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Effects of Liquid Manure Application Techniques on Ammonia Emission and Winter Wheat Yield

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Abstract: Ammonia emissions following liquid manure application impair human health and threaten natural ecosystems. In growing arable crops, where immediate soil incorporation of the applied liquid manure is not possible, best-available application techniques are required in order to decrease ammonia losses. We determined ammonia emission, crop yield and nitrogen uptake of winter wheat in eight experimental sites across Germany. Each individual experiment consisted of an unfertilized control (N0), broadcast calcium ammonium nitrate (CAN) application as well as four different techniques to apply cattle slurry (CS) and biogas digestate (BD). Fertilizer was applied to growing winter wheat at a total rate of 170 kg N ha^{-1} split into two equal dressings. The following application techniques were tested for both liquid manure types: (i) trailing hose (TH) application using untreated and (ii) acidified (~pH 6) liquid manure (+A), as well as (iii) a combination of open slot injection (SI) for the first dressing and trailing shoe (TS) application for the second dressing without and (iv) with the addition of a nitrification inhibitor (NI) for the first dressing. The highest ammonia emissions (on average 30 kg N ha^{-1}) occurred following TH application of BD. TH application of CS led to significantly lower emissions (on average 19 kg N ha^{-1}). Overall, acidification reduced ammonia emissions by 64% compared to TH application without acidification for both types of liquid manures. On average, the combination of SI and TS application resulted in 23% lower NH_3 emissions in comparison to TH application (25% for the first application by SI and 20% for the second application by TS). Supplementing an NI did not affect ammonia emissions. However, decreasing ammonia emissions by acidification or SI did not increase winter wheat yield and nitrogen uptake. All organically fertilized treatments led to similar crop yield (approx. 7 t ha^{-1} grain dry matter yield) and above-ground biomass nitrogen uptake (approx. 150 kg ha^{-1}). Yield (8 t ha^{-1}) and nitrogen uptake (approx. 190 kg ha^{-1}) were significantly higher for the CAN treatment; while for the control, yield (approx. 4.5 t ha^{-1}) and above-ground biomass nitrogen uptake (approx. 90 kg ha^{-1}) were significantly lower. Overall, our results show that reducing NH_3 emissions following liquid manure application to growing crops is possible by using different mitigation techniques. For our field trial series, acidification was the technique with the greatest NH_3 mitigation potential.

Keywords: trailing hose; trailing shoe; open slot injection; nitrification inhibitor; acidification; biogas digestate; cattle slurry

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1. Introduction

Due to the growing human population, it is expected that animal husbandry will be doubled within this century [1,2] leading to increased ammonia (NH_3) emissions at the different stages of the manure management chain [3]. Besides animal housing and manure storage, spreading of liquid organic fertilizers is an important NH_3 emission pathway [1,4,5]. Ammonia emissions lead to the formation of particulate matter, which affects air quality and impairs human health [6–8]. Furthermore, NH_3 contributes to climate change [9], because nitrogen (N) deposition stimulates N transformation processes (mainly nitrification and denitrification) in the soil leading to the formation of the greenhouse gas nitrous oxide [10–12]. Acidification as well as eutrophication are additional problems associated with NH_3 emissions, especially when emitted NH_3 enters non-agricultural ecosystems [8,13–16]. Therefore, the international agreement on air pollution control and reducing national emissions of certain air pollutants (NEC Directive, National Emission Ceiling) defined limits for maximum NH_3 emissions [17]. Thus, the development of improved application techniques for liquid manures is mandatory [18,19]. Digestate from anaerobic fermentation, which has become increasingly popular over the last three decades due to rising global energy consumption [20], is associated with a high risk of NH_3 emission because pH and NH_4-N levels increase during the digestion process [21], leading to increased NH_3 emissions [22].

Ammonia emissions are only one aspect worth consideration when applying liquid manures. Crop yield [23], nutrient leaching [24,25] and the emission of greenhouse gases [11] are also relevant factors. In order to harmonize crop demand and nutrient availability, autumn application of liquid manure was drastically restricted for many crops, including winter wheat (*Triticum aestivum* L.) by German legislation in 2017 [26]. Therefore, slurries and digestates have to be applied near to the soil surface (e.g., trailing hose technique) in spring into the growing crop. Compared to autumn application, where immediate incorporation of liquid organic fertilizers into the soil before sowing of the next crop is possible, spring application is suspected to increase NH_3 emissions [19]. Thus, new application techniques are required aiming to reduce NH_3 emissions. Those techniques are based either on lowering the pH of the liquid organic fertilizer [27] or on reducing the contact area of the applied organic fertilizer with the atmosphere. The application by trailing shoe [28,29] or direct injection into the soil [30] are two prominent means to reduce the contact area to the atmosphere. Applying organic fertilizers with injection technique is oftentimes combined with the use of a nitrification inhibitor (NI) in order to reduce emission of the greenhouse gas N_2O [11], as well as nitrate leaching [31]. However, the stabilization of NH_4^+ may provoke additional NH_3-losses.

We applied cattle slurry (CS) and biogas digestate (BD) on two dates in spring to growing winter wheat in a network of field experiments in Germany to evaluate different application techniques. Application by trailing hose was regarded as standard and NH_3 emissions of optimized application techniques were compared with that standard. Those optimized application techniques were: trailing hose application of acidified liquid manure, open slot injection and open slot injection with the addition of a nitrification inhibitor. For the second dressing at each site, open slot injection was replaced by trailing shoe application in order to avoid crop damage. Furthermore, we put NH_3 emissions, yield and N uptake of organically fertilized treatments into perspective by also implementing a control without N fertilization and a treatment with mineral fertilization. Our objectives were:

- Determine the effects of the different application techniques on NH_3 emissions;
- Show if the effects of application techniques on NH_3 emission are consistent for CS and BD;
- Analyze the effects of weather conditions, soil, and fertilizer properties on NH_3 emissions and on the mitigation potential of optimized application techniques;
- Determine the effects of the different application techniques on yield and N uptake.

Those objectives lead to the following hypotheses:

1. The highest NH_3 emissions occur when using trailing hose technique and emissions are higher when applying BD compared to CS.
2. Acidification reduces NH_3 emissions for both types of liquid organic fertilizer.

3. Slot injection in combination with trailing shoe application on the second application date decreases NH_3 emissions for both types of organic fertilizer compared to trailing hose application and adding an NI does not affect NH_3 emissions.
4. Decreasing NH_3 emissions improves yield and N uptake.

2. Materials and Methods

2.1. Site Characteristics

The 2-year study (2019–2020) consisted of eight winter wheat (WW) field trials (Table 1) located in three different regions across Germany (Figure 1).

Table 1. Soil characteristics and weather conditions.

			Soil Characteristics								Weather Conditions	
Site	**Year**	**Soil Type**	**Sand** %	**Silt** %	**Clay** %	**pH**	**Bulk Density** g cm^{-3}	**CEC** mmolc kg^{-1}	C_{org} g kg^{-1}	N_{total} g kg^{-1}	**Precip.** mm	**Temp.** °C
BWa	2019	Calcaric Regosol	2	64	34	6.8	1.37	150	19.9	2.0	109	14.0
BWb	2020	Haplic Luvisol	2	71	27	6.8	1.35	130	12.3	1.3	169	11.5
LSa	2019	Plaggic Anthrosol	69	20	12	6.0	1.34	87	13.6	1.2	125	13.4
LSb	2020	Plaggic Anthrosol	41	51	8	6.1	1.36	93	17.0	1.6	89	11.6
SHa	2019	Luvisol	64	25	10	6.8	1.56	44	11.1	1.1	174	12.4
SHb	2019	Luvisol	56	33	11	6.4	1.59	48	12.6	1.2	174	12.4
SHc	2020	Luvisol	65	24	11	7.1	1.52	46	12.7	1.1	99	11.6
SHd	2020	Luvisol	76	16	7	6.4	1.33	37	13.7	1.4	98	11.9

The weather conditions refer to the winter wheat growing period between beginning of March to end of July. BW = Baden-Württemberg, LS = Lower Saxony, SH = Schleswig Holstein, a–d = different sites in each region, Bulk density = mean bulk density in the top soil layer (0–0.3 m), CEC = Cation-exchange capacity, C_{org} = Organic carbon, Precip. = cumulated precipitation, Temp. = Average temperature.

