_{canopy}) [m].

Friction velocity u^* :

$$u^* = (k * u) / \ln\left(\frac{z_u - d}{z_0}\right) \quad (8)$$

Zero-plane displacement height d :

$$d[m] = \frac{2}{3} * z_{canopy} \quad (9)$$

For the characterization of the atmospheric stability condition as the third input parameter for bLS calculations, the classification of Pasquill–Gifford classes for all 30 min intervals was estimated. This was achieved by calculating the standard deviation of the horizontal wind direction (σ_θ) [$^\circ$] at a 2 m height using a sonic anemometer (Table S2). This approximation of atmospheric stability was found to be viable for short-term considerations (10–60 min) [46]. The calculation of the mean and standard deviation values of wind directions for all 30 min intervals was performed by the Yamartino method [47].

For each flux estimate made by bLS, 50,000 particle trajectories were employed. The trajectories that touch the ground inside the source area and their respective vertical velocities were used to calculate $C \times F^{-1}$, which is explained in detail by [48]. The performance of the bLS model is influenced by atmospheric conditions/turbulence, and filtering ensures that only data with high accuracy is included [13]. Intervals were discarded if one of the following restrictions applied: first, $u^* < 0.1 \text{ m s}^{-1}$ (indicator for very low windspeed) [49] or, second, $z_0 > \text{canopy height}$. If data gaps occurred in case of discarded sampling intervals due to inapplicable u^* values, the following gap filling procedure was performed: If data gaps occurred during night time, no gap filling was applied, since NH_3 emissions during the night are assumed to be low and therefore negligible [50]. Data gaps during the day were linearly interpolated if they were 1 h or shorter. Longer gaps were corrected through mean diurnal variation [51], for which the average of the same time stamp of the previous and the next day is used. Daily sunrise and sunset times were extracted from the U.S. Naval Observatory (USNO AAD, 2024) database using the location coordinates of each individual site.

2.3.4. Dräger Tube Method

The NH_3 flux is calculated by the air volume (V) sucked through the chambers, the concentration (C), the temperature-dependent density (ρ) of NH_3 , the molecular weight conversion factor (U_N), the surface area conversion factor (U_F) and the time conversion factor (U_Z) Equation (10).

NH_3 flux from the fertilized area with the Dräger tube method:

$$F_{Ng} = V * C * 10^{-6} * \rho_{\text{NH}_3} * U_N * U_F * U_Z \quad (10)$$

The emissions detected with the Dräger tubes were combined with an empirical calibration for the consideration of environmental factors on chamber measurements [52]. The calibration approach was validated in various studies by comparison with the micrometeorological measurements (IDM and ZINST) used with different concentration measurement methods [21,27,53].

For the conversion, the effect of varying ambient wind speeds at a 2 m height (WS_{2m}) on chamber measurements (Equation (11)) is considered.

Empirical calibration of fluxes detected by the Dräger tube method:

$$\ln(F_{DTM}) = 0.444 * \ln(F_{Ng}) + 0.59 * \ln(WS_{2m}) \quad (11)$$

To cover the diurnal variation in NH_3 fluxes, the measurements are distributed over the day and integrated by the trapezoid rule. Measurements at the beginning and end of the emission period each day are important to avoid overestimation of the night time fluxes. DTM measurements therefore included 3–5 measurements per day during the experimental campaign.

Plots with missing measurements, which lead to an overestimation of the fluxes during the night, were excluded from further analysis. Additionally, the following criteria usually led to an overestimation of the fluxes and were therefore excluded from the data set: fewer than three DTM measurements per day or no measurements for more than two days in a row.

2.4. Statistics

Differences between measurement methods were initially explored by a graphical comparison of dynamics over time and afterwards by a numerical comparison of cumulative emissions through linear regression. To estimate the relative magnitude of differences in total cumulative emission, Alpha IHF was set as reference method. The final cumulative losses were compared by different criteria: The mean bias error (MBE, unit according to variable) and the relative root mean squared error (rRMSE in %) (Equations (12) and (13)), with y_i being the actual observations and $\hat{y}_i$ the predicted/reference values.

Mean bias error:

$$MBE = \frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (12)$$

Relative root mean squared error:

$$rRMSE = \sqrt{\frac{\frac{1}{n} \sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=0}^n (\hat{y}_i)^2}} * 100 \quad (13)$$

Given the inevitable occurrence of errors during measurements under field conditions and given the numerous factors contributing to differences in the true emissions of the 18 trials, an estimation of all individual variables in emissions is impossible. A recent study estimated the relative uncertainty in total emissions measured with micrometeorological methods at 24 and 31% of the measured value (standard deviation) [28]. In addition, the relative systematic error in micrometeorological methods (bLS and IHF) was estimated in measurements to be about 25%, as standard deviation among methods based on random-effects models. The rRMSE, a dimensionless form of RMSE, scales residuals against actual values, allowing for the comparison of different measurement techniques. Often, rRMSE is excellent if it is <10%, good if it is between 10 and 20%, fair if it is between 20 and 30% and poor if it is >30%. In the context of this study, considering ranges of uncertainty found in other experiments, the evaluation limits for the rRMSE are set as follows: excellent if <15%, good if <25%.

The difference in cumulative emissions estimated using the micrometeorological reference method Alpha IHF and the other tested methods was calculated. In case of high deviations occurring between Alpha IHF and Alpha IDM, Pearson correlation tests with environmental factors were conducted. Afterwards, if such deviations could be related to specific soil or weather parameters, the relevant values could be corrected after the

determination of a correction algorithm. Values with high deviations were corrected with the help of the regression between the cumulative NH_3 losses from the reference and the respective comparison method. This correction is conducted by using the reciprocal of the slope or the intercept from the regression equation. For the Alpha IDM, which has been developed further within this study, an additional data set from 2023 comprising 8 study sites (Table S3) with 20 measurement campaigns (with both Alpha IDM and Alpha IHF) was used to test the correlation and validity of the correction algorithm.

Statistical analysis was conducted using R version 4.2.1 (R Core Team, 2019). All graphical representations were created using appropriate R packages, including [ggplot2].

3. Results

3.1. Cumulative NH_3 Emissions Estimated by Different Methods

In most cases, the cumulative emissions of the measurement campaigns showed a saturation curve after the application of urea (Figure 1; three exemplary locations: North, Central 2 and South-West 1). While the measured cumulative emission curves of the individual campaigns generally agree between DTM and Alpha IHF, the processes determined with Leuning IHF/ZINST and Alpha IDM appear to deviate more strongly. At location North, NH_3 emissions lasted longer in contrast to location South-West 1. At location Central 2, a sharp increase in emission losses in the first four days occurred. This kinetic was recorded consistently with all methods, but with IDM, it was recorded at an upwardly deviating level. The median of the cumulative NH_3 emissions of the 18 measurement campaigns was $3.27 \text{ kg N ha}^{-1}$ (mean $5.97 \text{ kg N ha}^{-1}$). The trials in Central 2 had the highest emissions, with a median of $10.9 \text{ kg N ha}^{-1}$ (mean $12.8 \text{ kg N ha}^{-1}$), despite featuring the lowest application rate (50, 50 and 45 kg N ha^{-1}). Other than differences between locations, seasonal differences between campaigns show an influence on NH_3 emissions. Emissions were highest in the first campaign, with a median of 7.2 kg N ha^{-1} (mean $8.07 \text{ kg N ha}^{-1}$). The median of the cumulative NH_3 emissions detected with Alpha IHF was $2.57 \text{ kg N ha}^{-1}$ (mean $5.12 \text{ kg N ha}^{-1}$), and with DTM, it was $2.38 \text{ kg N ha}^{-1}$ (mean $4.05 \text{ kg N ha}^{-1}$).

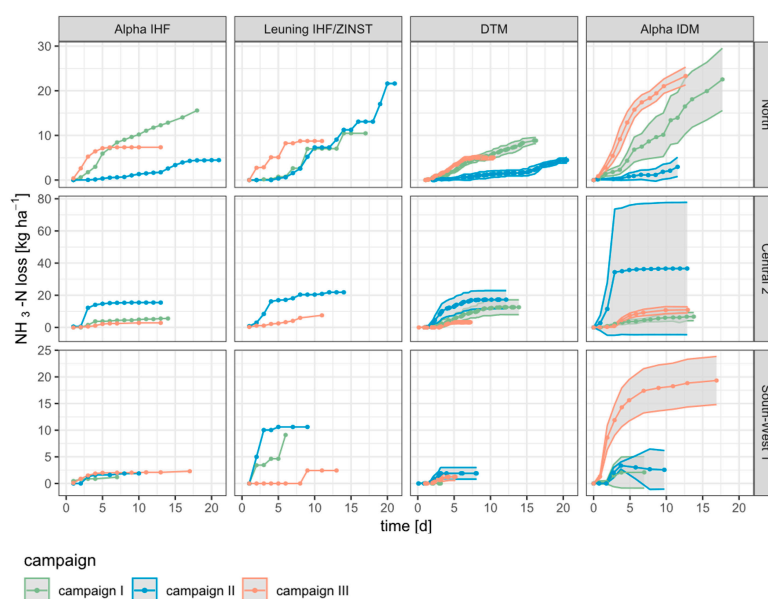


Figure 1. Cumulative NH_3 -N losses detected by the different methods: IHF with Alpha sampler ($n = 1$), IHF/ZINST with Leuning ($n = 1$), the DTM ($n = 4$) and Alpha sampler IDM ($n = 4$) in small plots at three exemplary locations, North (**top**), Central 2 (**middle**) and South-West 1 (**bottom**), in 2022 (Table 1). The different colours of the curves represent the campaigns and the grey areas represent the standard deviation for Alpha IDM and DTM.

3.2. Comparison of Cumulative NH_3 Emissions

The differences in cumulative NH_3 emissions detected by the reference Alpha IHF compared to the two small-plot methods and the Leuning IHF/ZINST are shown in Figure 2. Across all locations and campaigns, higher deviations were detected on average with Alpha IDM (median $6.45 \text{ kg N ha}^{-1}$, mean $8.53 \text{ kg N ha}^{-1}$) compared to Alpha IHF. For DTM, the deviation of losses had a median of $-0.24 \text{ kg N ha}^{-1}$ (mean $-0.45 \text{ kg N ha}^{-1}$), showing an underestimation of NH_3 losses, and for Leuning IHF/ZINST, on large plots, a median of $1.93 \text{ kg N ha}^{-1}$ (mean $3.19 \text{ kg N ha}^{-1}$) was observed. After the correction of the Alpha IDM values, the deviation was smaller and in the range of the second micrometeorological method Leuning (IHF/ZINST), with a median of $1.03 \text{ kg N ha}^{-1}$ (mean $2.24 \text{ kg N ha}^{-1}$) (Figure 2).

