Effect of Incorporation Techniques and Soil Properties on NH$_3$ and N$_2$O 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$_2$O) 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$_2$O 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$_2$O 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$_2$O emissions compared to surface application was observed. Therefore, an increase in N$_2$O 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

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 Sl2 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%.

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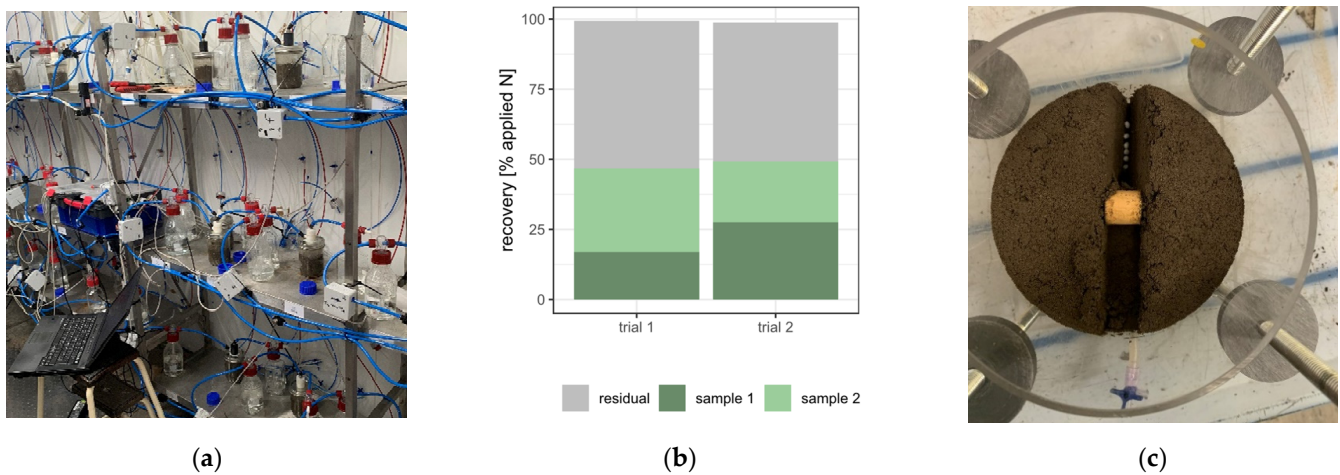
Figure 1. (**a**) Setup of flow chambers for NH_3 quantification, (**b**) recovery of the setup, and (**c**) application of urea with slit injection technique.

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 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% 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.

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

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 (CaCl₂) |
		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 Dürnast	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 NH_3 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 NH_3 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 NH_3 losses from the different treatments. The design of the experiment was based on findings from previous studies on NH_3 volatilization [22,23]. 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 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 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 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 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.

The tightness and NH_3 recovery efficiency of the system was evaluated in a separate trial with emissions from a 9.5 pH-controlled NH_4^+ bicarbonate solution (200 ppm, 5.5456 mM $(NH_4)_2SO_4$) in the same flow chamber facility (Figure 1b). Emitted NH_3 was captured with acid trap sampling in two separate trials subsequently. Sampled NH_3 and residual NH_4^+ in solution added up to a nitrogen recovery of 99% within the measurement uncertainty of the NH_4^+ concentration measurement for both trials.

2.3. NH₃ Analysis Flux Calculation

The NH_4^+ concentration in sulfuric acid was measured using an NH_3 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 ($M_{NH_3\ cum}$) (Equation (2)).

$$M_{NH_3\ cum} = \sum_{t1}^{ti} C_{NH_3} \times V_{acid} \qquad (2)$$

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)).

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

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, 79% N) 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, Kyōto, 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.

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

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 J mol^{-1} K^{-1}.

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

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)).

