Determination of ammonia emissions in multi-plot field trials to assess optimized application techniques for liquid manure in growing winter wheat

Dissertation
zur Erlangung des Doktorgrades (Dr. sc. agr.)
der Fakultät für Agrarwissenschaften
der Georg-August-Universität Göttingen

vorgelegt von
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geboren am 01.04.1991 in Dinslaken

Göttingen, Juni 2023

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Datum der mündlichen Prüfung: 01.09.2023

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Abbreviations

+A	Addition of acid
ANOVA	Analysis of variance
BD	Biogas digestate
BW	Baden-Württemberg
CAN	Calcium ammonium nitrate
CEC	Cation exchange capacity
C_{org}	Organic carbon
CPS	Calibrated passive sampling
CS	Cattle slurry
DT	Ammonia sensitive detector tube
DTM	Dynamic tube method (alternatively “Dräger tube method”)
DÜV	Düngeverordung (fertilizer ordinance)
EU	European Union
GL	Grassland
H_2SO_4	Sulfuric acid
HCl	Hydrochloric acid
HNO_3	Nitric acid
IHF	Integrated Horizontal Flux
LS	Lower Saxony
N	Nitrogen
N0	No nitrogen fertilization
N_2O	Nitrous oxide
NH_3	Ammonia
NH_4^+	Ammonium
NI	Nitrification inhibitor
NO_3^-	Nitrate
pH	Potential of hydrogen (scale to rate acidity)
Precip.	Precipitation
PS	Passive sampler (acid trap to collect ammonia)
PTFE	Polytetrafluoroethylene
p-value	Probability value
R	Correlation coefficient
R^2	Coefficient of determination
S	Sulphur
SCM	Standard comparison method
SD	Standard deviation
SH	Schleswig Holstein
SI	Slot injection
TC	Transfer coefficient
Temp.	Temperature
TH	Trailing hose
TS	Trailing shoe
UV/Vis	Ultra violett/visible light
WW	Winter wheat

Part 1

General Introduction

Background and objectives

Historically nitrogen (N) was a limiting factor for agricultural production (*Sutton* et al., 2011a; *Sutton* et al., 2011b). About 40 % of the current global food production would not exist without synthetic N fertilizers (*Pfromm*, 2017; *Ti* et al., 2019). However, excess N is causing immense damage (*Sutton* et al., 2011b) and the emission of ammonia (NH_3) is a main constituent to that problem (*Bouwman* et al., 1997). Globally, major NH_3 sources (Figure 1) are in West and central Africa, India, Pakistan and China. Also in the European Union (EU), the atmospheric NH_3 concentration is increased (Figure 1). Hotspots are in northern Italy and southwest Spain. Northwest Germany, the Netherlands and Belgium have also a comparatively high atmospheric NH_3 concentration (*van Damme* et al., 2018).