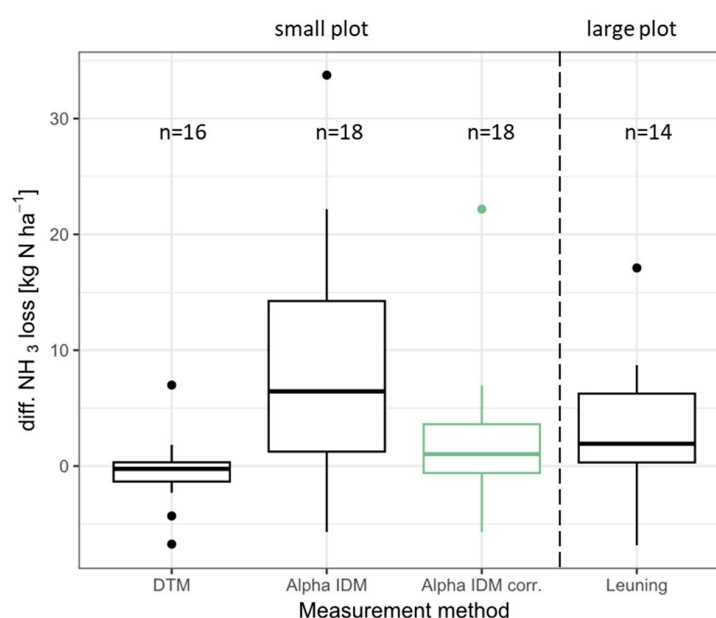


Figure 2. Difference in cumulative NH_3 emissions from urea applied to winter wheat between the reference method Alpha IHF and the two small-plot methods, DTM and Alpha IDM, and the large-plot method, Leuning IHF/ZINST (black), as well as after the application of the correction factor 0.27 on Alpha IDM (green), with the number of replicates in black.

The cumulative losses of the two small-plot methods, DTM and Alpha IDM, and the Leuning IHF/ZINST method are related to the reference method Alpha IHF in scatterplots (Figure 3).

The cumulative losses of the DTM and Alpha IHF showed high agreement, especially in the low measuring range $<5 \text{ kg N ha}^{-1}$ (Figure 3a). With a value of 11% (Table 3), the rRMSE is ranked into the excellent range according to the quality classes selected in this study. On the other hand, the cumulative losses of Alpha IDM and Alpha IHF show low agreement, with an rRMSE of 40%. The Alpha IDM method significantly overestimated NH_3 emissions. The Leuning IHF/ZINST method tended to detect higher emissions, but with an rRMSE of 21%, it is ranked in the acceptable evaluation limit.

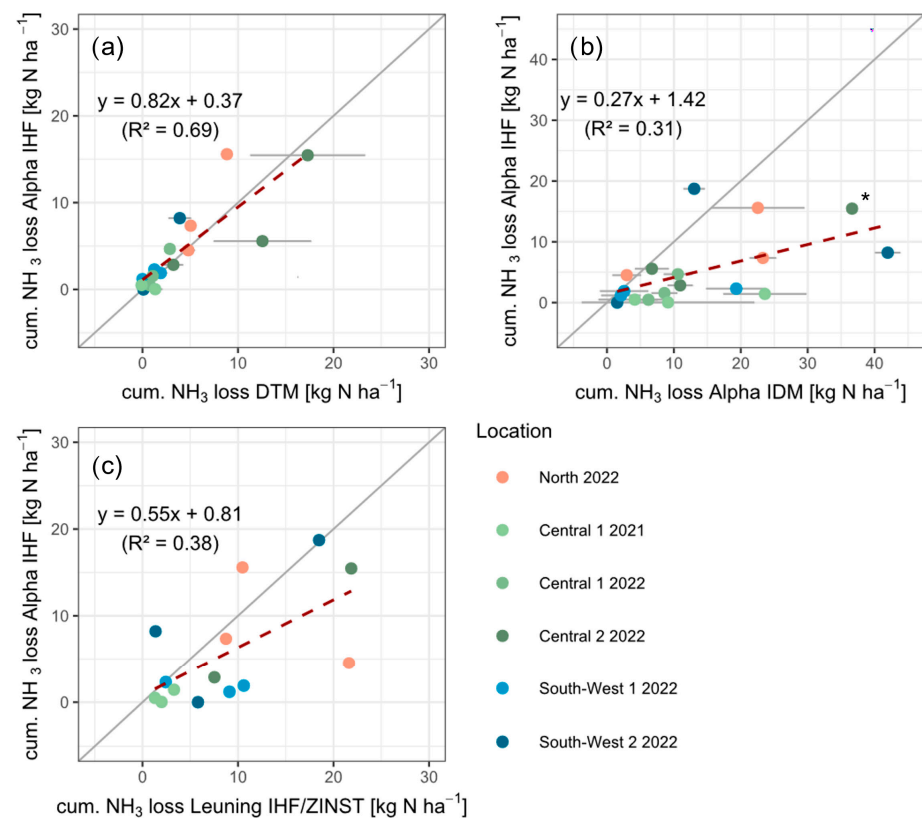


Figure 3. Comparison of the reference method IHF with Alpha sampler with (a) DTM and (b) IDM with Alpha sampler used in the small plots, as well as with (c) IHF/ZINST with Leuning sampler used in the large plots from 18 trials. Error bars represent the standard deviation of 4 replicates (DTM and Alpha IDM). The red dotted line represents the orthogonal regression line equal to the equation shown. The solid grey line represents a 1:1 slope. * standard deviation is 41 kg N ha^{-1} of Central 2, 2022.

Table 3. Comparison of the reference method Alpha IHF with (a) IHF/ZINST with Leuning sampler, (b) the DTM and (c) Alpha sampler used in the small plots by different criteria: the relative root mean squared error (rRMSE) and the mean bias error (MBE). Wind speed and temperature measured at 2 m.

Method	rRMSE [%]	MBE [kg N ha^{-1}]	With Posterior Correction
Alpha IHF ~ DTM	10.68	−0.43	No
Alpha IHF ~ Alpha IDM	39.78	+8.53	No
Alpha IHF ~ Alpha IDM corr. correction factor of 0.27:			
WS (2 m) $< 2.1 \text{ m s}^{-1}$ $\wedge$ temp (2 m) $> 10^\circ \text{C}$	19.63	+2.24	Yes
no correction: WS (2 m) $> 2.1 \text{ m s}^{-1}$ $\vee$ temp (2 m) $< 10^\circ \text{C}$			
Alpha IHF ~ Leuning IHF/ZINST	20.95	+3.19	No

3.3. Correlating Deviation of Cumulative NH_3 Emissions of Alpha IDM from Reference Alpha IHF Method with Environmental Factors

Figure 3b shows higher deviations for Alpha IHF regardless of location. The analysis of various soil parameters (e.g., cation exchange capacity or sand content) showed no correlation with this deviation. The correlation analysis revealed standardized wind and

air temperature as the meteorological parameters with the strongest influence on the detected NH_3 loss differences between Alpha IHF and Alpha IDM (Figure 4). This was initially demonstrated using the data set for the 18 trials examined in this study and subsequently verified using a further test data set from 2023 ($n = 20$ trials, Table S3) using wind speed, temperature and the differences in loss between Alpha IHF and Alpha IDM, respectively (Table S4). The NH_3 loss differences tended to be higher in domains with low wind speeds and high temperatures occurring in fertilization campaign three, while the differences tended to be small at higher wind speeds and temperatures below 10°C (Figure 4). The negative correlation ($R = -0.36$) between standardized wind and NH_3 loss difference indicates that NH_3 loss differences are significantly lower under windy conditions ($p = 0.028$). Consequently, emissions are overestimated at low wind speeds (Figure 4 left). A positive correlation ($R = 0.42$, $p = 0.008$) was observed between temperature and NH_3 loss difference (Figure 4 right).

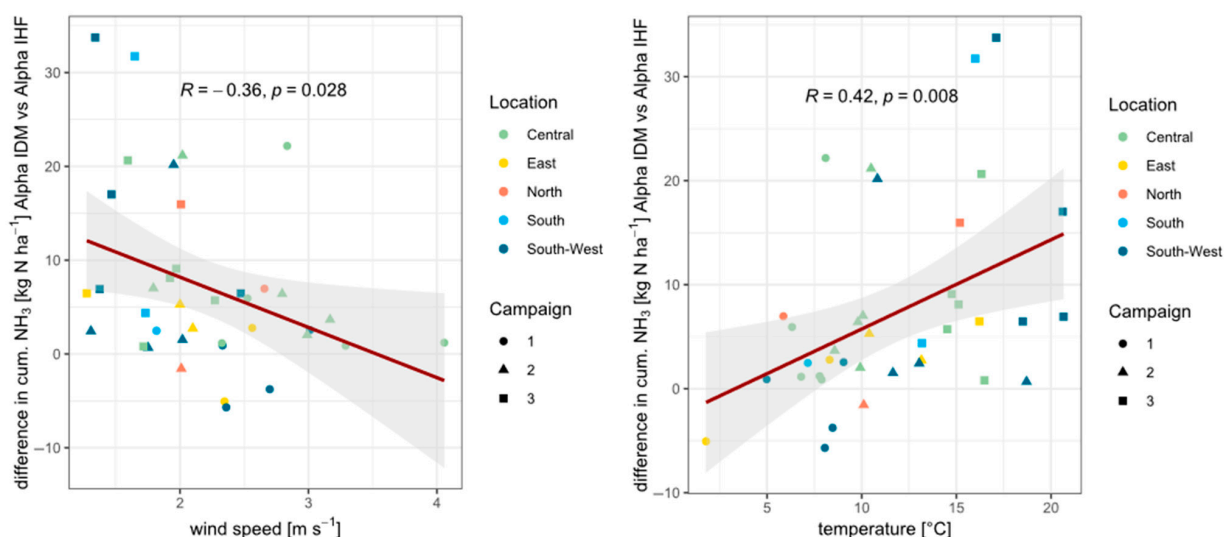


Figure 4. Correlation between the difference in cum. NH_3 emissions (Alpha IDM vs. Alpha IHF) and wind speed at the individual sites (**left**) and temperature at the individual sites (**right**) with regression lines (95% confidence intervals) and Pearson correlation coefficients from trials over 5 regions in 2021–2023.

These correlations are based on both data sets for the years 2021 to 2023. For the data set presented in this study, the two concomitant criteria, average wind speed $<2.1 \text{ m s}^{-1}$ $\wedge$ average temperature $>10^\circ\text{C}$, over a whole measurement campaign were identified for the correction of cumulative emissions with a factor of 0.27. This factor is derived from the correlation between Alpha IHF and Alpha IDM (Figure 3b) using the reciprocal of the slope of the regression line. Applying this correction, the rRMSE is reduced to 19.6% and the MBE to $+2.2 \text{ kg N ha}^{-1}$, i.e., to a similar acceptable deviation range compared to the Leuning IHF/ZINST (Table 3). The resulting rRMSE for the validation data set (2023, $n = 20$) after correction is 9.0%, with an MBE of $+1.0 \text{ kg ha}^{-1}$, and for all trials from 2021 to 2023 ($n = 38$), the resulting rRMSE is 10.3% and the MBE is $+1.6 \text{ kg ha}^{-1}$ (Figure 5, Table S4).