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

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 $-20\ ^\circ C$ 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 $^\circ C$) 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 614^1/4) and stored at $-20\ ^\circ C$ 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.

$$r = \frac{N_{min,end}}{\left(N_{min,start} + N_{fertilizer}\right)} \tag{7}$$

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.
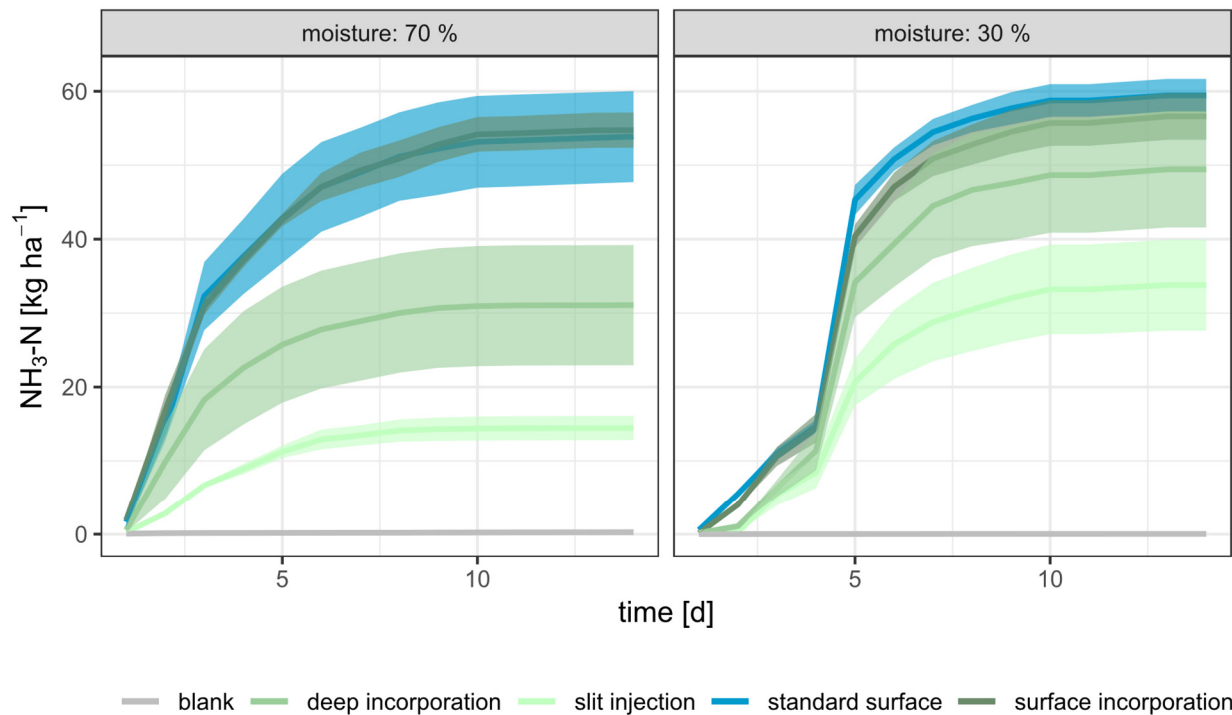
Figure 2. Cumulative NH_3-N losses from urea applied to the sandy soil of the investigated soils from different application techniques, including standard surface application, surface incorporation, deep incorporation, and slit injection, from sandy soil at two moisture levels (70 and 30 % WHC); lines 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.