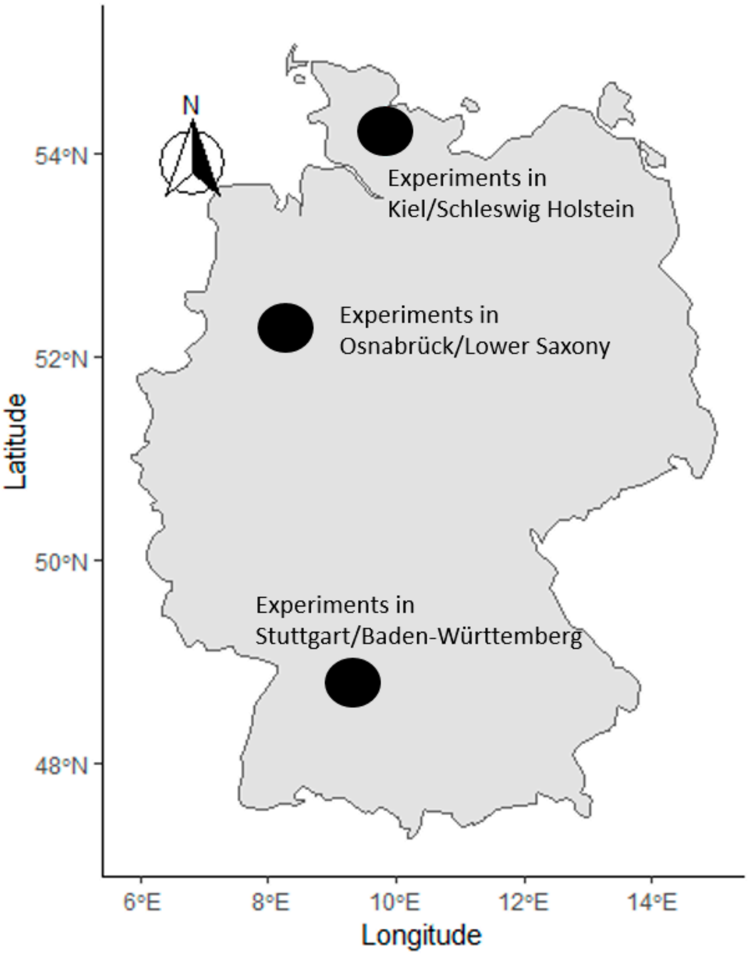

Figure 1. The three experimental regions across Germany.

Two sites were located in Baden-Württemberg (BWa, BWb) and Lower Saxony (LSa, LSb), whereas the remaining four sites were located in Schleswig-Holstein (SHa, SHb, SHc, SHd). On all sites, a winter oilseed rape–winter wheat crop rotation was followed. The sites were selected due to differences in soil and climate conditions (Table 1), affecting NH_3 volatilization and practicability of the manure application techniques. Climatic conditions (temperature, precipitation and wind speed) during the growing season (March until July) were measured at each site by a nearby weather station. Topsoil samples (0–0.3 m depth) were taken from each experimental site before the start of the WW growing period in early spring to determine physical and chemical properties of the soils. The samples were dried at 105 °C until constant weight. Soil pH was determined using 10^{-2} M $CaCl_2$ as extractant. Standardized methodology was used for cation exchange capacity (CEC) determination [32] and soil texture analysis [33]. Organic carbon and N content of the soil samples were analyzed by dry combustion [34]. Soil bulk density was measured based on soil cores collected at 0–0.1, 0.1–0.2 and 0.2–0.3 m depth at four places at each experimental site using stainless steel cylinders (100 cm^3 volume) that were then dried at 105 °C to constant weight. We derived soil types from the World Reference Base for Soil Resources [35]. Table 1 shows the results from the initial soil analyses.

2.2. Experimental Layout and Treatments

The field trials consisted of a control without N fertilization (N0), a calcium ammonium nitrate (CAN) treatment and four treatments with different techniques to apply CS and BD. In accordance with the German legislation [26], the maximum rate of 170 kg total N ha^{-1} via organic fertilizers was applied, split up into two equal rates of 85 kg N ha^{-1} at the end of March/start of April (end of tillering) and at the end of April (sprouting). For the CAN treatment, we applied 85 kg total N at each of the two dressings. We derived CS and BD from local farms close to the experimental sites, leading to slight variations regarding the NH_4-N application rates of individual experiments (Table 2).

Table 2. Weather conditions during the first 48 h after application as well as properties of the liquid organic fertilizers used at the individual application dates.

		Weather			Cattle Slurry					Biogas Digestate				
Site	**App.**	**Precip. mm**	**Temp. °C**	**Wind ms^{-1}**	**NH_4-N kg ha^{-1}**	**DM %**	**pH**	**pH Acid**	**Acid l m^{-3}**	**NH_4-N kg ha^{-1}**	**DM %**	**pH**	**pH Acid**	**Acid l m^{-3}**
BWa	1	2.4	10.0	0.8	31	5.1	6.8	5.8	1.6	51	7.6	7.6	6.2	6.6
	2	0.0	7.8	1.7	47	7.7	6.7	5.8	2.2	48	7.4	7.9	6.1	6.6
BWb	1	0.0	12.6	2.1	48	5.8	6.9	5.9	2.2	46	7.5	7.6	6.0	7.0
	2	0.0	14.8	2.8	49	5.6	6.8	5.9	1.7	46	8.6	7.8	6.2	4.3
LSa	1	4.8	5.0	0.9	38	9.1	6.9	6.0	2.9	45	6.0	7.7	6.5	6.2
	2	2.2	16.2	2.4	45	9.4	7.1	6.0	4.0	45	8.1	7.4	6.1	6.9
LSb	1	0.0	2.7	0.4	48	9.1	7.5	6.7	3.7					
	2	0.8	11.6	0.9	61	8.0	7.8	6.1	5.0					
SHa	1	6.0	7.6	2.4	48	5.6	8.0	NA	NA	51	5.5	7.7	7.4	2.2
	2	0.2	13.5	5.4	44	5.6	8.0	5.8	2.6	49	5.3	7.8	NA	4.5
SHb	1	1.0	3.8	3.8	48	7.8	7.3	NA	NA	51	5.5	7.7	7.4	2.2
	2	1.6	6.8	4.3	47	6.0	7.8	6.6	2.3	45	5.2	7.7	NA	3.4
SHc	1	0.0	4.7	3.7	49	8.3	7.9	4.0	5.8	57	4.4	7.7	6.7	4.5
	2	0.0	9.8	6.8	48	9.0	7.8	3.8	6.8	53	4.7	7.8	4.3	7.1
SHd	1	1.1	6.4	7.1	48	9.2	7.6	4.3	5.5	47	9.2	7.4	7.2	4.3
	2	1.0	9.8	3.5	48	8.6	7.6	5.2	4.0	55	4.8	7.8	3.8	7.3
Average					47	7.5	7.4	5.6	3.6	49	6.4	7.7	6.2	5.2

Precip. = cumulated precipitation, Temp. = Average temperature, Wind = Average wind speed, DM = Dry matter, NH_4-N = Amount of NH_4-N applied during each fertilization campaign, pH = pH of cattle slurry or biogas digestate without acidification, pH acid = pH of cattle slurry or biogas digestate with acidification, Acid = Amount of 98% sulfuric acid added to cattle slurry or biogas digestate in treatments with acidification, App = fertilizer application campaign [1 = End of March/Start of April, 2 = Middle/End of April], BW = Baden-Württemberg, LS = Lower Saxony, SH = Schleswig Holstein, a–d = different sites in each region, NA = not available.

In addition, the digestate source materials varied between sites. In SH and BW, the digestate was primarily based on maize silage, while slurry was only a minor component. In LS, the same slurry that was applied in the field experiments was used as the primary component for the digestate. To fulfill crop N demand, an additional CAN application

(40 kg ha^{-1} N for the experiments in LS and 60 kg ha^{-1} N for the experiments in SH) in all treatments (except N0) was performed during the bolting/heading development stage of the WW. Due to high N mineralization in both years, this mineral N application was not necessary for the two trials in Baden-Württemberg. CS and BD were applied by trailing hose (TH) and open slot injection (SI) technique to 0.05 m soil depth using a custom-made slurry spreader for small-plot trials based on an application technique from Samson Agro A/S (Viborg, Denmark). For TH application of CS and BD, untreated and acidified (+A) substrate was used. For acidification, the pH was adjusted to 6.0 by adding sulfuric acid (H_2SO_4). Substrate and acid were thoroughly mixed within a 1-m^3 tank before application. However, subsequent laboratory analysis of the pH in the acidified organic fertilizers revealed that the final pH in the applied products deviated slightly from the target pH value (Table 2). For SI application of CS and BD untreated substrate, as well as substrate plus a nitrification inhibitor (+NI) was used. For the NI treatments, the active ingredient 3,4-dimethylpyrazol phosphate was used as a commercially available product (2019: Entec-FL® by Eurochem Agro, application rate 6 L ha^{-1}; 2020: Vizura® by BASF, application rate 2 L ha^{-1}). The NI was added directly while the tank of the slurry spreader was filled and subsequently homogenously mixed with the respective substrate (either CS or BD). In order to avoid crop damage, the second application at each site was performed by trailing shoe (TS) instead of SI using the same custom-made slurry spreader. An NI was not added to the substrate for the second application (i.e., both CS and BD treatments were identical for the second application). All ten treatments (Table 3) were set up in a randomized block design with four replicates, except for the site LSb. This site consisted of only six treatments (N0, CAN and all four CS treatments). Generally, the plot size was 9 × 9 m, except for the sites SHa and SHb in 2019 where it was 9 × 6 m due to limited field area. To minimize cross contamination via NH_3 volatilization, unfertilized interspaces of 9 m surrounded the plots. For all organically fertilized treatments, the distance between the slurry bands was set to 0.25 m. Average width of the slurry bands or slits for TH, SI and TS application were 8.4, 4.3 and 5.7 cm. This led to an average soil coverage of 34, 17 and 23% for TH, SI and TS application.