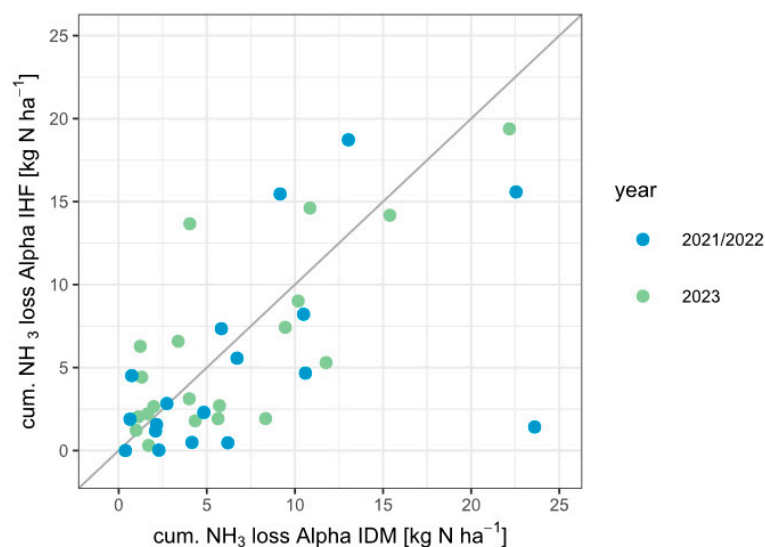


Figure 5. Comparison of the reference method IHF with Alpha sampler and IDM with Alpha sampler used in the small plots, applying the Alpha IDM with a correction factor for calculation, with campaign-averaged weather conditions (wind speed $<2.1 \text{ m s}^{-1}$ and average temperature $>10 \text{ }^{\circ}\text{C}$) from 38 trials in year 2021 to 2023. The solid grey line represents 1:1 slope.

4. Discussion

This study presents a data set of 18 measurement campaigns in winter wheat across Germany. Four measurement techniques were used to measure NH_3 emissions from urea, two applied on large plots and two in a small-scale multiplot design. Alpha sampler with IDM was used for the first time in such an experimental design, and Alpha IHF was set as reference method. Results from NH_3 emission studies are often biased due to the research group conducting the experiment and the measurement method used [28]. This centrally coordinated study covering five sites in Germany provides a unique and extensive data set to compare and evaluate the applied methods. Scale effects due to the size of the measurement plots are debated but not discussed in the present study.

4.1. Alpha IDM in Small Plots

The initial hypothesis (b) expecting the Alpha IDM approach to provide higher agreement with the Alpha IHF than DTM was not confirmed. Other studies have shown a relative difference in cumulative emissions of 6–28% for IHF, ZINST and IDM/bLS compared to the average emissions assessed by micrometeorological methods [54]. Within the different concentration measurement methods used with bLS, differences of 1–13% in applied total ammoniacal nitrogen (TAN) were found [28]. In this study, a high rRMSE of 39.78% and an MBA of $+8.5 \text{ kg N ha}^{-1}$ were determined from uncorrected NH_3 losses obtained by Alpha IDM.

The use of Alpha samplers for IDM with long time intervals reaches the applicability limits of the IDM model, as the parameterization with the Monin–Obukhov similarity theory (MOST) is only valid for shorter time intervals [55]. The assumption of stationarity within averaging intervals of 24 h is not plausible. Therefore, weather data was used at 30 min intervals. However, there is a distortion of the turbulence parameter due to the long averaging intervals used for the concentrations. This could be a contributing factor to the differences between Alpha IHF and Alpha IDM emissions. This effect could be overcome by a higher temporal resolution, like 3–6 h concentration sampling, with Alpha samplers improving the accuracy of IDM. Due to low sensitivity and limitations in equipment or site availability, this is not always possible. Nevertheless, there is a difference

between the IHF and IDM methods. Thus, IHF measures concentration and wind profiles directly from multiple heights within the boundary layer. On the other hand, the IDM method assumes that the wind profile can be based on the application of MOST by the utilization of measurements at a single height while applying similarity relationships. Filtering removes periods with more extreme conditions where the assumptions are more likely to be violated [49]. At the same time, removed data (often from night time) and linear interpolation can lead to overestimation.

Cumulative ammonia emissions obtained by Alpha IDM showed good agreement with the reference for the two first fertilizer application timings across sites and experimental years. The influence of the third split application on deviations from the reference method is shown by the data set, as mostly lower wind speeds and comparatively high temperatures prevail. Therefore, cumulated ammonia emissions obtained by small-plot measurements with IDM require correction with a factor of 0.27 (within the limits for campaign-averaged wind speed $<2.1 \text{ m s}^{-1}$ $\wedge$ air temperature $>10^\circ\text{C}$) to yield an acceptable deviation compared to the Alpha IHF reference. The factors are considered to be the best threshold criteria for identifying the need for correction of cumulated NH_3 emissions by Alpha IDM, while they are not necessarily explanatory for the observed differences. The applicability of the factor may be influenced by site-specific factors. Specific canopy traits, like fully developed winter wheat flag leaf or ear appearance under the specified wind and temperature conditions of the third measurement campaigns, may also account for the higher uncertainties of Alpha IDM and be related to the applied Alpha sampler sampling heights. In addition, while low wind speeds are often found to be critical for micrometeorological flux calculations [45], the use of Pasquill–Gifford classes for characterizing atmospheric stability conditions in inverse dispersion modelling has been found to lead to erroneous results under specific conditions (WindTrax users guide 2024). In future measurements following this approach, atmospheric stability parameters for inverse dispersion modelling should be obtained from 3D sonic wind speed measurements. However, by using the correction factor, hypothesis (a) on the quantitative accuracy of NH_3 loss measurements of Alpha samplers combined with IDM in small plots can be accepted, while improvement in Alpha IDM is still needed and should be investigated. As one approach, conducting measurements at different heights in small plots should also be considered. This could entail a more accurate representation of background concentrations and the possibility to quantify potential cross contamination between plots. An additional circular plot should be included in further trials, if the space is available, e.g., with Alpha IHF as reference, to validate and correct absolute flux estimates obtained by Alpha IDM.

4.2. Dräger Tube Method in Small Plots

The initial hypothesis (b), according to which the DTM was expected to be less consistent with the Alpha IHF compared to the Alpha IDM approach, cannot be confirmed. The DTM shows a high agreement with the Alpha IHF, with an rRMSE of 11% and an MBE of $-0.4 \text{ kg N ha}^{-1}$.

Generally, enclosure methods feature critical disadvantages in measuring absolute emissions. They modify the environment of the emitting surface compared to ambient conditions by changing the air flow (e.g., turbulence, wind speed and vertical wind profile), along with precipitation, radiation, temperature and soil conditions [56]. A review of chamber and micrometeorological methods to quantify NH_3 emissions from field-applied fertilizer has concluded that enclosure methods, as well as dynamic chambers like wind tunnels, which proved to be the most suitable technique to mimic wind conditions, are a reliable tool for the relative comparison of emissions [57]. For enclosed methods, a relative difference in cumulative emissions of 41–76% for DTM and wind tunnels compared to the

average emissions estimated using micrometeorological methods was reported [54]. Some studies observed close agreement of the DTM to measurements made with IDM on liquid manures [27,53], while others observed the opposite, especially with organic (incorporated) fertilizers, due to the heterogeneity regarding unknown fertilizer quantity, placement and a rather small measurement area [21]. In this study, the agreement between DTM and IDM was closer for the urea fertilizer measurements due to the more evenly distributed application within the area covered by the DTM soil rings. However, the DTM does not integrate over large areas and is therefore not robust to spatial heterogeneity or heterogeneous fertilizers such as slurry [28]. In addition, organic fertilizers can lead to a contamination of the chamber system, which can make reliable measurements challenging [30]. The application error of this study is expected to be small in this measurement, since the urea granules were weighed exactly for the corresponding area of the soil rings. Nevertheless, the measured emissions may differ between methods, as small application heterogeneity in plots due to fertilizer spreaders is not representable in small-chamber measurements on soil rings. The results of the present study have shown that DTM is suitable for quantitative NH_3 emission measurement from urea fertilizer under these specific experimental conditions in comparison to the Alpha IHF reference.

The DTM provides direct spot measurements, measured during daytime, when emissions were expected to be the highest, as the highest temperatures and wind speeds were observed during daytime. Although measurements in the morning and in the evening are connected to lower temperatures and wind speeds, emissions were also detected during that time. As no sampling was carried out at night, the lowest daytime emissions may not have been recorded, which may lead to an overestimation of night time emissions with the DTM. Next to this overestimation, underestimation occurred as well, as the initial flows were measured at specific moments when concentrations were partially below the detection limit of the Dräger tubes [29]. For these cases, accumulating samplers with longer exposure times have a great advantage in terms of detecting low emissions. An underestimation of emissions detected with DTM of 34% of applied TAN in comparison with other measurement methods was also reported by other studies [28]. Due to the low number of measurement points and no continuous measurement, no high short-term emission peaks could be detected. This is more likely to be the case with organic fertilizers for which accumulating samplers with longer exposure times performed better (Alpha IDM).

Overall, measurements with the DTM are difficult, both in the very low range due to the detection limits of the point measurements and also in the high range due to the measurement intervals of the individual measurements. In addition, the amount of work involved in field tests with mineral fertilizers is very high, as the emission process can be long, as shown at location North (Figure 1). NH_3 losses detected with the DTM are reliable when the limits and uncertainties of this method are considered.

4.3. Leuning IHF/ZINST

For hypothesis (c), the results obtained by Leuning sampler IHF/ZINST and the reference Alpha IHF showed an acceptable agreement, as emissions were within the expected range of possible deviations. However, emissions showed a tendency to be overestimated with the IHF Leuning method (MBE of $+3.2 \text{ kg N ha}^{-1}$).

Relative standard deviations of 23% and 52% are reported when using IHF between replicate plots [20]. The deviations of the Leuning IHF/ZINST from the Alpha IHF found here are within this range. The data in this study is not based on replications within one trial but on measurements by different research groups at different locations, which can cause higher deviations. The positive bias of the IHF, partly due to the contribution of horizontal turbulent diffusion, can cause a systematic overestimation of 5–20% depending

on stability [6]. There are various ways to adjust the profiles. In 2020, a new method was proposed, which decreased overestimated emissions by a relative factor of 10% for 160 experiments [43]. This adjustment was chosen for the Alpha IHF calculations in this study as well. This comparison points out that a similar kind of adjustment procedure for Leuning sampler IHF could also be considered. Overall, the use of Leuning samplers as concentration measurement for IHF should be carefully examined and an alternative concentration measurement method should possibly be used, e.g., Alpha sampler.

4.4. Challenges During Concentration Measurements

The use of Alpha and Leuning samplers requires manual handling in several steps, including preparation, set up, collection and laboratory analysis, during which systematic or random errors can possibly occur. In addition, the general disadvantage of concentration measurements with Leuning samplers is the high laboratory effort due to the complex extraction and long drying steps. Replicates in the field are difficult due to the large area required. Furthermore, it is difficult to ensure rotation while preventing samplers from falling down during strong winds, leading to data loss. The IHF results were more robust than the ZINST results, which are more prone to application errors and data loss due to the small number of samplers. Application of ZINST is clearly restricted by its strict prerequisites, such as deriving the empirical ratio of horizontal flux at ZINST height to the emission rate from the plot with specific size and surface roughness, as well as requiring large uniform fields [21]. The concentrations measured with the Dräger tubes were determined visually through a coloured gradient on the tube, potentially being source of random or systematic errors. While this method requires a lot of fieldwork, it eliminates the need for laboratory measurements, as the results of measurements are directly available.