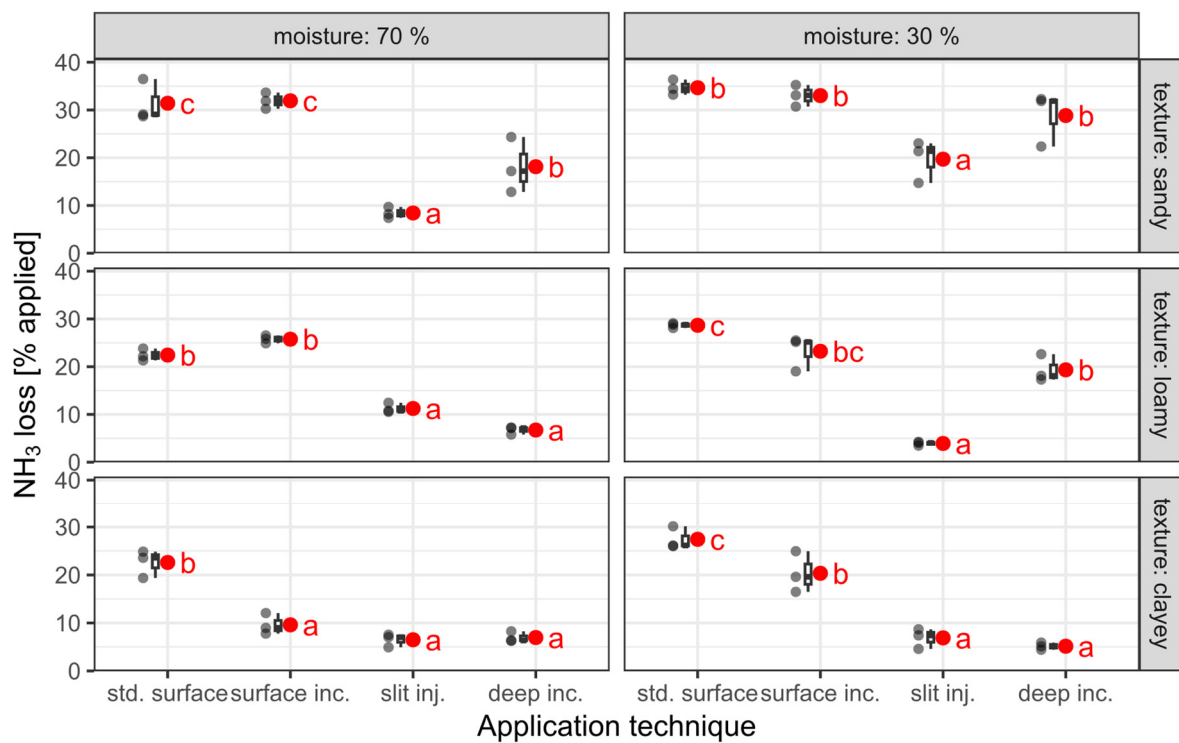
Figure 3. NH$_3$ losses [% of N applied] from urea fertilizer applied with standard (std.) surface, surface incorporation (inc.), slit injection (inj.), and deep incorporation (inc.) technique on three different soils (loamy, sandy, clayey) at two different moisture levels (70 and 30% WHC); replicates 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.
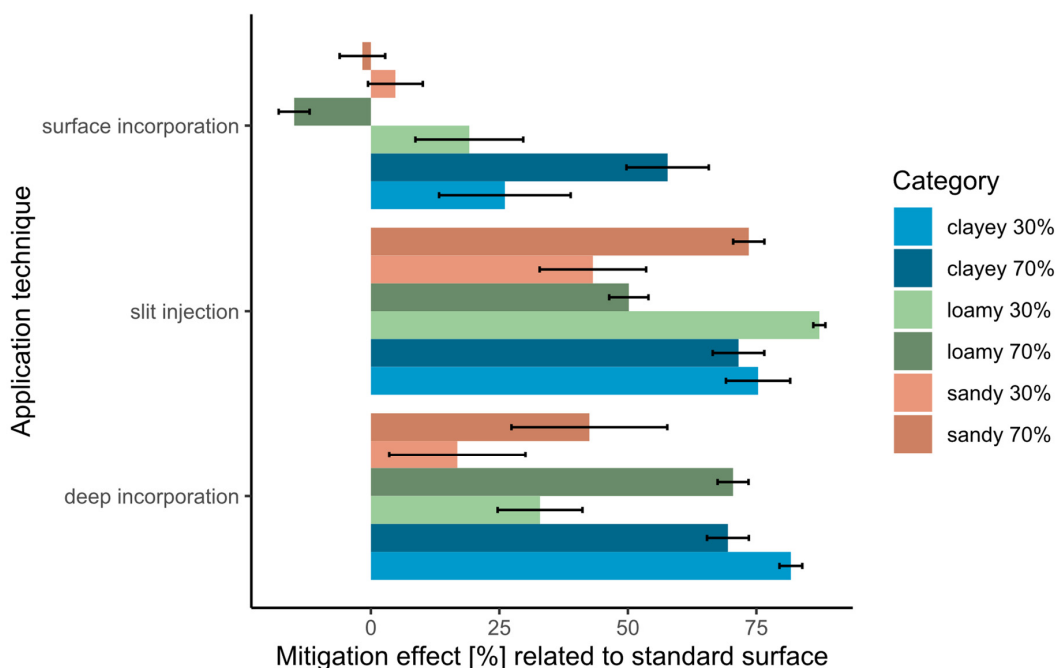
Figure 4. NH_3 mitigation effect [%] related to the cumulative loss of standard surface treatment with losses of surface incorporation, slit injection, and deep incorporation technique on three different soils (loamy, sandy, clayey) at two different moisture levels (70 and 30% WHC) each.