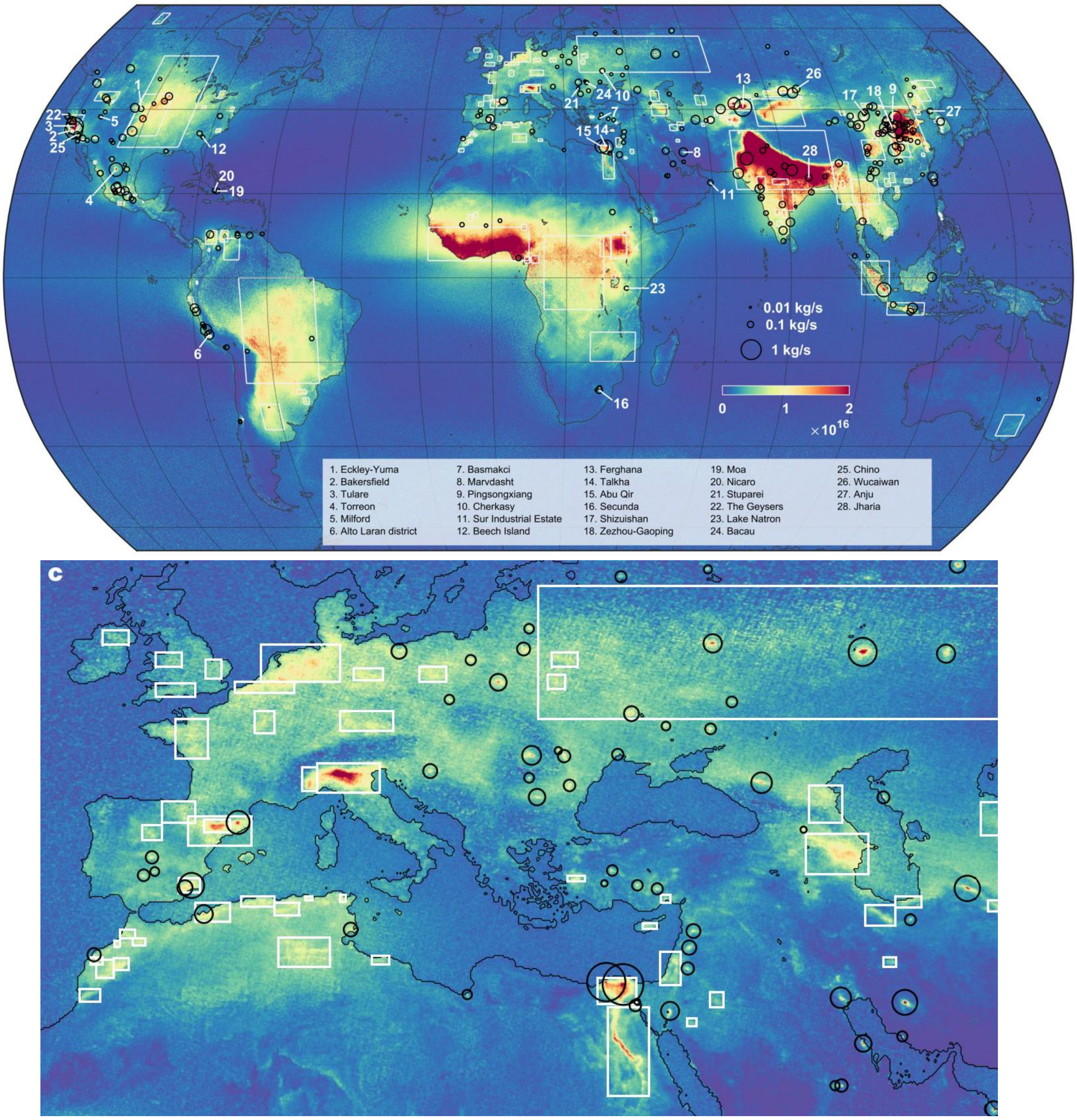

Figure 1: Global and European NH_3 source areas and hotspot locations (*van Damme* et al., 2018). Nine-year NH_3 average (in molecules cm^{-2}) with identified hotspots, their associated flux estimates (black circles), and source areas (white rectangles).

Within the atmosphere, NH_3 leads to the formation of particulate matter, impairing human health and life expectancy (*Bauer* et al., 2016; *Lelieveld* et al., 2015; *van Damme* et al., 2018). It is estimated that the annual health cost due to NH_3 emissions is between US$18–140 billion for the European Union alone (*Sutton* et al., 2011a; *Ti* et al., 2019). Furthermore, the excess of NH_3 leads to acidification and eutrophication of natural ecosystems (*Bobbink* et al., 2010; *Galloway* et al., 2003; *Hertel* et al., 2013; *Paerl* et al., 2014; *van Damme* et al., 2018). Ammonia emissions also contribute to climate change (*Shindell* et al., 2009), since N deposition stimulates nitrification and denitrification in the soil leading to the formation of the greenhouse gas nitrous oxide (*Arp* and *Stein*, 2003; *Ruser* and *Schulz*, 2015; *Saggar* et al., 2013). Thus, the international agreement on air pollution control and reducing national emissions of certain air pollutants (National Emission Ceiling Directive) defined limits for maximum NH_3 emissions forcing EU member states to cut emissions. Identifying sectors responsible for the highest NH_3 emissions is therefore mandatory. Globally, livestock husbandry (Figure 2) is the biggest emitter of NH_3 directly related to human activities (*Bouwman* et al., 1997). Besides of animal housing and manure storage, spreading of organic fertilizers is an important NH_3 emission pathway (*Emmerling* et al., 2020; *Erisman* et al., 2008; *Wulf* et al., 2002), which globally accounts for 6.2 million tons of NH_3-N emissions per year (*Beusen* et al., 2008). The development of optimized spreading techniques is therefore necessary in order to reduce emissions (*Webb* et al., 2005; *Webb* et al., 2010).