4.5. Combination of Quantitative Methods with Qualitative Passive Flux Sampler

Absolute emission measurements can be combined with qualitative/semi-quantitative NH_3 concentration measurements using passive samplers like sulfuric acid traps or denuders to assess NH_3 emission in plot experiments with many treatments [21]. Ammonia collected by passive samplers on fertilized small plots is then compared with absolute NH_3 emissions collected on standard plots with known rates of NH_3 to determine a transfer coefficient, which is called the standard comparison method [58,59]. Sulfuric acid traps have also been combined with the DTM as absolute emission measurements, which proved to be reliable in field studies [27] and can be used for determining the quantitative NH_3 losses in field trials with multiple plots. However, the need for a quantitative method that is easy to use and implement in small-plot field trials remains. The DTM has proven to be suitable in this study, but there are clear limitations, and the amount of workload involved makes it difficult to implement in field trials. Quantitative NH_3 losses could be detected by Alpha sampler and the backward Lagrangian stochastic dispersion method within small plots. This approach would not need large additional plot size or electricity nor multiple samplings throughout the day. Nevertheless, as described before, more experiments with the Alpha IDM approach are needed to cover various weather conditions and refine the model and sampling approach for the Alpha IDM.

5. Conclusions

This study compared two small-plot NH_3 measurement approaches to a micrometeorological reference method based on a comprehensive, multi-annual data set collected throughout Germany. To date, this study is the first to provide such a comprehensive comparison between methods and to test passive flux Alpha samplers in combination with inverse dispersion modelling to determine NH_3 emissions from mineral fertilizers on small

plots. In addition, two micrometeorological approaches were compared, of which integrated horizontal flux (IHF) measurements employing Alpha samplers were in acceptable agreement with IHF/ZINST using Leuning samplers.

The comparison showed a good agreement of the DTM dynamic chamber method with the reference method Alpha IHF for cumulative emissions from homogeneously surface-applied urea fertilizer. Nevertheless, this method has strong limitations, and its application should be carefully considered, particularly regarding the fertilizer application method and the required fieldwork. With respect to Alpha samplers in combination with inverse dispersion modelling, there was good agreement with the reference for early- and middle-of-spring applications. This method is therefore recommended by the authors. Deviations from the reference, particularly in late-spring applications, were related to specific weather threshold values of average air temperature and wind speed within an experimental campaign. A correction factor was derived, which could be considered for the same weather soil and canopy conditions in future investigations. To ensure reliable measurements with Alpha IDM, further improvements should be considered, such as utilizing multiple measurement heights, concentration measurements at higher time resolution or derivation of atmospheric stability parameters from 3D sonic wind speed measurements.

The results of this study show that quantitative ammonia loss measurements from small-plot measurements are feasible under specific conditions. Therefore, providing a supplementary micrometeorological reference measurement on a larger plot is recommended. This can serve as an additional validation and correction of results obtained in a multiple-small-plot set up until more valid and robust small-plot methods are available.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/environments12080255/s1>, Figure S1. Experimental design of the field trials, Table S1. Mean air temperature, wind speed at 2 m height, standardized rain and relative humidity during the measurement campaigns for each year and location, Table S2. Pasquill–Gifford classes used for characterization of the atmospheric stability condition as input parameter for the IDM calculations, Table S3. Overview of the study sites in 2023, Table S4. rRMSE and MBE of NH₃ loss differences between Alpha IHF and Alpha IDM from small plot trials in 2023 ($n = 20$) in winter wheat the two concomitant criteria average wind speed $<2.1 \text{ m s}^{-1}$ AND average temperature $>10^\circ \text{C}$ over a whole measurement campaign were identified for the correction of cumulative emissions with a factor of 0.27.

Author Contributions: H.G.: Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Data Curation, Writing—Original Draft, Writing—Review and Editing, Visualization. J.B.: Methodology, Investigation, Data Curation, Writing—Review and Editing. J.F.: Methodology, Investigation, Data Curation, Writing—Review and Editing. A.K.: Methodology, Investigation, Data Curation, Writing—Review and Editing. S.K.: Conceptualization, Methodology, Data Curation, Writing—Review and Editing, Project Administration. A.S.P.: Conceptualization, Methodology, Validation, Formal Analysis, Writing—Original Draft, Writing—Review and Editing, Supervision, Project Administration, Funding Acquisition. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

The following abbreviations are used in this manuscript:

NH ₃	Ammonia
DTM	Dynamic chamber Dräger tube method
IHF	Integrated horizontal flux
ZINST	Height z, independent of stability
rRMSE	Relative root mean squared error
MBE	Mean bias error

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5 Overall discussion

5.1 Overview of the main findings

The research questions of this work (3.1) have been answered by the publications presented.

Influence of different incorporation techniques and soil properties on NH₃ mitigation (Götze et al., 2023):

How effective are different practice-oriented fertilizer incorporation techniques in reducing NH₃ emissions across diverse soil conditions, and to what extent do soil properties modulate their mitigation performance? How significant is the risk of pollution swapping due to increased N₂O emissions after incorporation?

- All urea incorporation techniques examined showed great potential for reducing NH₃ emissions compared to standard surface application.
- Slit injection achieved the highest NH₃ reduction of up to 87%, followed by deep incorporation with 82%.
- The reduction effect correlated positively with the clay content of the soil and was greatest on clayey soil.
- The highest cumulative NH₃ emissions occurred at low soil moisture (30% WHC) on sandy soil (34% of the applied N).
- Surface incorporation showed a significant reduction only on clayey soil and was largely ineffective on sandy and loamy soils.
- Pollution swapping to N₂O was observed with surface incorporation and higher moisture.

Effectiveness of urease and nitrification inhibitors compared to incorporation (Götze et al., 2025b):

How effectively do different urea mitigation strategies, including practical incorporation techniques and alternative urease inhibitors used alone or in combination with nitrification inhibitors, reduce NH₃ losses while influencing N₂O emissions and potential pollution-swapping effects under agricultural soil conditions?

- Slit injection achieved the highest NH₃ emission reduction (79.6%) compared to inhibitor treatments.

- Sole application of urease inhibitor (2-NPT) reduced NH_3 by 40.6% and the combined application with a nitrification inhibitor (2-NPT + MPA) by 46.7%.
- Although combined use of urease and nitrification inhibitor reduced NH_3 emissions, the effect was lower than reported in meta-studies for other inhibitors.
- Combined use of urease and nitrification inhibitor treatment initially showed the strongest N_2O reduction, but emissions increased exponentially later on and reached the level of the standard treatment.
- Isotopocul analysis showed that six weeks after fertilization, nitrification was the dominant process for N_2O production.

Evaluation of measurement methods for replicated small plot field trials (Götze et al., 2025a):

How accurately can NH_3 emissions from field-applied synthetic fertilizers be quantified using simultaneous measurements from replicated plots needed for evaluation of mitigation measures. How well do different multi-plot measurement approaches perform when validated against micrometeorological reference methods?

- The Inverse Dispersion Modeling with Alpha samplers initially significantly overestimated NH_3 emissions (rRMSE 40%).
- This deviation strongly correlated with low wind speed ($<2.1 \text{ m s}^{-1}$) and high temperature ($>10^\circ\text{C}$) conditions.
- By applying a correction factor of 0.27 under these specific atmospheric conditions, the accuracy of Inverse Dispersion Modeling with Alpha samplers could be improved to an acceptable level (rRMSE 19.6%).
- Thus, the Inverse Dispersion Modeling with Alpha sampler method was in the same range of deviation from the Integrated Horizontal Flux with Alpha sampler reference as the established micrometeorological method Integrated Horizontal Flux or ZINST with Leuning sampler (rRMSE 21%), which was also performed.
- The Dräger Tube Method showed good agreement with the micrometeorological reference method Alpha sampler with Integrated Horizontal Flux, with a relative root mean square error (rRMSE) of 11%.

5.2 Connection between the studies and interpretation of main findings

The studies are positioned within the overall goal of quantifying and reducing reactive nitrogen losses from urea fertilizers in agricultural systems to achieve the NH_3 reduction target for 2030 by 29% (European Parliament, 2016). First, the fundamentals regarding the dependence of incorporation efficiency on soil texture and moisture were determined in laboratory mesocosm experiments under controlled conditions considering the risk of pollution swapping to N_2O . These were then expanded with a focus on chemical reduction strategies by using inhibitors. Finally, measurement techniques required to verify the lab-determined reduction effects through incorporation and inhibitors were investigated and validated under real field conditions on replicated small plots.

Mechanisms of NH_3 reduction measures

The effectiveness of incorporation techniques for reducing NH_3 emissions heavily depends on the depth (Prasertsak et al., 2002) of incorporation and soil conditions (Fröhl et al., 2025; Pelster et al., 2018). The closed slit injection simulated in the laboratory experiment, in which urea was placed in a 5 cm deep slit and then closed, consistently showed the highest reduction in NH_3 emissions. Deep incorporation (simulated plow incorporation, 5 cm) was also very effective but showed significantly higher variability. Surface incorporation (shallow mixing to 2 cm), on the other hand, may in some cases (e.g. on sandy soils) have no reduction effect but could even lead to an increase in NH_3 emissions. The results support the hypothesis that the higher the clay content and thus the cation exchange capacity of the soil, the greater the reduction effect of incorporation (Pelster et al., 2018). This is because NH_4^+ binds to clay particles and thus does not contribute to rapid volatilization (Wang et al., 2025). The highest efficiency by using slit injection is explained by the complete coverage and compaction of the soil, which reduces macropores and maximizes contact between fertilizer and soil matrix. Slit injection is used as a benchmark for comparison with inhibitors due to the first results and has been confirmed as the most effective measure in the second study.

The NH_3 reduction observed with the specific inhibitors 2-NPT and MPA was within the range of meta-analyses, but lower than in studies that mainly investigated the inhibitor NBPT (Fan et al., 2022). This emphasizes the need for individual inhibitor studies also considering the experimental setup and conditions to ensure a comparable analysis. The observed N_2O emission following superficial incorporation in wetter soils and the delayed but exponential increase in N_2O with urease plus nitrification inhibitor confirm the risk of pollution swapping (Drury et al., 2017). The isolation of

nitrification as the main source of N_2O emissions suggests that the combined effect of urease inhibitor, delaying hydrolysis (Wang et al., 2020) and nitrification inhibitor, delaying NH_4^+ oxidation, stabilizes the NH_4^+ pool for longer. Then, once the nitrification inhibitor effect wears off, NH_4^+ is available for nitrification.

Validation of quantitative small plot measurements for mitigation measure comparison

The studies show that the reduction potential, 50 to 80% (Bittman et al., 2014), assumed in policy measures (European Parliament, 2016) for surface incorporation cannot be fully confirmed, especially on sandy or dry soils. Recent field trials also observed a significant increase in NH_3 emissions at dry and sandy sites (Brokötter et al., 2024a). This has direct implications for the adaptation of efficient fertilization practices to local conditions. As another example confirming the importance of regional conditions, a recent meta-modeling approach, applying Tier 3 methodology with 2776 NH_3 emission measurements (Hutchings et al., 2024) also highlighted the effects of soil clay content, rainfall and air temperature. All of these results emphasize the importance of investigating mitigation measures under real field conditions and at different locations in order to determine regionally suitable reduction factors.