3.2. N Recovery NH_3 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).
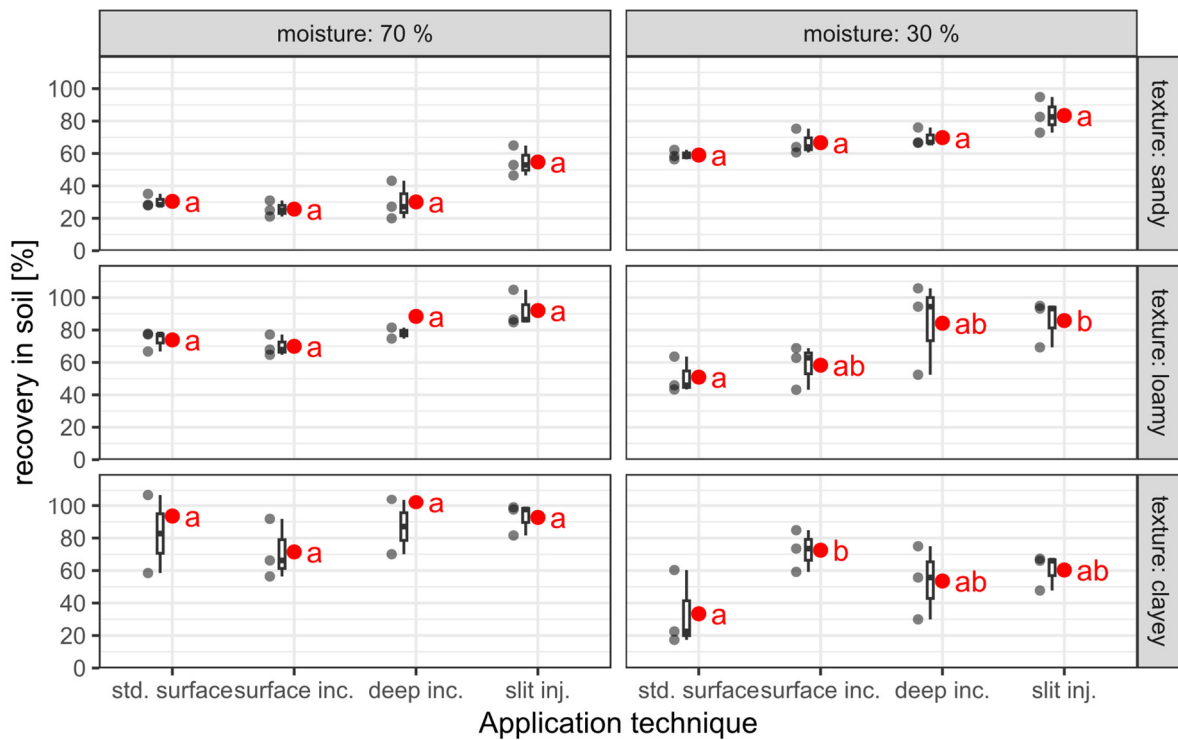
Figure 5. Recovery of mineral N content in three different soils (sandy, loamy, clayey) at two different moisture levels (70 and 30% WHC) with standard (std.) surface, surface incorporation (inc.), slit injection (inj.), and deep incorporation (inc.) technique after incubation for two weeks with start 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			
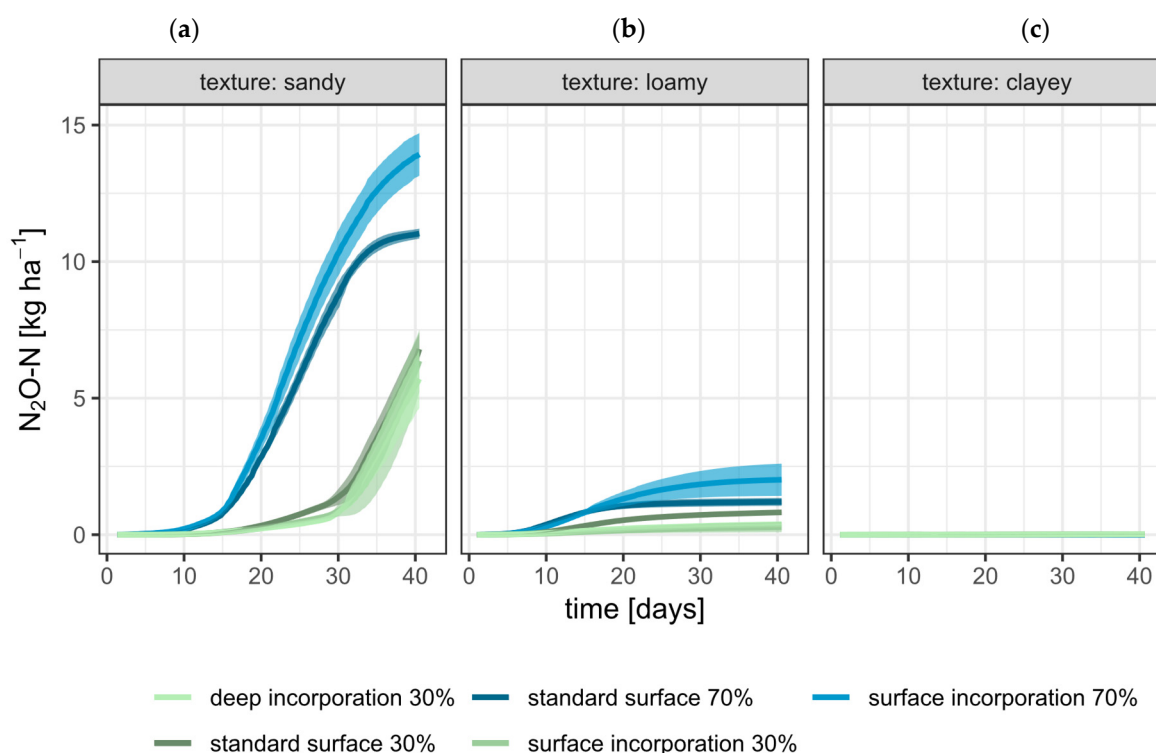
Figure 6. Cumulative losses of N$_2$O-N from urea applied with different application techniques, including standard surface, surface incorporation, and deep incorporation, on sandy (**a**), loamy (**b**), and clayey soil (**c**) at two moisture levels of 70% and 30% WHC; lines depict mean values (*n* = 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$_2$O 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$_2$O 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$_2$O 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,

NH_3 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 NH_3 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 NH_3 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 NH_4^+ ions, as sand does not have many functional groups that can adsorb NH_4^+ ions [29]. The resulting increased risk of NH_3 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 NH_4^+ ions, and NH_3 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 NH_3 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 NH_3 emissions for urea incorporated with slit injection in 5 cm depth since NH_4^+ bound to cation exchange sites does not contribute to rapid NH_3 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 NH_3 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 NH_3 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 N_2O 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 NH_4^+-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 $N_2O/(N_2O + N_2)$ 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 NH_4+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$_2$O 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$_2$O 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$_2$O emissions from urea applied with surface incorporation, deep incorporation, and slit injection compared to urea applied with standard surface technique are therefore recommended.

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