Table 3. Treatment description.

Abbreviation	Substrate	Application Technique
N0	No nitrogen fertilization	
CAN	Calcium ammonium nitrate	Broadcast
CS:TH	Cattle slurry	Trailing hose
CS:TH+A	Acidified (pH ~6.0) cattle slurry	Trailing hose
CS:SI/TS	Cattle slurry	Slot injection (app. 1) Trailing shoe (app. 2)
CS:SI+NI/TS	Cattle slurry + NI (app. 1) Cattle slurry (app. 2)	Slot injection (1. app.) Trailing shoe (app. 2)
BD:TH	Biogas digestate	Trailing hose
BD:TH+A	Acidified (pH ~ 6.0) biogas digestate	Trailing hose
BD:SI/TS	Biogas digestate	Slot injection (app. 1) Trailing shoe (app. 2)
BD:SI+NI/TS	Biogas digestate + NI (app. 1) Biogas digestate (app. 2)	Slot injection (1. app.) Trailing shoe (app. 2)

App.1 = First application, App. 2 = Second application, NI = Nitrification inhibitor.

2.3. Measurement of Ammonia Emissions

At all sites, NH_3 measurements were performed in all plots for the first two dressings. The amount of NH_3-N collected by passive samplers (PS; i.e., open plastic bottles filled with a sulfuric acid solution) placed in the middle of each plot was calibrated by performing simultaneous measurements with the dynamic tube method (DTM) in all plots of the CS:TH treatment [36].

For DTM measurements, the chamber system was centered on the slurry band, covering 11.5 of the 25 cm distance between slurry bands, which equals 46% of the total area. The NH_3 concentration within the chamber system was measured with a gas analysis detector tube (3–70 ppm, Drägerwerk AG, Lübeck, Germany) after exchanging a specified air volume using an automated pump (X-ACT 5000, Dräger, Lübeck, Germany). NH_3 fluxes were calculated following the procedure described by Pacholski [36] and the proportion of the area covered by the chambers, which contained all the applied fertilizer, was related to the total area between two slurry bands by using the factor 0.46. Subsequently, NH_3 fluxes were cumulated by linear interpolation between DTM measurements.

For the PS, the mean of the collected NH_3-N in the N0 plots was considered as background and therefore subtracted from the measured NH_3-N values in each plot. This procedure can result in values below zero, since NH_3-N collected in N0 plots is only an approximation for determining the background.

The transfer coefficient (TC) required for calibrating PS results was obtained by dividing DTM CS:TH treatment mean by PS CS:TH treatment mean (Equation (1)):

$$\mathrm{TC} = \left(\frac{\text{treatment mean DTM cumulated } \left(\text{kg N ha}^{-1}\right)}{\text{treatment mean PS cumulated } \left(\text{mg N L}^{-1}\right)} \right) \tag{1}$$

2.4. Yield and Nitrogen Use Efficiency

Yield data were determined by taking two subsamples of 0.5 m^2 in each plot when the WW reached harvest maturity. Plants were cut above the soil surface and subsequently divided into the fractions ear and culm. Both fractions were dried for 48 h at 58 °C and the ears were threshed afterwards to obtain the grain dry matter yield (t ha^{-1}) of each individual plot. Grain as well as culm samples were milled to 1 mm and the dry matter N content was analyzed by near infrared spectroscopy (Foss NIRSystems, Silver Springs, MD, USA). N uptake (kg ha^{-1}) of grain and above-ground biomass (grain + culm) was calculated by multiplying N concentration (%) and dry matter yield (kg ha^{-1}) of each individual plot. Furthermore, the apparent N use efficiency (aNUE) was calculated for grain and whole plants as shown in Equation (2) according to Sistani et al. [37]:

$$\mathrm{aNUE} = \frac{\text{Total N uptake by treatment} - \text{Total N uptake by treatment N0}}{\text{Total N applied}} \tag{2}$$

2.5. Analyses of Variance (ANOVA)

We assessed the effect of various fixed factors on NH_3 emissions, the NH_3 mitigation potential of optimized application techniques (acidification, SI/TS), yield, N uptake and aNUE by computing ANOVA models using IBM SPSS statistics 29. The NH_3 mitigation potential was defined as the relative reduction of NH_3 emissions in a plot with optimized application technique compared to the average NH_3 emissions in the TH treatment with the corresponding type of liquid organic fertilizer (CS or BD). It was calculated according to Equation (3) [38]:

$$\text{Mitigation potential } (\%) = \frac{(\text{mean NH}_3 \text{ in TH treatment}) - (\text{NH}_3 \text{ in treated plot})}{(\text{mean NH}_3 \text{ in TH treatment})} * 100 \tag{3}$$

For all ANOVA models, we took into account all possible interactions between fixed factors included in the respective model. Due to our study design, the random factor block (within site) was also included in all ANOVA models. Tuckey tests were then performed for all ANOVA models to analyze significant differences ($p \leq 0.05$) between groups when comparing more than two groups. In Table A1, all ANOVA models are described in detail.

2.6. Correlation of Soil Parameters, Weather Conditions and Fertilizer Properties with NH_3 Emissions and NH_3 Mitigation Potential

For TH treatments with CS and BD application, correlation coefficients (R) and the significance of the slope were calculated for the relationship of several parameters with the average NH_3 emissions per treatment at each application. Additionally, CS:TH and BD:TH treatment means were correlated with all parameters in a "joint" analysis. For the treatments CS:TH+A, BD:TH+A, CS:SI/TS and BD:SI/TS, R values and significance of slope were calculated for the relationship of the same parameters with the average NH_3 mitigation potential per treatment. Additionally, CS:TH+A and BD:TH+A as well as CS:SI/TS and BD:SI/TS treatment mean mitigation potential were correlated with all parameters in a "joint" analysis. Parameters were divided into the sections soil parameters, weather conditions and fertilizer properties. For describing the strength of the relationship between parameters and NH_3 emissions/mitigation potential we used the terms negligible ($R < 0.3$), slight ($R = 0.3$–< 0.4), slight to medium ($R = 0.4$–< 0.5), medium ($R = 0.5$–< 0.6), medium to strong ($R = 0.6$–< 0.7), strong ($R = 0.7$–< 0.8) and very strong ($R < 0.8$).

3. Results and Discussion

3.1. Ammonia Emission

3.1.1. Ammonia Emissions following Trailing Hose Application without Acidification

As expected, the highest NH_3 emissions occurred using trailing hose application without acidification (Table 4). Obviously, this is due to the comparatively large contact area between the liquid organic fertilizer and the atmosphere [22]. Averaged across all sites and both types of fertilizer (CS/BD), 25% of the applied ammoniacal N was lost as NH_3. This is comparable to previous findings [39], where 20% of the applied ammoniacal N was lost as NH_3. However, compared to broadcast application, which was the standard application technique in the past, trailing hose application is already considered as a NH_3 mitigation technique [19]. BD application by trailing hose led to significantly higher NH_3 emissions than CS application (Table 3). Considering both applications per site, we calculated average NH_3-N emissions of 30 kg ha^{-1} per site for BD, while applying CS led to average NH_3-N emissions of 19 kg ha^{-1} (Table 4).

However, the variation in NH_3 emissions between the different application campaigns and individual experimental fields was high. Usually, BD has a higher pH and NH_4-N content compared to the input material for the biogas fermentation process [21], which might explain the increased NH_3 emissions [22]. For our experiments it has to be kept in mind that the applied BD was not based on the CS applied in the field trials (except for the experiments in LS) and therefore the pH value and NH_4-N concentration of the BD are not directly comparable to the applied CS.