For such comparative measurements on small plots, the Dräger Tube Method provided reliable snapshots of homogeneous surface application of urea, even though it has methodological limitations. Recent studies indicate that Dräger Tube Method should be applied only when no feasible alternatives are available and when high NH_3 emissions are anticipated (Kelsch et al., 2025). On the other hand, the need for correction for the Inverse Dispersion Modeling with Alpha samplers under conditions of low wind speed and high temperature indicates a violation of the assumptions of the Monin - Obukhov similarity theory at long sampling intervals (24 hours) (Flesch et al., 2005). However, the successful derivation and application of a correction factor validates the Inverse Dispersion Modeling with Alpha samplers as a fundamentally suitable method for replicated small plot experiments, considering specific weather limits. Furthermore, mandatory monitoring (EMEP/EEA, 2023) can be ensured by this method with its advantageous practicality.

5.3 Contribution to current research

Quantification and refinement of emission factors

This work provides urgently needed quantitative data on the efficiency of NH_3 reduction measures (various incorporation methods and little-researched inhibitors) under varying conditions. The results reveal limitations and potential that have not been sufficiently explored to date. On the one hand, there is the great potential of slit incorporation and on the other hand, the insufficient efficiency of surface incorporation under certain conditions (dry and sandy soils). In addition, the risk of pollution swapping was observed under certain conditions. This highlights that site-specific adaptations of mitigation strategies (e.g. deep incorporation on sandy soils) and concludes that regionalization of reduction factors is necessary to achieve political reduction targets.

Establishment of robust measurement technology for small plots

The decisive contribution to the current state of research is the validation of Inverse Dispersion Modeling with Alpha samplers as a practical, cost-effective, and less intrusive method for quantitative NH_3 flux measurement on small, replicated field plots. The empirically derived correction factors for the Inverse Dispersion Modeling with Alpha samplers under critical weather conditions significantly increase the accuracy of this method. This overcomes the scaling problems of wind tunnels or large-scale micrometeorological methods and is essential for the statistical evaluation of agricultural practices. This allows mitigation measures to be effectively evaluated and regionalized and enables the required monitoring in order to evaluate the success of measures aimed at achieving emission reduction targets.

5.4 Limitations and future research

The laboratory experiments on incorporation techniques and inhibitor use were conducted under controlled conditions (constant temperature and humidity, no plant nitrogen uptake), which limits their direct transferability to real field conditions. While N_2O isotopocule analysis identified nitrification as the dominant N_2O source under inhibitor use, extended measurements with high-resolution isotope sampling are required to assess N_2O kinetics.

Overall, field trials with the incorporation and inhibitor strategies are urgently needed to confirm the results under real site and weather conditions, e.g. precipitation (Fröhl et al., 2025), for a practice-oriented evaluation and reliable consideration. Thus, an individualized choice of appropriate mitigation measures should be taken, not only due to site characteristics but also with regard to technical feasibility. Other options within the 4R strategies offer alternative, for example, increasing the number of nitrogen applications with lower amounts per dose (Finck et al., 2024).

For validation of these mitigation approaches, the methods for small plot measurements need to be developed further. The Dräger tube method is limited due to the high field effort and susceptibility to measurement errors in the low concentration range (Kelsch et al., 2025), which makes its application in long-term experiments difficult. The Inverse Dispersion Modeling with Alpha samplers requires further refinement through measurements at multiple heights above canopy and an adjusted temporal resolution of concentration measurements (shorter than 24 hours) to improve accuracy under varying meteorological conditions. The use of 3D sonic anemometers for more precise determination of the atmospheric wind profile is recommended to reduce uncertainties in the Inverse Dispersion Model.

Next to reflecting regional site conditions, field experiments are essential to demonstrate the economic value of NH_3 mitigation through increased plant-available nitrogen. While urease and nitrification inhibitors have shown potential to improve nitrogen use efficiency and grain protein concentration (Brokötter et al., 2024b), these benefits must be quantified more precisely under field conditions.

Finally, there is a knowledge gap regarding the long-term environmental impacts of inhibitors. For example, an initial study indicates that the use of nitrification inhibitors leads to a sustained reduction in ammonia-oxidising bacteria even after several years without inhibitor application (Groven et al., 2025). Data from long-term studies on the persistence of these substances in the environment is incomplete and the specific effectiveness of various inhibitor products has not yet

been sufficiently researched (Biewald et al., 2025). In particular, further studies are needed to investigate the impact on microbial communities that do not belong to the target group and the potential for entering the food chain, in order to rule out possible risks to the ecosystems and human health (Biewald et al., 2025).

6 Conclusion

In this work, different incorporation techniques and inhibitors products as mitigation measures for NH_3 emissions from mineral fertilizer were investigated to analyze their effectiveness, considering soil types, soil moisture contents as well as pollution swapping in form of N_2O losses in laboratory trials. Additionally, measurement methods for quantifying NH_3 emissions were applied in replicated agronomic field plot trials allowing statistical comparison of different fertilizers and measures.

The results demonstrate that incorporating urea is effective but practical applicability by farmers has still to be assessed. Deep slit injection of urea has proven to be the most effective NH_3 reduction measure and avoids additional cost for inhibitors. However, its practical transferability depends on soil properties (e.g. clay content and moisture) and the availability of suitable machinery. Inhibitors are a viable alternative for achieving NH_3 emission reduction, especially when incorporation is not technically feasible. Nevertheless, their efficiency depends heavily on the specific inhibitor product. Moreover, the risk of pollution swapping to N_2O must also be taken into account, especially with regard to soil properties during surface incorporation as well as weather conditions for nitrification inhibitors.

The quantitative determination of NH_3 losses in small plot field trials has been shown to be feasible by the evaluated measurement methods. This is essential in order to evaluate the efficiency of reduction strategies in a statistically reliable manner under field conditions and to reduce uncertainties in emission inventories by facilitating monitoring. The newly established Alpha sampler which Inverse Dispersion Modeling approach in such small plot setup demonstrated reliable performance when adjusted using the empirically derived correction factor. Given the substantially lower labor demands and fewer methodological constraints, it should be prioritized for future small plot emission studies in contrast to the Dräger Tube.

Achieving the goals of nitrogen efficiency and climate protection requires a combination of advanced, site-specific fertilization practices and continuous validation and improvement of measurement methods. Incorporation, where technically feasible and the development of inhibitors with targeted, long-lasting effects are promising options for more sustainable nitrogen fertilization.

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8 Attachment

8.1 Supplement Publication 1

Götze, H., Saul, M., Jiang, Y., Pacholski, A., 2023. Effect of Incorporation Techniques and Soil Properties on NH₃ and N₂O Emissions after Urea Application. *Agronomy* 13, 2632.
<https://doi.org/10.3390/agronomy13102632>



Supplementary Materials

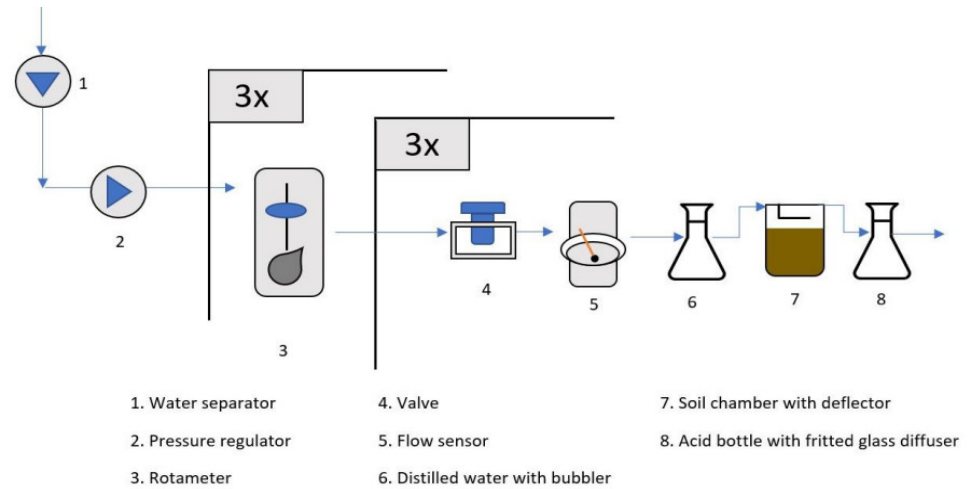


Figure S1 Set-up flow chambers for NH_3 loss quantification

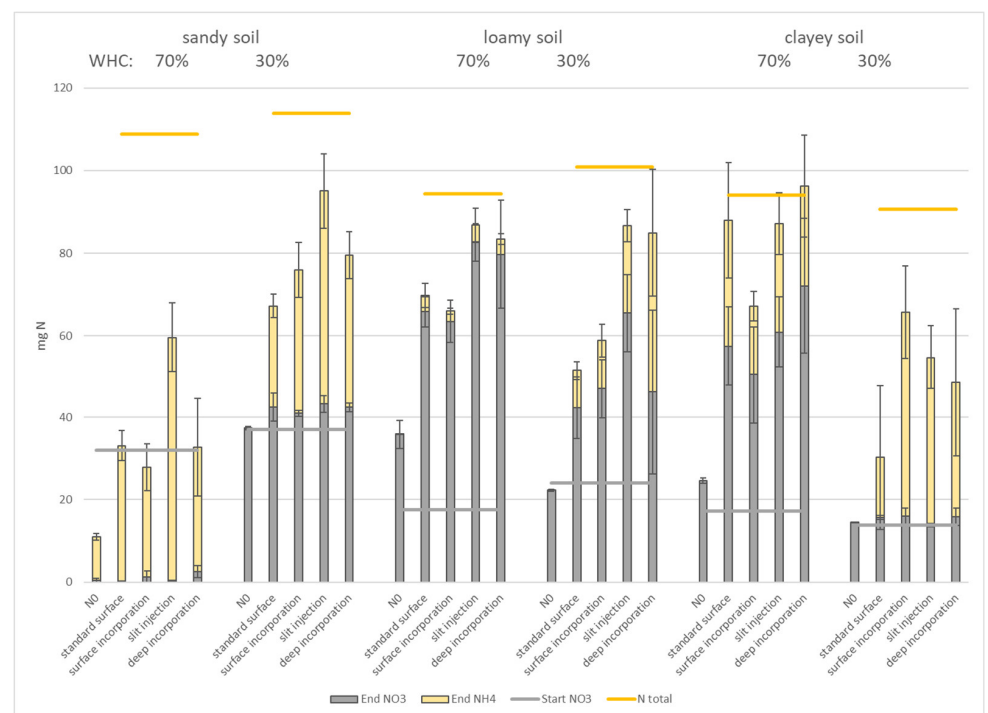


Figure S2 Mineral N content in three different soils (sandy, loamy, clayey) and two different moisture levels (70 and 30 % WHC) of NH_3 experiment after incubation for two weeks with start NO_3 (grey line) and total N from fertilizer and start NO_3 (yellow line)