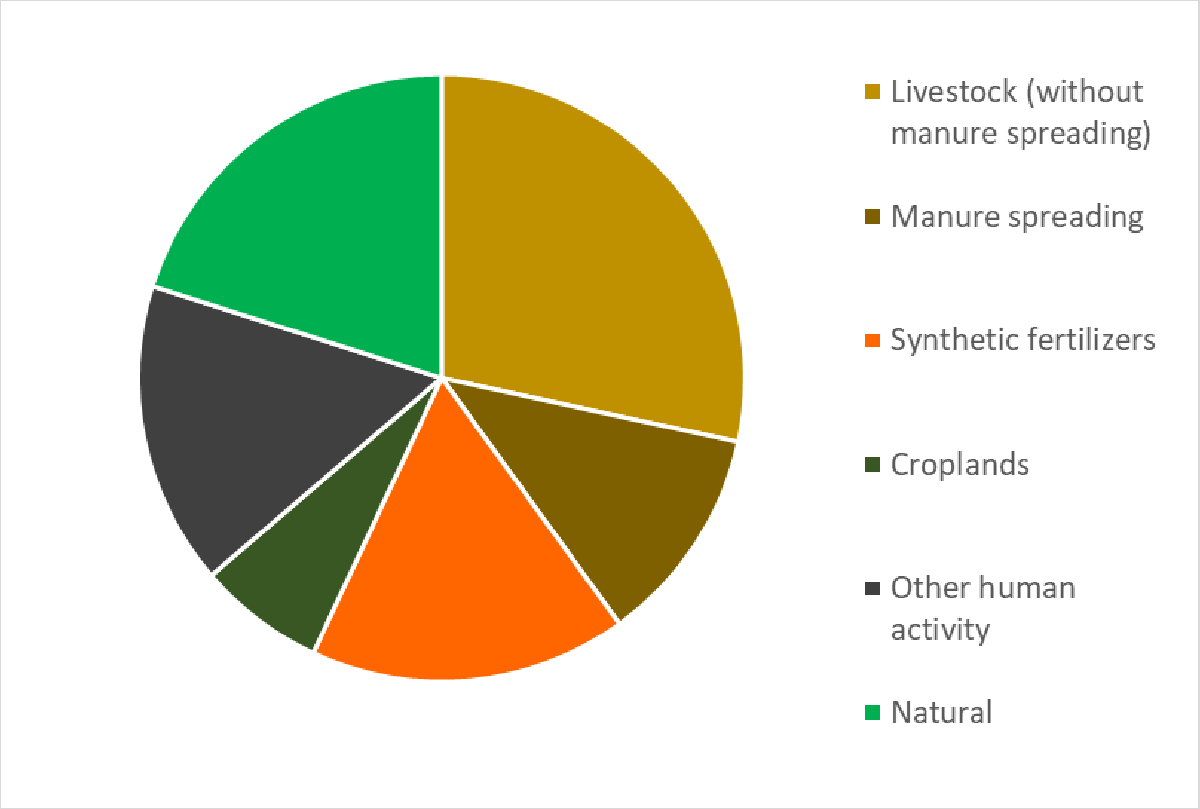

Figure 2: Global ammonia emitter according to *Bouwman* et al. (1997). Manure spreading was highlighted as a sub-category of livestock-husbandry based on data from *Beusen* et al (2008).

In Germany, NH_3 emissions need to be reduced while simultaneously considering specific requirements. German legislation (*DÜV*, 2020) drastically restricted autumn application of liquid manure for many crops, including winter wheat (*Triticum aestivum* L.). In 2022, winter wheat was cultivated on 28,880 km^2 (*Statista*, 2023a), accounting for approximately 8 % of Germany's landmass and the average grain yield was 7.6 t ha^{-1} (*Statista*, 2023b). Nitrogen fertilization is a key variable that determines yield and protein content of winter wheat (*Rinno* et al., 1970). For elite winter wheat with high protein content, the N demand is 260 kg ha^{-1}, while winter wheat produced for feeding animals has a demand of 210 kg N ha^{-1} (*Landwirtschaftskammer*, 2023). However, in autumn shortly after sowing, winter wheat has only a minor N demand. Thus, restricting fertilization in autumn makes sense in order to reduce nitrate leaching into groundwater aquifers (*Gasser*, 1961). Therefore, liquid manures have to be applied in spring into the growing crop.