Overall, the average pH of the BD was only slightly higher than the average pH of the CS (7.7 versus 7.4; Table 2). Furthermore, we found no evidence that increased NH_4-N application rates (range 31–61 kg N ha^{-1}; Table 2) led to higher NH_3 emissions in this study (Table 5). Thus, other liquid manure characteristics such as CEC and pH buffer capacity [40] might also be relevant for the increased NH_3 emissions following BD application, but were not directly analyzed in the present study. Generally, acidifying BD required more acid than acidifying CS (Table 2), indicating that the buffer capacity of BD was higher than that of CS. Thus, the pH of the BD might have stayed on a comparatively high level after application, possibly explaining the comparatively high NH_3 emissions following BD application by TH compared to the CS:TH treatment. Monitoring the pH of liquid manure after application in future studies could validate this hypothesis.

NH_3 emissions following TH application varied between sites (Tables 6 and A2). For individual sites, we calculated NH_3-N emissions between 4.8 and 38.1 kg ha^{-1} following CS:TH application and for the BD:TH treatment emissions ranged between 15.9 and 47.2 kg NH_3-N ha^{-1} (Table 6). In order to explain these differences, we analyzed the relationships of several parameters with the average NH_3 emissions (kg N ha^{-1}) of CS:TH and BD:TH treatments during each application. Additionally, the mean NH_3 emissions (kg N ha^{-1}) for the TH treatments with CS and BD application were correlated with those parameters in a "joint" analysis (Table 5). Regarding the pH of the applied liquid organic fertilizer, we found a significant correlation for the "joint" analysis. However, the correlation coefficient of 0.37 (Table 5) indicated only a small effect on the amount of NH_3 emissions, although it is well known that a high pH shifts the NH_3/NH_4^+ ratio towards NH_3, which increases NH_3 emissions [27]. Our calculation revealed that soil pH affected NH_3 emissions significantly with a slight to medium (R = 0.47) effect strength. Similarly to the pH of the liquid organic fertilizer, a high soil pH shifts the NH_3/NH_4^+ ratio towards NH_3 increasing NH_3 emissions [1,41]. CS application responded slightly stronger to the soil pH than BD application (Table 5), indicating that the pH buffering capacity of BD might be higher, which possibly decreased soil pH effects. Adsorption of NH_4^+ to the soil's cation exchange sites might reduce NH_3 emissions [40], however, in our two-year field study the soil CEC only affected NH_3 emissions following CS application (R = 0.53), but not for BD application (R = −0.01; Table 5).

Table 4. Effect of treatment, application technique, fertilizer type and application date on NH_3 emissions across sites.

			NH_3-N Emissions				
	kg ha^{-1}		**% TAN Applied**		**% Total N Applied**		**Sample Size**
Treatment [1]		***		***		***	
N0	0.0	a					64
CAN	0.0 [5]	a	0.0 [5]	a	0.0 [5]	a	64
CS:TH	19.0	d	20.4	d	11.2	d	64
CS:TH+A	8.0	b	8.9	bc	4.7	b	64
CS:SI/TS	14.3	c	15.2	c	8.4	c	64
CS:SI+NI/TS	14.1	c	15.0	c	8.3	c	64
BD:TH	30.3	f	30.7	f	17.8	f	56
BD:TH+A	10.5	bc	10.6	b	6.2	bc	56
BD:SI/TS	25.0	e	25.4	e	14.7	e	56
BD:SI+NI/TS	25.1	e	25.3	de	14.8	e	56
Application technique [2]		***		***		***	
TH	24.3	c	25.2	c	14.3	c	120
TH+A	9.2	a	9.7	a	5.4	a	120
SI/TS	19.3	b	19.9	b	11.3	b	120
SI+NI/TS	19.2	b	19.8	b	11.3	b	120
Fertilizer type [3]		***		***		***	
CS	13.8	a	14.9	a	8.1	a	256
BD	22.7	b	23.0	b	13.4	b	224
Application date [4]		n.s.		n.s.		n.s.	
App. 1	8.7	n.s	18.1	n.s	10.2	n.s	240
App. 2	9.3	n.s	19.3	n.s	10.9	n.s	240
Site		***		***		***	

Different lower case letters indicate significant differences ($p \leq 0.05$) between groups. n.s = Not significant, *** = $p < 0.001$, TAN = Total ammonium nitrogen, N = Nitrogen, N0 = No nitrogen fertilization, CAN = Calcium ammonium nitrate, CS = Cattle slurry, BD = Biogas digestate, TH = Trailing hose, +A = Acidification, SI = Slot injection, TS = Trailing shoe, NI = Nitrification inhibitor, App. = Application, [1] = mean across sites, [2] = mean across site and fertilizer type, [3] = mean across site and application technique, [4] = mean of organically fertilized treatments across sites, [5] = numerically negative mean values were set to zero.

Table 5. Correlation coefficients for the effects of soil, weather and fertilizer characteristics differentiated for cattle slurry and biogas digestate on the NH_3 emissions for the trailing hose treatment as well as on the NH_3 mitigation potential of acidification and trailing shoe/open slot application.

		Effect on NH_3 Emissions			**Effect on Mitigation Potential** [1]					
	Parameter	**TH Treatments**			**Acidification**			**SI/TS Treatments**		
		CS	BD	CS+BD	CS	BD	CS+BD	CS	BD	CS+BD
Soil	Sand content	0.35	−0.18	0.04	0.05	0.07	0.06	0.03	0.69 **	0.32
	Silt content	−0.39	0.23	−0.05	−0.02	−0.11	−0.06	−0.12	−0.69 **	−0.36 *
	Clay content	−0.22	0.07	−0.03	−0.11	0.02	−0.05	0.16	−0.64 *	−0.20
	pH	0.56 *	0.43	0.47 **	−0.45	−0.39	−0.43 *	−0.15	−0.67 **	−0.38 *
	Bulk density	0.43	0.13	0.25	−0.43	−0.70 **	−0.56 **	0.08	−0.09	0.00
	CEC	−0.53 *	−0.01	−0.22	0.08	0.22	0.14	0.11	−0.48	−0.15
	C_{org}	−0.49	−0.23	−0.34	−0.09	0.22	0.05	−0.01	−0.30	−0.12
	N_{total}	−0.47	−0.18	−030	−0.06	0.12	0.02	−0.06	0.12	−0.2
Weather	Temperature	−0.12	−0.11	−0.09	0.48	0.16	0.34	0.20	−0.26	0.00
	Wind speed	0.83 ***	0.22	0.48 **	−0.22	−0.25	−0.24	−0.24	−0.10	−0.19
	Precip.	−0.36	−0.58 *	−0.43 *	0.23	−0.05	0.10	0.45	0.55 *	0.48 **
Fertilizer	DM	0.08	−0.27	−0.23	−0.05	0.42	0.15	−0.15	−0.29	−0.14
	pH	0.40	0.19	0.37 *	0.33	−0.35	0.01	−0.27	−0.39	−0.31
	NH_4-N	0.11	0.18	0.21	0.18	−0.12	0.06	−0.3	0.00	−0.23
	Acid amount				−0.15	0.74 **	0.24			

Correlation with weather parameters was performed using data obtained from the first 48 h after application. The acid amount refers to the amount of sulfuric acid (standardized for 98% H_2SO_4) used for acidification. [1] % NH_3 mitigation compared to the trailing hose treatment with the same type of fertilizer, * = Slope significance level of $p \leq 0.05$, ** = Slope significance level of $p \leq 0.01$, *** = Slope significance level of $p < 0.001$, TH = Trailing hose application, SI = Slot injection, TS = Trailing shoe application, CS = Cattle slurry, BD = Biogas digestate, CS/BD = Correlation was performed including data from both types of fertilizer, CEC = Cation-exchange capacity, Corg = Organic carbon, Ntotal = Total nitrogen, Precip. = Precipitation, DM = Dry matter.

Regarding the weather conditions within the first 48 h after application, we could not find a significant temperature effect, although the partition of NH_3 between liquid and gaseous phase shifts towards the gaseous phase with increasing temperature [42] leading to increased NH_3 emissions. Additionally, more water evaporates due to higher temperature, increasing the NH_3 concentration in the liquid phase [22]. For the wind speed we found a very strong correlation (R = 0.83) regarding CS, but again not for BD application (R = 0.22; Table 5). High wind speed increases the air exchange rate [43], which decreases the NH_3 concentration in the air layer close to the applied organic fertilizer [22]. This leads to an increased concentration gradient between the relatively high NH_3 concentration in the liquid phase and ambient air, increasing NH_3 volatilization [22]. However, the methodology used for this study does not directly measure increased NH_3 emissions induced by high air exchange rates, since the air exchange rate in the chamber system is not influenced by the actual wind speed [43]. Instead, the measured NH_3 emissions are adjusted for wind speed using an empirical formula [43]. Since treatment CS:TH and not treatment BD:TH was used to scale relative differences between plots, correlation of wind speed and NH_3 emissions is stronger for the CS treatment. Increased precipitation significantly decreased NH_3 emissions (R = −0.43 in the "joint" analysis, Table 5). According to Misselbrook et al. [44] rainfall decreases NH_3 emissions by washing the applied NH_3/NH_4^+ in the liquid phase of the organic fertilizer into the soil.