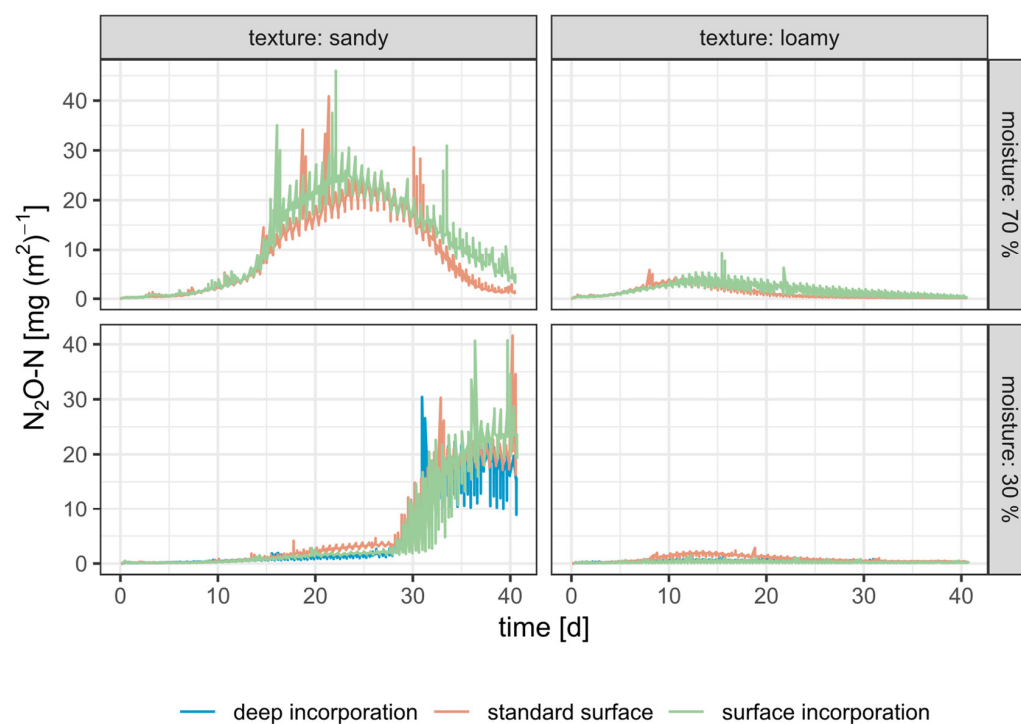
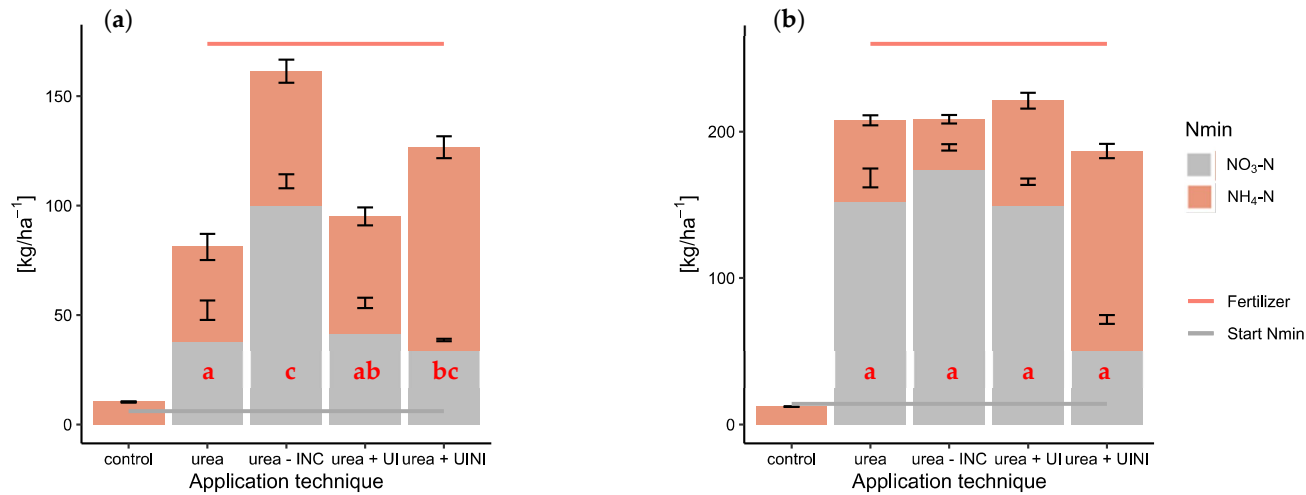


Figure S3 Fluxes of $\text{N}_2\text{O-N}$ from urea applied with different application techniques, standard surface, surface incorporation and deep incorporation, on sandy and loamy soil in two moisture levels 70 % and 30 % WHC

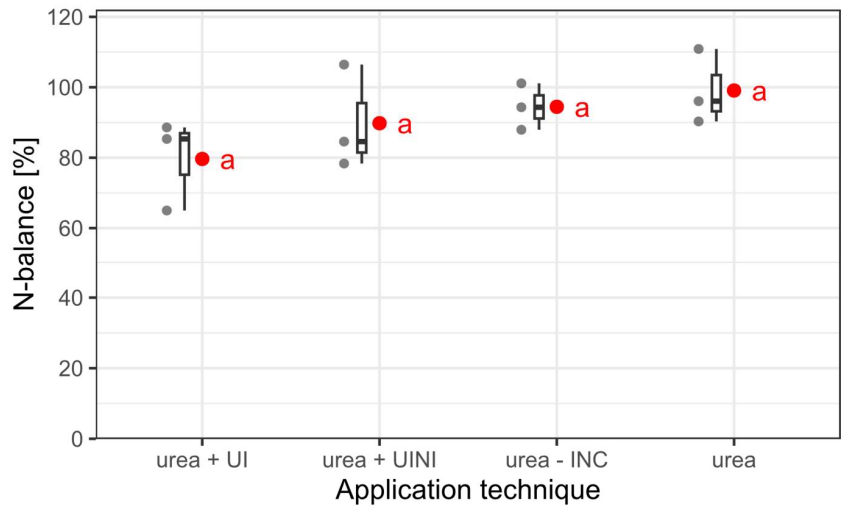
8.2 Supplement Publication 2

Götze, H., Buchen-Tschiskale, C., Eder, L., Pacholski, A., 2025b. Effects of inhibitors and slit incorporation on NH_3 and N_2O emission processes after urea application. *Agric. Ecosyst. Environ.* 378, 109307. <https://doi.org/10.1016/j.agee.2024.109307>

1 Supplement



2
3 **Figure S1.** Mineral N content in the NH₃ Exp. (a) after two weeks and the N₂O Exp. after 37 days (b) of incubation with start Nmin
4 of the soil (grey line) and applied fertilizer N (orange line). Red letters indicate the compact letter display (Means not sharing any
5 letter are significantly different by the Sidak test at the 5% level of significance with 95% confidence)
6



7
8 **Figure S2.** Nitrogen balance (%) from urea fertilizer applied with standard surface application (urea), slit injection technique (urea
9 - INC), urea + UI and urea + UINI; replicates and boxplots are in black, and red indicates the mean values and compact letter display
10 (Means not sharing any letter are significantly different by the Sidak test at the 5% level of significance with 95% confidence). n=3.
11

12 **Table S1.** Summary of mixing endmember isotopic signatures of particular pathways (bD – bacterial denitrification, nD – nitrifier
13 denitrification, fD – fungal denitrification, Ni – nitrification) and reduction fractionation factors (reduction) with respective
14 references. For the model input, each value is corrected with the respective mean isotopic signature of the substrate: for $\delta^{18}\text{O}_{\text{N}_2\text{O}}$
15 – soil water ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$) for bD, nD, and fD. The respective substrate-corrected values were applied as a model input for $\delta^{18}\text{O}_{\text{N}_2\text{O}}$. For
16 $\delta^{15}\text{N}^{\text{SP}}_{\text{N}_2\text{O}}$ no substrate correction is needed. As the isotopic endmember ranges of nD and bD overlap considerably, a mean value
17 was used for the 2D model.

	Literature values		Substrate isotope values ^f	Substrate-corrected values
Pathway	$\delta^{15}\text{N}^{\text{SP}}_{\text{N}_2\text{O}}$ (‰)	$\delta^{18}\text{O}_{\text{N}_2\text{O}}$ (‰)	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ (‰)	$\delta^{18}\text{O}_{\text{N}_2\text{O}}$ (‰)
bD ^a	-1.9±5.6	20.0±3.3	-8.4	11.6±11.7
nD ^b	-5.8±7.7	15.9±3.5	-8.4	7.5±11.9
fD ^c	33.6±6.4	48.5±6.6	-8.4	40.1±15
Ni ^d	34.7±4.0	23.5±2.9		

Reduction^e -6.1±1.4

^aToyoda, Mutobe, Yamagishi, Yoshida, and Tanji (2005) doi:10.1016/j.soilbio.2005.01.009, R. L. Sutka et al. (2006) doi:10.1128/AEM.72.1.638–644.2006, Lewicka-Szczebak et al. (2014) doi:10.1016/j.gca.2014.03.010, Lewicka-Szczebak et al. (2016) doi:10.5194/bg-13-1129-2016

^bFrame and Casciotti (2010) doi:10.5194/bg-7-2695-2010, R. L. Sutka et al. (2006) doi:10.1128/AEM.72.1.638–644.2006

^cMaeda et al. (2015) doi:10.1038/srep09697, Rohe et al. (2014); Rohe, Well, and Lewicka-Szczebak (2017) doi:10.1002/rcm.7909, R. Sutka, Adams, Ostrom, and Ostrom (2008) doi:10.1002/rcm.3820

^dFrame and Casciotti (2010) doi:10.5194/bg-7-2695-2010, R. L. Sutka et al. (2006) doi:10.1128/AEM.72.1.638–644.2006,

^eJinuntuya-Nortman, Sutka, Ostrom, Gandhi, and Ostrom (2008) doi:10.1016/j.soilbio.2008.05.016, Lewicka-Szczebak et al. (2015); Lewicka-Szczebak et al. (2014), Menyailo and Hungate (2006) doi.org/10.1029/2005GB002527, Ostrom et al. (2007) doi:10.1029/2006JG000287, Well and Flessa (2009) doi:10.1002/rcm.4216