Besides animal slurry, biogas digestate has become an increasingly popular type of liquid manure over the last three decades in Germany, since it is a climate-friendly way to meet rising energy demands (*Herrmann* et al., 2017; *Náthia-Neves* et al., 2018). Thus, energy from biogas production increased from 65 to 5,880 megawatts in the period 2000 - 2021 (*Statista*, 2023c), so that currently biogas digestate accounts for 33 % of the applied liquid manure in Germany (*DESTATIS*, 2023). However, this might be associated with increased NH_3 emission, since the digestion process increases pH and NH_4-N concentration of the substrate (*Möller* and *Müller*, 2012).

Until 2030, Germany has to cut NH_3 emissions by 29 % compared to the reference year 2005 (*European Environment Agency*, 2016). However, the combination of application into growing crops, where immediate incorporation into the soil to reduce NH_3 emissions (*Webb* et al., 2010) is not possible, and the increased use of biogas digestate as fertilizer might lead to even higher NH_3 emissions.

This thesis aimed to resolve this conflict of interest by testing several optimized techniques to apply slurry and biogas digestate in a network of winter wheat field experiments in Germany. Therefore, NH_3 emissions needed to be quantified in replicated field trials with liquid manure application. However, standard methods for the quantification of NH_3 emissions require large experimental areas und expensive equipment (*Pacholski* et al., 2006) so that their implementation in multi-plot field experiments is very difficult (Roelcke et al., 2002). Therefore, calibrated passive sampling (*Gericke* et al., 2011; *Pacholski*, 2016) was used as an alternative method for multi-plot field trials. Calibrated passive sampling combines two separate approaches: (1) acid traps, which passively collect emitted NH_3 (*Vandré* and *Kaupenjohann*, 1998) and (2) the dynamic tube method (*Pacholski* et al., 2006).

Therefore, the first objectives of this thesis were:

- To evaluate potential problems when using acid traps and dynamic tube method in multi-plot field experiments with liquid manure application
- To assess the best practice for using calibrated passive sampling to quantify NH_3 emissions under those conditions

Subsequently, this evaluation enabled to:

- Analyze the effects of different optimized application techniques on NH_3 emissions
- Determine the effects of fertilizer properties and site conditions on NH_3 emissions and the NH_3 mitigation potential of optimized application techniques

- Finally, the effect of those optimized application techniques on winter wheat yield and N uptake was assessed to enable an agronomic evaluation

Ammonia emission measurement for multi-plot field experiments with liquid manure application

Micrometeorological methods

Micrometeorological methods analyze gas fluxes without disturbing environmental conditions. They require a horizontally homogeneous surface and large treatment areas to ensure that concentration measurements reflect the source/sink strength (*McGinn* and *Janzen*, 1998). The large sampling area minimizes the sampling problem (*Denmead*, 1983), but makes their usage in multi-plot field experiments almost impossible (*Pacholski* et al., 2006; *Roelcke* et al., 2002). Another challenge is that they require very accurate and rapid measurements of small gas concentrations (*Denmead*, 1983). One micrometeorological method is the integrated horizontal flux (IHF) method (*Denmead*, 1983; *Leuning* et al., 1985; *Misselbrook* et al., 2005; *Wilson* et al., 1983). For the IHF, a measurement pole is placed in the center of circular plots (Figure 3; strip wise IHF designs also exist (*Wilson* and *Shum*, 1992)) to collect NH_3-N at different heights (*Denmead*, 1983). Cup anemometers measure the wind speed at the corresponding heights (*Mannheim* et al., 1995) and NH_3 fluxes are subsequently calculated by statistical models based on two-dimensional mass balance (*Mannheim* et al., 1995; *McGinn* and *Janzen*, 1998; *Wilson* et al., 1983). For those models, the amount of NH_3 passing through the upwind edge of the plot minus NH_3 leaving the downward edge is related to NH_3 emitted at the surface between the two edges (*McGinn* and *Janzen*, 1998). However, this method requires relatively high wind speeds (> 1 m s^{-1}), so that the horizontal mass transport is higher than the vertical transport (*Mannheim* et al., 1995), since the IHF assumes no net movement of gas above the upper measurement height (*McGinn* and *Janzen*, 1998). Furthermore, the measurement of background NH_3 concentrations is difficult when the wind direction frequently changes (*Mannheim* et al., 1995).