Overall, we confirmed our initial hypotheses that the highest NH_3 emissions occurred when using trailing hose technique and emissions were higher when applying BD compared to CS.

Table 6. Ammonia emissions (kg ha^{-1}) for each trial site and fertilizer application campaign.

								CS													BD										
Site	**App.**	**N0**			**CAN**			**TH**			**TH+A**			**SI/TS**			**SI+NI/TS**			**TH**			**TH+A**			**SI/TS**			**SI+NI/TS**		
BWa	1	0	±0.8	a	−0.4	±0.8	a	4.3	±2.7	abc	2.3	±1.1	ab	1.8	±2.3	ab	2.5	±2.1	ab	6.0	±3.7	bc	2.2	±2.1	ab	6.2	±1.7	b	7.9	±4.0	c
BWa	2	0	±2.6	a	−0.8	±2.9	a	7.0	±5.3	abc	3.8	±3	ab	5.6	±4.6	ab	2.6	±3.2	a	15.5	±4.4	bc	6.1	±4.3	ab	17.1	±4.9	c	14.8	±5.2	bc
BWa	1 + 2	0	±2.3	a	−1.2	±3.3	a	11.3	±7.2	bc	6.1	±3.5	ab	7.4	±6.1	ab	5.1	±4.8	ab	21.5	±6.9	cd	8.3	±5.8	ab	23.3	±5.8	d	22.7	±7.0	d
BWb	1	0	±2.7	a	−0.3	±2.3	a	8.4	±0.9	ab	4.6	±4	a	6.9	±2.1	a	6.0	±4.1	a	35.9	±7.6	d	3.5	±1.4	a	27.9	±7.1	cd	18.1	±3.3	bc
BWb	2	0	±2.8	ab	−1.9	±4.4	a	10.7	±3.2	cd	−1.9	±3	a	8.6	±2.3	cd	7.3	±2.7	bc	10.8	±1.9	cd	6.2	±2.3	bc	13.9	±4.3	cd	15.6	±3.4	d
BWb	1 + 2	0	±5.0	a	−2.2	±6.0	a	19.1	±3.3	c	2.7	±6.4	ab	15.5	±3.6	c	13.3	±6.1	bc	46.7	±6.3	e	9.7	±1.7	abc	41.8	±10.2	de	33.7	±4.5	d
LSa	1	0	±1.5	ab	−0.2	±1.7	a	5.8	±0.8	e	0.8	±0.5	ab	2.4	±0.7	abc	2.8	±1.0	bcd	10.8	±1.0	f	0.5	±0.9	ab	4.8	±0.9	cde	5.6	±2.1	de
LSa	2	0	±1.4	a	0.0	±1.7	a	5.2	±3.1	b	0.2	±2.3	a	2.1	±1.9	ab	1.6	±0.8	ab	5.1	±1.8	b	−0.7	±1.5	a	2.8	±2.4	ab	3.5	±2.5	ab
LSa	1 + 2	0	±2.6	a	−0.2	±2.0	a	11.0	±3.1	cd	1.0	±1.9	a	4.5	±1.5	ab	4.4	±1.3	ab	15.9	±1.8	d	−0.2	±1.8	a	7.6	±2.5	bc	9.1	±4.0	bc
LSb	1	0	±0.7	a	0.4	±1.0	a	1.8	±0.8	ab	0.8	±0.7	ab	2.5	±1.3	b	1.5	±0.6	ab												
LSb	2	0	±1.2	a	0.1	±0.2	a	3.0	±1.0	b	0.2	±0.9	a	1.8	±0.4	ab	2.4	±2.1	ab												
LSb	1 + 2	0	±1.7	a	0.5	±1.1	a	4.8	±1.2	c	1.0	±1.4	ab	4.3	±1.4	c	3.9	±2.2	bc												
SHa	1	0	±0.9	ab	−1.1	±0.8	a	5.3	±2.2	b	1.5	±1.2	ab	3.9	±1.2	ab	5.7	±2.6	b	5.8	±4.0	b	4.7	±0.5	ab	3.9	±3.4	ab	4.7	±4.1	ab
SHa	2	0	±3.8	ab	−2.0	±4.4	a	13.0	±6.4	c	6.8	±4.6	abc	11.4	±3.3	bc	13.6	±5.4	c	13.6	±6.6	c	10.2	±4.3	b	13.0	±3.4	c	15.1	±3.4	c
SHa	1 + 2	0	±3.0	a	−3.1	±4.5	a	18.3	±7.6	b	8.3	±4.9	ab	15.3	±4.2	b	19.3	±3.6	b	19.4	±6.2	b	14.9	±4.4	b	16.9	±5.7	b	19.8	±6.2	b
SHb	1	0	±1.6	a	0.2	±1.1	ab	10.1	±1.0	cd	5.4	±2	bc	5.1	±1.1	abc	7.7	±1.4	cd	15.7	±2.8	e	11.6	±1.5	de	12.3	±2.9	de	10.3	±3.6	cd
SHb	2	0	±3.3	a	0.3	±2.6	ab	13.5	±6.6	cde	5.3	±1.4	abc	8.2	±3.0	abcd	12.3	±5.6	cde	18.8	±5.3	e	10.2	±3.2	bcde	14.9	±4.2	cde	15.9	±4.3	de
SHb	1 + 2	0	±2.4	a	0.5	±3.2	a	23.6	±5.6	cde	10.7	±2.9	ab	13.3	±3.5	bc	20.0	±6.0	bcd	34.5	±6.0	e	21.8	±6.0	cd	27.2	±6.2	de	26.2	±6.1	de
SHc	1	0	±3.0	ab	−3.3	±5.2	a	21.3	±3.3	d	19.2	±9.1	d	13.1	±4.0	bcd	14.9	±3.5	cd	24.3	±9.6	d	4.1	±6.9	abc	19.7	±4.9	d	18.3	±5.3	d
SHc	2	0	±1.8	a	0.1	±2.5	a	16.8	±8.3	bc	6.6	±8.2	ab	16.6	±6.8	bc	14.9	±5.3	abc	22.9	±7.8	bc	9.0	±9.2	ab	21.8	±6.6	bc	25.9	±5.2	c
SHc	1 + 2	0	±2.6	a	−3.2	±7.0	a	38.1	±10.5	cd	25.8	±13.6	bc	29.7	±6.7	bcd	29.8	±4.7	bcd	47.2	±11.3	d	13.1	±9.7	ab	41.5	±9.6	cd	44.2	±7.2	cd
SHd	1	0	±3.9	ns.	0.7	±6.8	ns.	17.4	±8.2	ns.	9.7	±8.8	ns.	17.6	±5.4	ns.	9.6	±4.3	ns.	11.8	±4.7	ns.	3.2	±10.5	ns.	9.2	±7.4	ns.	10.1	±9.1	ns.
SHd	2	0	±2.9	ab	−1.8	±2.6	a	8.6	±4.1	cd	−1.4	±1.9	a	6.5	±2.7	bc	7.1	±1.1	bcd	14.8	±4.3	d	2.5	±2.5	abc	7.5	±2.3	cd	9.9	±4.8	cd
SHd	1 + 2	0	±2.7	a	−1.1	±6.5	a	26.0	±9.4	c	8.3	±8.5	abc	24.1	±4.0	bc	16.7	±4.7	abc	26.6	±6.6	c	5.7	±10.6	ab	16.7	±7.9	abc	20.0	±12.8	bc

Different lower case letters indicate significant differences ($p \leq 0.05$) between treatments within site and/or fertilization campaign. ± indicates the standard deviation, App. = Application campaign, N = Nitrogen, N0 = No nitrogen fertilization, CAN = Calcium ammonium nitrate, TH = Trailing hose, +A = Acidification, SI = Slot injection, +NI = Substrate + Nitrification inhibitor, TS = Trailing shoe, BW = Baden-Württemberg, LS = Lower Saxony, SH = Schleswig Holstein, a–d = Different sites in each region, ns. = Not significant.

3.1.2. Ammonia Emissions following Trailing Hose Application with Acidification

In our second hypothesis, we stated that acidification reduces NH_3 emissions for both types of liquid manure (CS and BD). On average, acidification reduced NH_3 emissions by 65% for CS and by 63% for BD compared to TH application without acidification (Table 7). Those findings are in accordance with results reported in previous studies [27,45]. However, the mitigation potential for each individual field experiment ranged from 10 up to 100% compared to the TH treatment with the corresponding type of liquid organic fertilizer (Table A3).