^fmean value of lab water from Rohe et al. (2017) doi:10.1002/rcm.7909

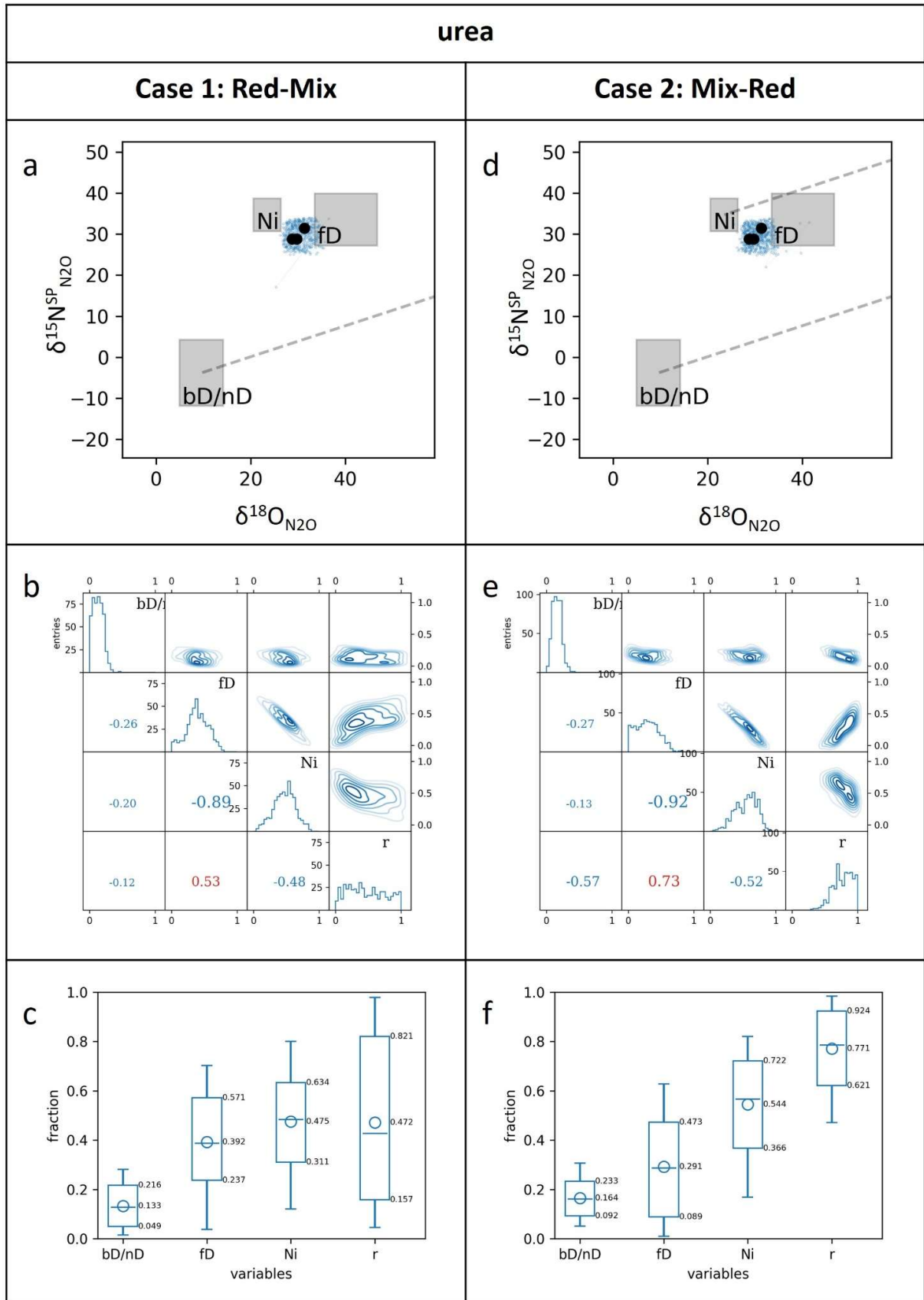


Figure S3. FRAME results of N₂O production/consumption process analyses of the urea treatment. Panels (a) and (d) show the observed N₂O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares

34 indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni
35 (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N₂O reduction by
36 denitrification, along which the isotopocule ratios of the remaining N₂O are expected to increase if N₂O is reduced. Values are based
37 on Table S1. Panel (b) and (e) show variable correlations based on model runs, using Histograms (on the diagonal) calculated from
38 the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients
39 (bottom-left). Panel (c) and (f) summarizes statistics on the simulation results of fractions of the different N₂O production processes
40 and the residual unreduced N₂O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively.
41 The box encloses the 68% confidence interval (CI), and the whiskers show 95% CI.

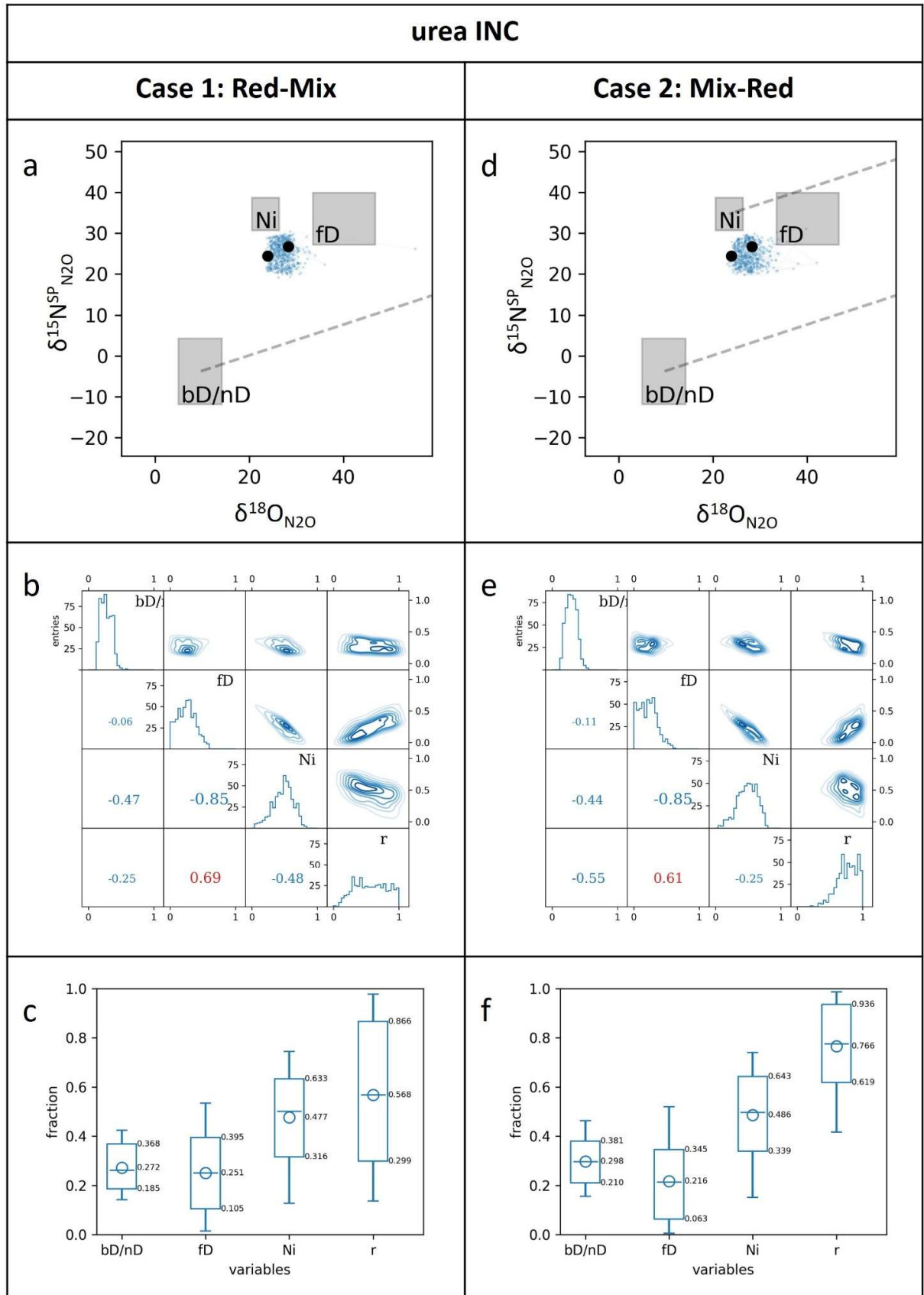


Figure S4. FRAME results of N_2O production/consumption process analyses of the urea - INC treatment. Panels (a) and (d) show the observed N_2O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares

45 indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni
46 (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N₂O reduction by
47 denitrification, along which the isotopocule ratios of the remaining N₂O are expected to increase if N₂O is reduced. Values are based
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49 the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients
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51 and the residual unreduced N₂O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively.
52 The box encloses the 68% confidence interval (CI), and the whiskers show 95% CI.

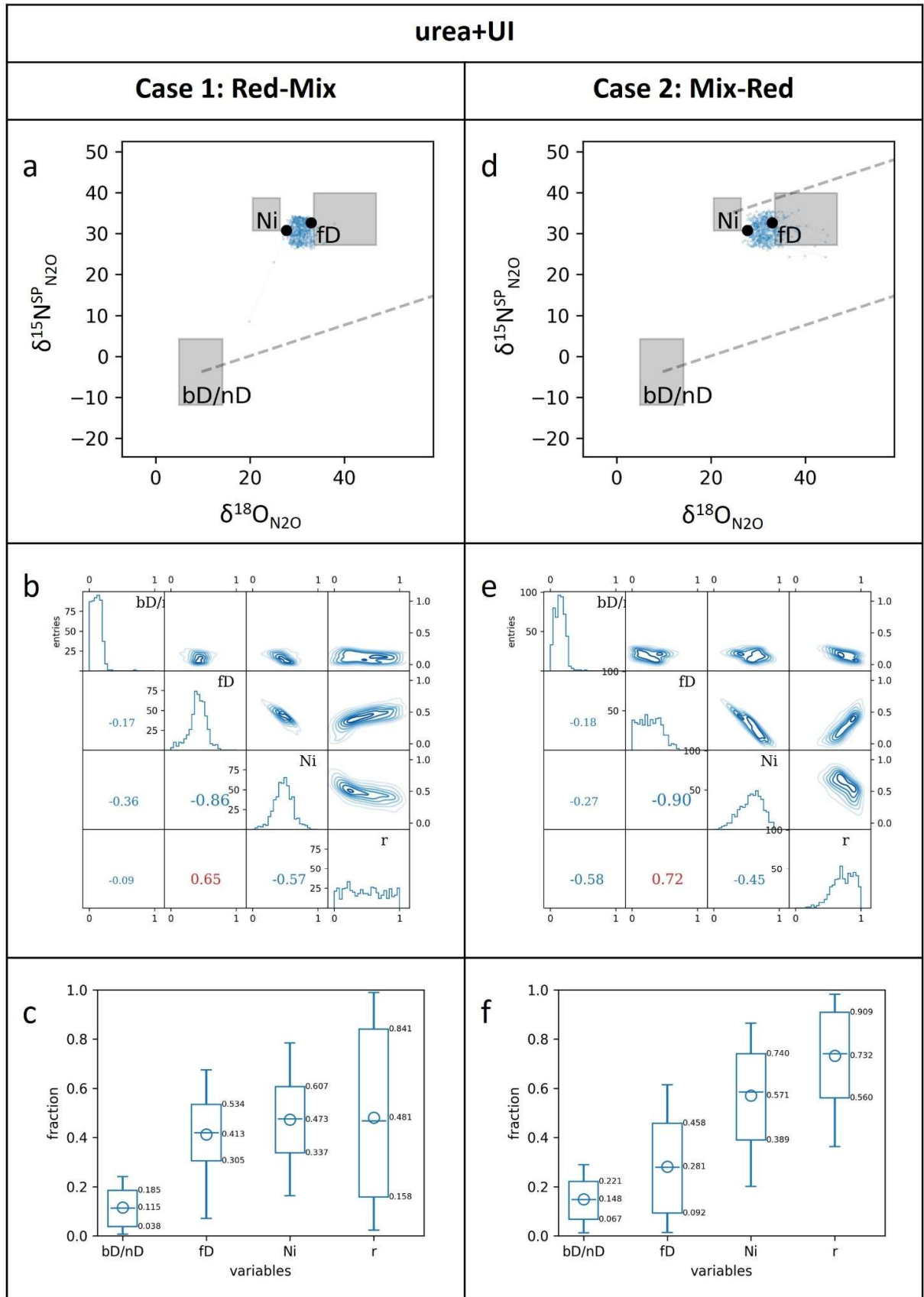


Figure S5. FRAME results of N_2O production/consumption process analyses of the urea+UI treatment. Panels (a) and (d) show the observed N_2O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares

56 indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni
57 (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N₂O reduction by
58 denitrification, along which the isotopocule ratios of the remaining N₂O are expected to increase if N₂O is reduced. Values are based
59 on Table S1. Panel (b) and (e) show variable correlations based on model runs, using Histograms (on the diagonal) calculated from
60 the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients
61 (bottom-left). Panel (c) and (f) summarizes statistics on the simulation results of fractions of the different N₂O production processes
62 and the residual unreduced N₂O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively.
63 The box encloses the 68% confidence interval (CI), and the whiskers show 95% CI.