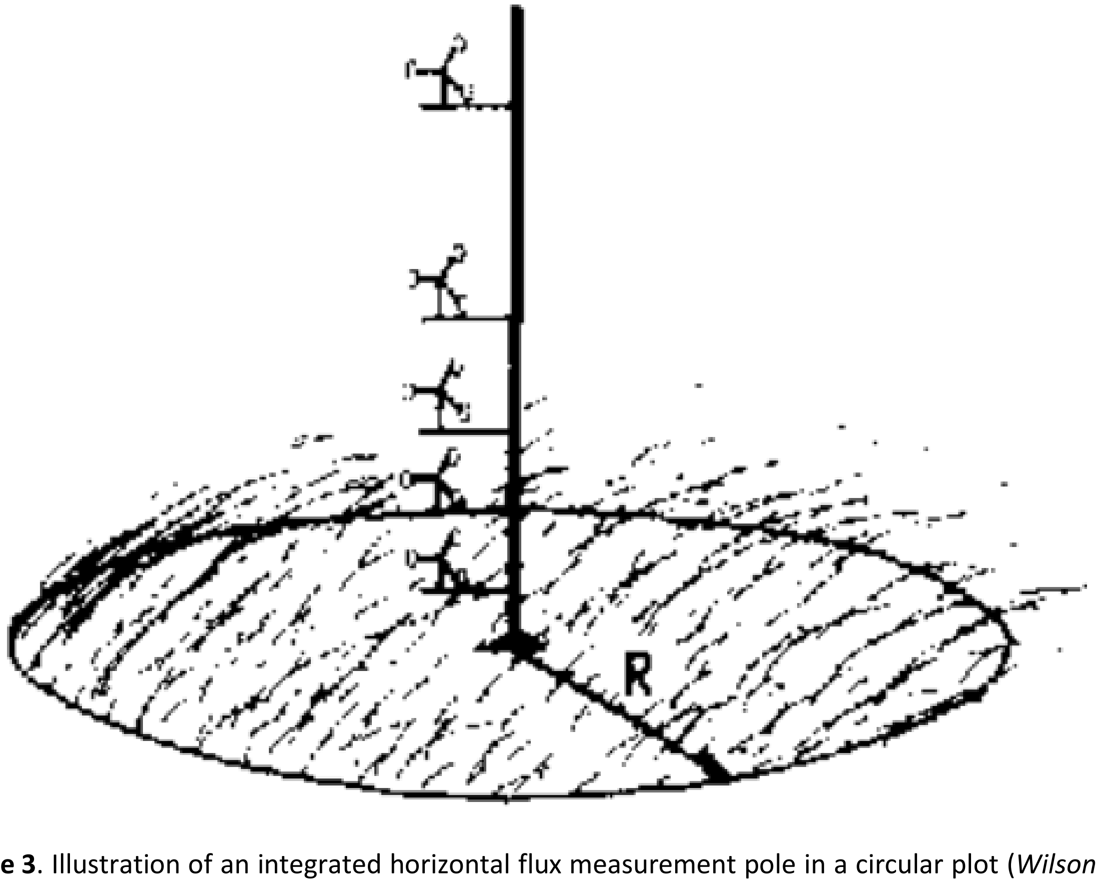

Figure 3. Illustration of an integrated horizontal flux measurement pole in a circular plot (*Wilson* and *Shum*, 1992).

Wind tunnels

Another approach to quantify NH_3 emissions is the use of surface chambers and wind tunnels (*McGinn* and *Janzen*, 1998). The general concept of a wind tunnel (Figure 4) is to assess the difference between the input and output of NH_3 in the system (*Loubet* et al., 1999). Wind tunnels require smaller sampling areas than micrometeorological methods (*Pedersen* et al., 2020), improving their feasibility for multi-plot field experiments. A great variety of different systems was developed (*Lockyer*, 1984; *Braschkat* et al., 1993; *Sommer* and *Misselbrook*, 2016; *Saha* et al., 2010). One general problem of those systems is that they require the adjustment of microclimatic conditions inside the tunnel to those outside (*Braschkat* et al., 1993). One particular challenge is precipitation. Wind tunnels might lead to wrong results when they cannot be removed before rain events and replaced thereafter (*Pacholski*, 2016). Therefore, caution is required when extrapolating results obtained from wind tunnel measurements (*McGinn* and *Janzen*, 1998). Furthermore, small differences between the soil temperature inside and outside the system might lead to condensation at the walls, affecting NH_3 measurements (*Lockyer*, 1984; *McGinn* and *Janzen*, 1998).