Table 7. Influence of fertilizer type, application date and nitrification inhibitor on the NH_3 mitigation potential (% NH_3 mitigation compared to the trailing hose treatment with the same type of fertilizer) of acidification and slot injection/trailing shoe application across sites.

	Acidification		**SI/TS Treatments**	
Fertilizer type		n.s.		*
CS	65.1	n.s.	26.4	b
BD	63.0	n.s.	18.2	a
Average	64.1		22.3	
Application date		*		n.s.
1. app.	57.0	a	25.2	n.s.
2. app.	71.2	b	20.0	n.s.
Average	64.1		22.6	
NI	n.a.			n.s.
−NI (1. app.)	n.a.		25.2	n.s.
+NI (1. app.)	n.a.		25.8	n.s.

Different lower case letters indicate significant differences ($p \leq 0.05$) between groups. * = $p \leq 0.05$, n.s. = Not significant, SI = Slot injection, TS = trailing shoe, CS = Cattle slurry, BD = Biogas digestate, app = Application (for SI/TS treatments the 1. app. was applied as SI and 2. app. was applied as TS), −NI = No Nitrification inhibitor regarding the 1. app. by slot injection, + NI = Addition of nitrification inhibitor regarding the 1. app. by slot injection, n.a. = not applied.

Overall, the type of fertilizer (CS vs. BD) did not influence the relative mitigation potential (Table 5). That means that the absolute reduction of NH_3 emissions was higher for BD, since emissions were generally higher following BD application (Table 4).

The individual soil and weather conditions at the trial sites (Table 1), as well as the fertilizer properties (Table 2) might have influenced the mitigation potential of acidification. To explain differences between the mitigation potential of individual experiments, we analyzed the influence of these parameters on the average NH_3 mitigation potential (Table 5). With increasing soil pH, the NH_3 mitigation potential of acidification was slightly reduced (R = −0.43; Table 5), i.e., when the soil pH is high, the relative influence of the CS/BD pH is lower. Also, an increasing soil bulk density led to a decreased NH_3 mitigation potential of acidification (R = −0.56; Table 5). This effect was more pronounced for BD (R = −0.70) than for CS (R = −0.43). According to the correlation analysis, the pH of the acidified organic fertilizer did not affect the efficiency of acidification (Table 5). The target pH was set to 6.0 and slight deviations from that target (Table 2) did not affect the general efficiency of the acidification. For BD we found a strong relationship (R = 0.74) between the amount of H_2SO_4 added for acidification and the mitigation potential, whereas for CS the mitigation potential was not affected by the amount of acid (R = −0.15). On average, over all application dates (Table 2), more acid was required for acidifying BD (5.2 $l\ m^{-3}$) than for acidifying CS (3.6 $l\ m^{-3}$), indicating that the buffer capacity of BD was generally higher. This indicates that the pH of the BD might have increased relatively quickly after application when not enough acid was added, although initially the target pH was reached [46,47]. However, it must be considered that the regular use of H_2SO_4 might led to excess sulfur (S), which might induce sulfate leaching. For our experiments, about

60 kg S ha^{-1} was applied with 20 m^3 of acidified BD, while the S demand of winter wheat is around 25–30 kg ha^{-1}. Therefore, we advise to add H_2SO_4 only when conditions favor NH_3 emissions. Furthermore, for commercial techniques such as the SyreN system [48], acid is added immediately before soil application using a static mixer installed in the output line of the slurry tanker [27]. This differs from the method used for this study, where the liquid manure was acidified prior to application in a tank, enabling an exact pH measurement of the acidified liquid manure. According to the "Verification of Environmental Technologies for Agricultural Production", the SyreN system reduces NH_3 emissions by 49% for CS and by 40% for pig slurry compared to trailing hose application [48], which is lower than the mitigation potential found in this study (65% for CS; Table 7).

Overall, we can confirm our initial hypothesis that acidification reduces NH_3 emissions for both types of organic fertilizer. We identified soil pH and bulk density as important factors influencing the mitigation potential of acidification. Furthermore, the pH buffer capacity of the applied liquid manure seems to play a vital role regarding the efficiency of acidification. Monitoring the pH after application might increase our understanding concerning the influence of that factor.

3.1.3. Ammonia Emissions following Slot Injection and Trailing Shoe Application

In our third hypothesis, we stated that reducing the contact area of the applied liquid fertilizer and the atmosphere by slot injection or trailing shoe application decreases NH_3 emissions for both types of organic fertilizer. Following SI (first application) and TS application (second application), on average only 17 and 23% of the soil surface were covered with organic fertilizer, while TH application resulted in a soil surface coverage of 34%. This illustrates that SI combined with TS application clearly reduced the contact area of the applied liquid fertilizer with the atmosphere, which according to Hansen et al. [49] should result in lower NH_3 emissions. In our multi-site multi-year field trial series, we found significantly reduced NH_3 emissions for both types of organic fertilizer compared to their respective TH treatment (Table 4). The overall NH_3 mitigation potential of the CS:SI/TS treatment was 26%, while for the BD:SI/TS treatment it was significantly lower (Table 5), where NH_3 emissions were on average reduced by 18% (Table 7). However, considering that BD application generally leads to higher emissions (Table 4), absolute reduction is comparable for CS and BD. Interestingly, the time period of application did not significantly influence the mitigation potential (Table 7), although the first application at each site was performed using SI (17% of surface area covered by fertilizer), while the second was performed using the TS technique (23% covered).

We also tested the sub hypothesis that adding an NI does not affect NH_3 emissions by slot injection. The addition of an NI to NH_4 containing fertilizers such as CS or BD means that the conversion from NH_4-N to NO_3-N is inhibited [31], which could theoretically lead to an increase in NH_3 emissions due to prolonged presence of NH_4^+. However, our data showed that the mitigation potential of SI and SI+NI treatments were comparable (Table 7), confirming our hypothesis. Usually NH_3 emissions occur shortly after application [50,51], where the effect of the NI might be negligible.

For individual applications, we found NH_3 mitigation potentials between −39 (sometimes emissions in the SI/TS treatment were higher than in the TH treatment) and 60% for CS and BD:SI/TS treatment (Table A3). Under some conditions, those application techniques might lead to smearing of soil, inhibiting infiltration of liquid manure [52], possibly explaining increased emissions following the application of liquid organic fertilizers. However, it should be noted that these increased emissions were not significantly different (Table 6) from the corresponding TH treatment with the same type of organic fertilizer.

In order to explain differences in the mitigation potential between individual experiments, we correlated several parameters with the average mitigation potential of CS:SI/TS and BD:SI/TS treatment. CS:SI/TS and BD:SI/TS treatment means were also correlated with those parameters in a "joint" analysis (Table 5). Soil texture (sand (R = 0.69), silt (R = −0.69) and clay (R = −0.64)) had a strong effect on the mitigation potential of BD, but the mitigation potential of CS was not significantly affected (Table 5). Besides other factors, the potential for soil compaction depends on soil texture [53]. Therefore, efficiency of SI and TS application might be decreased in soils with high clay and/or silt content. Similarly, the NH_3 mitigation potential of BD:SI and BD:TS treatment was significantly reduced with increasing soil pH ($R = -0.67$; Table 5). As mentioned above, a high soil pH leads to generally increased NH_3 emissions [22]. Since SI and TS application leads to increased contact of soil and BD, this effect might be even more pronounced, possibly explaining the reduced mitigation potential following SI/TS application. However, it remains unclear why soil pH and texture only affected NH_3 emission from BD application.

It is generally accepted that rainfall decreases NH_3 emissions as the NH_4^+ is washed into the soil [44]. Sanz-Cobena et al. [54] reported that this effect is even more pronounced for surface application than for shallow injection. This is in contrast to our findings, where the NH_3 mitigation potential for SI/TS application was significantly increased ($R = 0.48^{**}$; Table 5) when rainfall occurred within 48 h after application. Overall, our data confirmed our initial hypothesis. However, compared to acidification, the NH_3 emissions of SI in combination with TS application on the second application date was significantly higher (Table 4).

3.2. Crop Yield and N Uptake

We found the significantly highest crop yield, N uptake and aNUE (7.9 t grain dry matter yield, 162 kg grain N uptake, 189 kg total N uptake, 40% aNUE for grain and 47% aNUE for total above-ground biomass) following CAN application (Table 8). When looking at individual trial sites (Table 9), N uptake of above-ground biomass following CAN application was always higher than N uptake in the N0 treatment, except for the site BWa, which was characterized by long-term organic fertilization leading to the highest soil N_{total} content (Table 1). For our experiments, we based fertilization on total N instead of NH_4-N. Therefore, the proportion of plant available mineral N was lower for all organically fertilized treatments compared to the CAN treatment (Table 2). Nitrogen applied via mineral fertilizers such as CAN is generally better available for plant uptake than N applied via organic fertilizers such as CS or BD. Furthermore, even when applying equivalent amounts of NH_4-N, yield and nitrogen uptake of WW are somewhat higher after applying CAN than after using slurry, due to the lower NH_3 emissions following CAN application [55]. This is in line with our data, as we did not find relevant NH_3 emissions following CAN application calculated across all sites (Table 4) or for each individual campaign per site (Table 6). This is confirmed by many previous studies [56–58], where low NH_3 emissions following CAN application were reported. Overall, the better plant availability from mineral N and very low NH_3 emissions can explain the higher yield and aNUE in the CAN treatment found in this study.