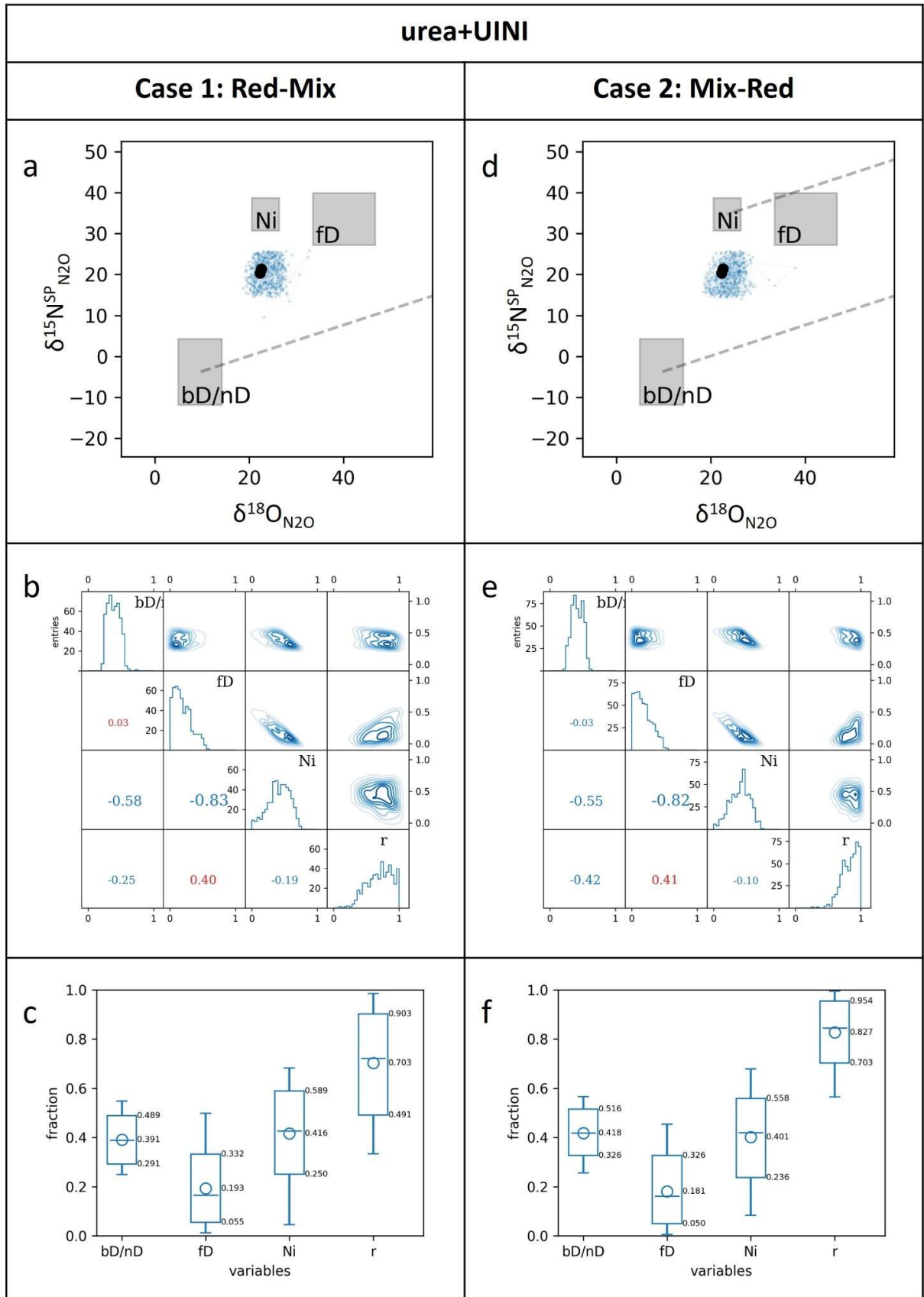


Figure S6. FRAME results of N_2O production/consumption process analyses of the urea+UINI treatment. Panels (a) and (d) show the observed N_2O isotopocule ratios (black dots) and the simulated results (blue dots) for both calculation scenarios. Gray squares

indicate the endmember ranges of bD (bacterial denitrification) /nD (nitrifier-denitrification), fD (fungal denitrification) and Ni (nitrification). The slope of the grey broken lines shows the ratio of the isotopocule fractionation factors for N₂O reduction by denitrification, along which the isotopocule ratios of the remaining N₂O are expected to increase if N₂O is reduced. Values are based on Table S1. Panel (b) and (e) show variable correlations based on model runs, using Histograms (on the diagonal) calculated from the variables building the Markov chains, contour-plots (top-right) showing the correlation and their correlation coefficients (bottom-left). Panel (c) and (f) summarizes statistics on the simulation results of fractions of the different N₂O production processes and the residual unreduced N₂O fraction (r). The open circles and horizontal lines indicate the mean and median values, respectively. The box encloses the 68% confidence interval (CI), and the whiskers show 95% CI.

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8.3 **Supplement Publication 3**

Götze, H., Brokötter, J., Fröhl, J., Kelsch, A., Kukowski, S., Pacholski, A.S., 2025a. Assessment of Different Methods to Determine NH₃ Emissions from Small Field Plots After Fertilization. *Environments* 12, 255. <https://doi.org/10.3390/environments12080255>

Article

Assessment of Different Methods to Determine NH_3 Emissions from Small Field Plots After Fertilization

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Supplementary Material

Figure S1. Experimental design of the field trials.

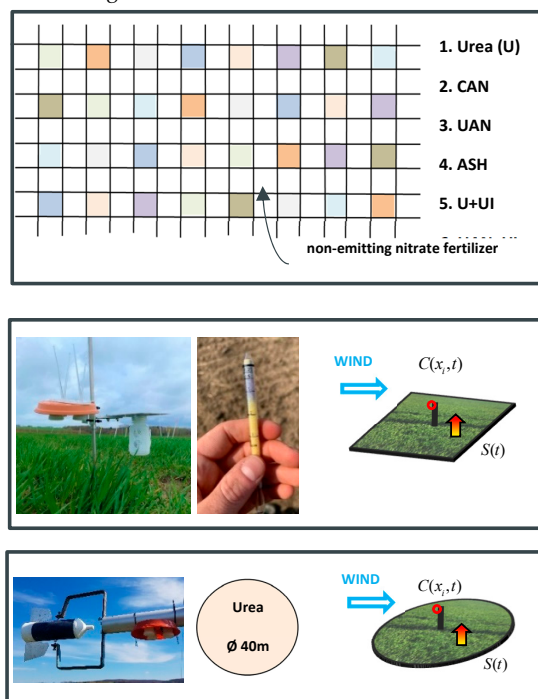


Table S1. Mean air temperature, wind speed at 2 m height, standardized rain, and relative humidity during the measurement campaigns for each year and location.

Region	Year	Temperature [°C]			Wind [m s ⁻¹]			Rain [mm d ⁻¹]		
		I	II	III	I	II	III	I	II	III
North	2022	5.86	10.11	15.19	2.66	2.01	2.01	1.28	0.22	1.11
Central 1	2021	8.09	8.57	14.75	2.83	3.17	1.97	0.58	1.76	3.12
Central 1	2022	6.32	10.06	14.52	2.53	1.79	2.27	0.42	0.25	2.42
Central 2	2022	6.8	10.49	15.12	2.33	2.02	1.92	0.29	0.2	1.44
South-West 1	2022	4.98	18.71	20.62	2.33	1.75	1.47	3.3	1.65	2.63
South West 2	2022	8.05	11.65	17.1	2.36	2.02	1.34	0.14	2.53	0.98

Table S2. Pasquill-Gifford-Classes used for characterization of the atmospheric stability condition as input parameter for the IDM calculations.

Pasquill-Gifford-Class	Stability	σ_θ
A	Extremely unstable	> 25
B	Moderately unstable	< 25
C	Slightly unstable	< 20
D	Neutral	< 15
E	Slightly stable	< 10
F	Moderately stable	< 5
G	Extremely stable	< 2.5

Table S3. Overview of the study sites in 2023.

Region	Campaigns	Application date	Application rate kg N ha ⁻¹	BBCH	Method	Latitude degrees °	Longitude degrees °	Sand %	Silt %	Clay %	CEC cmol kg ⁻¹	Soil pH
East	I-BB, II-BB, III-BB	16.03., 18.04., 26.05.2023	69.7, 52.3, 52.3	24, 30, 59	Alpha IHF Alpha IDM	51.832900	11.69310	15.5	65.1	19.3	17.9	7.1
	I-BG, II-BG	27.02., 02.05.2023	58.8, 58.8	21, 45	Alpha IHF Alpha IDM	52.619600	12.78490	71.6	19.8	8.5	6.9	6.4
Central	I-ME, II-ME, III-ME	21.03., 19.04., 25.05.2023	60, 50, 43	21, 30, 51	Alpha IHF Alpha IDM	52.220190	10.29272	79.1	12.0	8.9	8.3	6.6
	I-SI, II-SI, III-SI	20.03., 20.04., 24.05.2023	60, 50, 45	22, 32, 51	Alpha IHF Alpha IDM	52.111969	10.41136	17.6	69.4	13.0	13.5	6.3
South-West	I-EW, II-EW, III-EW	07.03., 14.04., 24.05.2023	90, 70, 70	23, 31, 51	Alpha IHF Alpha IDM	48.518299	7.869955	38.6	41.3	20.1	13.9	6.8
	I-HO, II-HO, III-HO	21.03., 03.05., 13.06.2023	70, 70, 70	26, 32, 69	Alpha IHF Alpha IDM	48.713643	9.195351	3.2	72.0	24.7	15.6	7.1
South	I-DN, III-DN	16.03., 20.05.2023	90, 90	25, 37	Alpha IHF Alpha IDM	48.407268	11.69187	13.7	64.7	21.5	13.8	6.8
	III-DN	04.05.2023	90	32	Alpha IHF Alpha IDM	48.402234	11.69302	15.9	56.9	27.1	17.8	6.5

Table S4. rRMSE and MBE of NH₃ loss differences between Alpha IHF and Alpha IDM from small plot trials in 2023 (n=20) in winter wheat the two concomitant criteria average wind speed <2.1 m s⁻¹ AND average temperature >10 °C over a whole measurement campaign were identified for the correction of cumulative emissions with a factor of 0.27

		rRMSE %	MBE kg/ha
2021/22 (n=18)	Raw data	39.78	+8.53
	Corrected values	19.63	+2.24
2023 validation dataset (n=20)	Raw data	28.81	+5.88
	Corrected values	8.97	+1.02
2021-23 all years (n=38)	Raw data	24.03	+7.14
	Corrected values	10.26	+1.59

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