For the organically fertilized treatments, we hypothesized that decreasing NH_3 emissions will result in higher yield, N uptake and aNUE. Since acidification and reduced contact area of the applied liquid manure with the atmosphere (i.e., SI/TS application) decreased NH_3 emissions compared to the TH treatment, we expected increased yield, N uptake and aNUE for those treatments. However, averaged by fertilizer type (CS and BD), all application techniques (TH, TH+A, SI/TS, SI+NI/TS) revealed similar values for all parameters (Table 8). We did not find a significant difference compared to TH application for any of the parameters. When looking at the total above-ground biomass N uptake of individual experiments (Table 9), we also did not find any significant differences between organically fertilized treatments except for the site LSa, where N uptake of the BD:TH+A treatment was higher than N uptake of all CS treatments. Thus, we cannot confirm our initial hypothesis that decreased NH_3 emissions will result in increased yield parameters. As Tilling et al. [59] pointed out, N uptake depends on soil and plant water status. In both experimental years, the WW growing season from March to the end of July was characterized by rather dry conditions (Table 1), so N uptake may have been reduced due to water stress. Therefore, comparatively small differences regarding the amount of plant available mineral N between organically fertilized treatments might have been insignificant for crop yield. However, organic fertilization increased the yield compared to the N0 treatment and CAN application led to even higher yield (Table 8), indicating that increased levels of mineral N lead to higher yield.

Table 8. Effect of treatment, application technique, fertilizer type on grain dry matter yield, N uptake grain, N uptake total above-ground biomass, as well as apparent nitrogen use efficiency for grain (aNUE grain) and total above-ground biomass (aNUE total) across sites.

	Grain DM Yield t ha^{-1}		**N Uptake Grain** kg N ha^{-1}		**N Uptake Total** kg N ha^{-1}		**aNUE Grain** %		**aNUE Total** %	
Treatment [1]		***		***		***		***		***
N0	4.5	a	75	a	88	a				
CAN	7.9	c	162	c	189	c	40	b	47	b
CS:TH	6.8	b	127	b	145	b	24	a	29	a
CS:TH+A	6.7	b	130	b	148	b	25	a	27	a
CS:SI/TS	6.5	b	126	b	143	b	24	a	26	a
CS:SI+NI/TS	6.9	b	134	b	152	b	28	a	30	a
BD:TH	6.7	b	126	b	143	b	24	a	26	a
BD:TH+A	6.6	b	128	b	146	b	26	a	29	a
BD:SI/TS	7.0	b	137	b	156	b	29	a	32	a
BD:SI+NI/TS	7.0	b	136	b	155	b	29	a	31	a
Application technique [2]		n.s.		n.s.		n.s.		n.s.		n.s.
TH	6.8	n.s.	129	n.s.	147	n.s.	25	n.s.	28	n.s.
TH+A	6.9	n.s	130	n.s	149	n.s	26	n.s	28	n.s
SI/TS	6.8	n.s	131	n.s	149	n.s	26	n.s	29	n.s
SI+NI/TS	7.0	n.s.	135	n.s.	153	n.s.	28	n.s.	31	n.s.
Fertilizer type [3]		**		**		**		**		*
CS	6.8	a	130	a	148	a	26	a	28	a
BD	6.9	b	132	b	151	b	27	b	29	b
Site		***		***		***		***		***

Different lower case letters indicate significant differences ($p \leq 0.05$) between groups. n.s = Not significant, * = $p \leq 0.05$, ** = $p \leq 0.01$, *** = $p < 0.001$, DM = Dry matter, N = Nitrogen, N0 = No nitrogen fertilization, CAN = Calcium ammonium nitrate, CS = Cattle slurry, BD = Biogas digestate, TH = Trailing hose, +A = Acidification, SI = Slot injection, +NI = Substrate + Nitrification inhibitor, TS Trailing shoe, [1] = mean across sites, [2] = mean across site and fertilizer type, [3] = mean across site and application technique.

Table 9. Nitrogen uptake (kg ha^{-1}) of winter wheat above-ground biomass.

			CS				**BD**			
Site	**N0**	**CAN**	**TH**	**TH+A**	**SI/TS**	**SI+NI/TS**	**TH**	**TH+A**	**SI/TS**	**SI+NI/TS**
BWa	230 ±13 a	215 ±35 a	280 ±23 a	220 ±36 a	257 ±22 a	272 ±42 a	258 ±28 a	245 ±9 a	275 ±35 a	272 ±42 a
BWb	99 ±20 a	158 ±6 b	135 ±28 ab	108 ±15 ab	119 ±14 ab	125 ±24 ab	131 ±27 ab	116 ±16 ab	141 ±35 ab	144 ±35 ab
LSa	61 ±6 a	220 ±24 d	118 ±12 b	129 ±14 b	119 ±11 b	124 ±18 b	131 ±30 bc	166 ±19 c	144 ±18 bc	134 ±11 bc
LSb	87 ±16 a	307 ±72 c	190 ±44 b	221 ±28 b	196 ±34 b	191 ±38 b				
SHa	73 ±10 a	179 ±18 d	124 ±18 b	139 ±10 bc	141 ±24 bc	141 ±23 bc	142 ±11 bcd	163 ±5 cd	158 ±8 bcd	169 ±29 cd
SHb	68 ±23 a	136 ±7 b	119 ±16 ab	133 ±22 b	120 ±15 b	124 ±18 b	120 ±27 b	122 ±24 b	121 ±28 b	122 ±18 b
SHc	48 ±17 a	177 ±30 c	133 ±44 bc	121 ±7 bc	122 ±34 bc	152 ±44 bc	107 ±27 ab	131 ±34 bc	134 ±35 bc	134 ±29 bc
SHd	37 ±3 a	123 ±32 c	97 ±7 bc	109 ±5 bc	73 ±13 ab	90 ±5 bc	110 ±14 bc	107 ±5 bc	118 ±22 c	108 ±22 bc

Different lower case letters indicate significant differences ($p \leq 0.05$) between treatments. ± indicates the standard deviation, BW = Baden-Württemberg, LS = Lower Saxony, SH = Schleswig Holstein, a–d = different sites in each region, N = Nitrogen, N0 = No nitrogen fertilization, CAN = Calcium ammonium nitrate, CS = Cattle slurry, BD = Biogas digestate, TH = Trailing hose, +A = Acidification, SI = Slot injection, +NI = Substrate + Nitrification inhibitor, TS Trailing shoe.

One concern regarding injection of liquid organic fertilizers in a growing cereal crop is that the injection system might damage plants resulting in lower yields [39]. Since yield, N uptake and aNUE did not differ between organically fertilized treatments, we cannot confirm this concern based on the data from our multi-site multi-year field trial series.

However, it has to be pointed out that in accordance with common farm practice, injection technique was only used for the first application at each site, minimizing the negative impact on plant growth.

We also combined injection with the use of an NI, that may reduce N losses by nitrate leaching [31], which should increase N availability. However, although dry matter yield, N uptake and aNUE were slightly increased for the SI+NI/TS treatment in comparison with other organically fertilized treatments (Table 8), that difference was not statistically confirmed. In addition, for individual experimental sites (Table 9), there was never a significant difference between treatments with and without NI application. Considering that the NI was only added into the liquid organic fertilizers at the first application, we assume that its influence was rather limited. In addition, both experimental years were characterized by dry conditions during the WW growing season (Table 1), which apparently minimized the impact of nitrate leaching on yield and N uptake. Therefore, the beneficial effect of supplementing liquid organic fertilizers with an NI in a growing winter wheat crop might be limited.

On average, we found slightly increased values for grain dry matter yield, N uptake grain, N uptake total above-ground biomass, aNUE grain and aNUE above-ground biomass following BD application compared to CS application (Table 8). One possible explanation is that slightly more NH_4-N was applied, when using BD compared to CS (Table 2). However, also NH_3 emissions were significantly increased with BD application (Table 4). Möller and Müller [21] pointed out that by transforming organic carbon compounds to methane during the anaerobic digestion process, the dry matter content (Table 2) is decreased, until only rather stable organic matter remains [60]. Therefore, the C:N ratio declines remarkably, decreasing the risk of bacterial N immobilization [61], which might explain the significantly improved yield, N uptake and aNUE (Table 8) in our experiments.

4. Conclusions

Our results show that a reduction ins NH_3 emissions following CS and BD application to growing crops is possible by using mitigation techniques such as acidification or open slot injection. In our field trial series, acidification was especially promising, but it has to be kept in mind that we acidified the liquid organic fertilizers prior to application within a tank to reach the target pH of 6.0, which differs from on-the-go acidification systems during the slurry application process used in farm practice. This must be taken into account when transferring our results into practice. In addition, it should be considered that the regular use of sulfuric acid for acidifying liquid organic fertilizers leads to excess sulfur in the soil and, as a result, leaching of sulfate into the groundwater might become a concern. Reducing the contact area of liquid organic fertilizers with the atmosphere by open slot injection or trailing shoe application also reduced emissions, but to a lesser extent compared to acidification. Unfortunately, the lower NH_3 emissions that resulted from the use of optimized application techniques did not lead to increased yield. However, both experimental years of this study were characterized by dry conditions during the winter wheat growing period. Therefore, mitigating NH_3 emissions might have a stronger yield effect for more humid years or climates. Compensating famers for using such application techniques for NH_3 emission mitigation might be the key for a wider acceptance of those techniques.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Appendix A

Table A1. List of ANOVA models.

Model Description	Dependent Variable(s)	Fixed Factors	Data Included
1. Treatment effect on NH_3 emissions across sites and application dates	NH_3 emissions (kg ha^{-1}) NH_3 emissions (% TAN applied) NH_3 emissions (% Total N applied)	Treatment Application date Site	All
2. Effect of application technique, fertilizer type, application date and site on NH_3 emissions	NH_3 emissions (kg ha^{-1}) NH_3 emissions (% TAN applied) NH_3 emissions (% Total N applied)	Application technique Fertilizer type Application date Site	All treatments except N0 and CAN
3. Effect of fertilizer type and application date on the NH_3 mitigation potential across sites	Acidification mitigation potential (%) SI/TS mitigation potential (%)	Fertilizer type Application date Site	Either CS and BD:TH+A or CS and BD:SI/TS
4. Effect of adding a nitrification inhibitor on the NH_3 mitigation potential across sites and fertilizer types	NH_3 mitigation of SI and SI+NI application (%)	Fertilizer type NI Site	CS:SI, CS:SI+NI, BD:SI and BD:SI+NI
5. Treatment effect on NH_3 emissions for individual sites and application dates	NH_3 emissions (kg ha^{-1})	Treatment	All
6. Treatment effect on NH_3 emissions for individual sites across both application dates	NH_3 emissions (kg ha^{-1})	Treatment Application date	All
7. Treatment effects on yield, N uptake and aNUE across sites	Grain dry matter yield (t ha^{-1}) N uptake grain (kg ha^{-1}) N uptake total above-ground biomass (kg ha^{-1}) aNUE grain aNUE total above-ground biomass	Treatment Site	All
8. Effect of application technique, fertilizer type and site on yield, N uptake and aNUE	Grain dry matter yield (t ha^{-1}) N uptake grain (kg ha^{-1}) N uptake above-ground biomass (kg ha^{-1}) aNUE grain (kg ha^{-1}) aNUE above-ground biomass (kg ha^{-1})	Application technique Fertilizer type Site	All treatments except N0 and CAN
9. Treatment effect on N uptake for individual sites	N uptake total above-ground biomass (kg ha^{-1})	Treatment	All

ANOVA = Analysis of variance, TAN = Total ammoniacal Nitrogen, N = Nitrogen, SI = Slot injection, TS = Trailing shoe, NI = Nitrification inhibitor, aNUE = apparent Nitrogen Use Efficiency, N0 = Control treatment without nitrogen fertilization, CAN = Calcium ammonium nitrate, CS = Cattle slurry, BD = Biogas Digestate, TH = Trailing hose, +A = Acidification.

Appendix B

Table A2. Ammonia emissions (% TAN applied) for each fertilizer application campaign.

				CS								BD							
Site	**App.**	**CAN**		**TH**		**TH+A**		**SI/TS**		**SI+NI/TS**		**TH**		**TH+A**		**SI/TS**		**SI+NI/TS**	
BWa	1	−1	±2	14	±8	7	±4	6	±7	8	±7	12	±7	5	±4	12	±3	16	±8
BWa	2	−2	±7	15	±11	11	±8	12	±10	6	±7	32	±9	13	±9	36	±10	31	±11
BWb	1	−1	±5	18	±2	9	±8	14	±4	13	±9	77	±16	8	±3	60	±15	39	±7
BWb	2	−4	±10	22	±6	−4	±6	18	±5	15	±6	23	±4	14	±5	30	±9	34	±7
LSa	1	0	±4	15	±2	2	±1	6	±2	7	±3	24	±2	1	±2	11	±2	12	±5
LSa	2	0	±4	12	±7	1	±5	5	±4	4	±2	11	±4	−1	±3	6	±5	8	±6
LSb	1	1	±2	4	±2	2	±1	5	±3	3	±1								
LSb	2	0	±0	5	±2	0	±2	3	±1	4	±4								
SHa	1	−3	±2	11	±5	3	±2	8	±3	12	±5	11	±8	9	±1	8	±7	9	±8
SHa	2	−5	±10	29	±15	16	±11	26	±8	31	±12	28	±13	20	±9	26	±7	31	±7
SHb	1	0	±3	21	±2	11	±4	11	±2	16	±3	31	±5	23	±3	24	±6	20	±7
SHb	2	1	±6	29	±14	11	±3	17	±6	26	±12	42	±12	23	±7	33	±9	35	±9
SHc	1	−8	±12	43	±7	42	±20	27	±8	30	±7	43	±17	7	±13	35	±9	32	±9
SHc	2	0	±6	35	±17	14	±17	35	±14	31	±11	43	±15	16	±17	41	±12	49	±10
SHd	1	2	±16	37	±17	20	±18	37	±11	20	±9	25	±10	6	±21	19	±16	21	±19
SHd	2	−4	±6	18	±8	−3	±4	13	±6	15	±2	27	±8	4	±4	14	±4	18	±9

±indicates the standard deviation, App. = Application campaign, CS = Cattle slurry, BD = Biogas digestate, CAN = Calcium ammonium nitrate, TH = Trailing hose, +A = Acidification, SI = Slot injection, +NI = Substrate + Nitrification inhibitor, TS = Trailing shoe, BW = Baden-Württemberg, LS = Lower Saxony, SH = Schleswig Holstein, a–d = Different sites in each region.

Appendix C

Table A3. Mitigation potential (%) of optimized techniques compared to trailing hose application.

		CS						BD					
Site	**App.**	**TH+A**		**SI/TS**		**SI+NI/TS**		**TH+A**		**SI/TS**		**SI+NI/TS**	
BWa	1	46	±27	57	±53	41	±49	64	±35	−3	±28	−31	±66
BWa	2	45	±43	20	±66	62	±46	61	±28	−11	±32	5	±34
BWb	1	46	±48	18	±24	29	±49	90	±4	22	±20	50	±9
BWb	2	117	±28	20	±21	32	±25	43	±21	−28	±39	−44	±32
LSa	1	86	±9	58	±13	51	±16	95	±8	55	±9	48	±19
LSa	2	95	±43	60	±35	69	±16	113	±30	45	±48	31	±50
LSb	1	54	±37	−39	±71	17	±34						
LSb	2	94	±31	38	±12	18	±73						
SHa	1	71	±22	26	±23	−8	±48	20	±8	33	±59	19	±70
SHa	2	47	±36	12	±26	−4	±41	25	±32	5	±25	−11	±25
SHb	1	47	±20	50	±11	23	±14	26	±10	22	±19	34	±23
SHb	2	61	±11	40	±22	9	±42	46	±17	21	±22	15	±23
SHc	1	10	±42	39	±19	30	±16	83	±28	19	±20	25	±22
SHc	2	61	±49	1	±40	11	±32	61	±40	4	±29	−13	±23
SHd	1	44	±50	−1	±31	45	±24	73	±89	22	±62	15	±77
SHd	2	116	±22	25	±32	17	±13	83	±17	49	±16	33	±32

±indicates the standard deviation, App. = Application campaign, CS = Cattle slurry, BD = Biogas digestate, CAN = Calcium ammonium nitrate, TH = Trailing hose, +A = Acidification, SI = Slot injection, +NI = Substrate + Nitrification inhibitor, TS = Trailing shoe, BW = Baden-Württemberg, LS = Lower Saxony, SH = Schleswig Holstein, a–d = Different sites in each region.

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