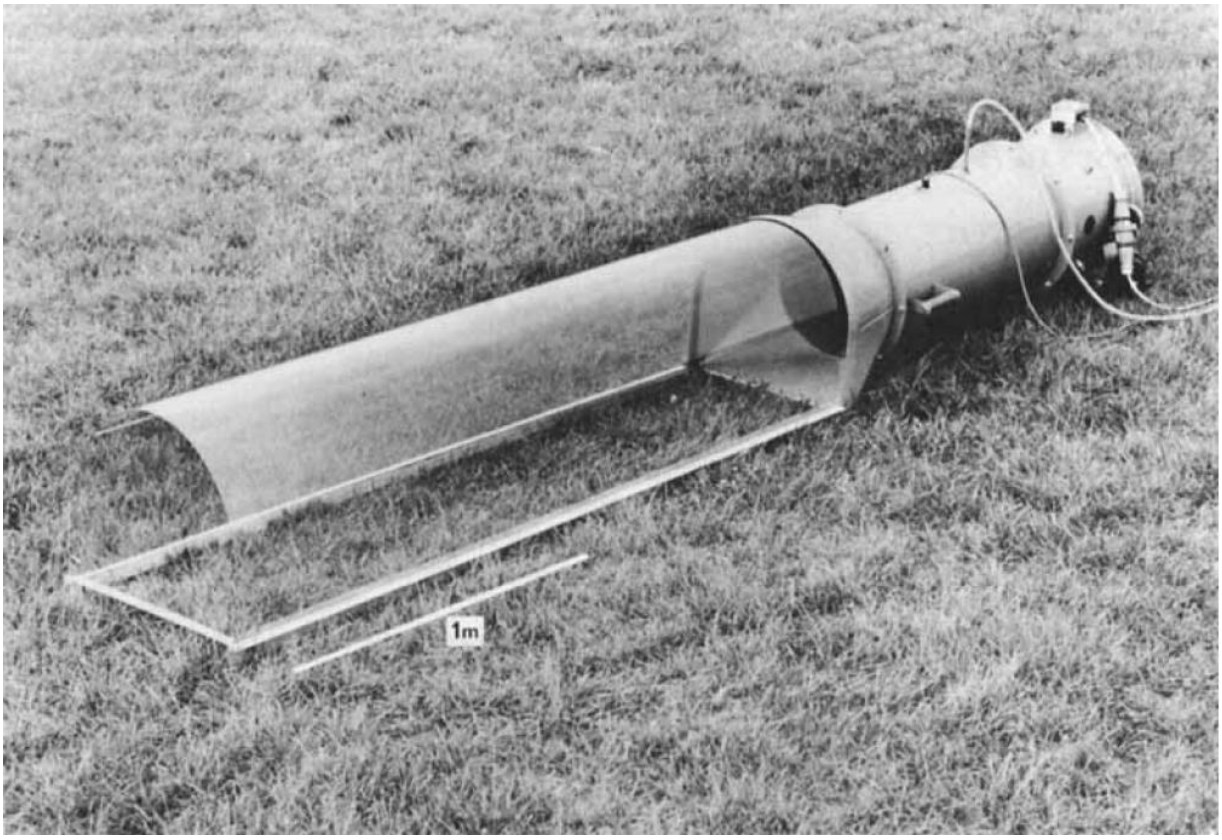

Figure 4: Exemplary design of a wind tunnel (*Lockyer*, 1984).

Dynamic tube method

The dynamic tube method (DTM) is a technique developed for multi-plot field trials (*Pacholski* et al., 2006). Compared to wind tunnels, the system is cheap, easy to translocate and it is only a short term measurement so that micro climatic conditions are not influenced (*Pacholski*, 2016).

The DTM comprises of four individual circular stainless steel chambers with 11.5 cm diameter connected by Polytetrafluoroethylene tubings (Figure 5). This chamber system is placed on the soil surface where fertilizer was applied. Subsequently, the air is exchanged at a constant rate using an automated pump to achieve an equilibrium NH_3 concentration within the system (*Pacholski*, 2016). This concentration is then measured in treated plots as well as in untreated control plots using glass tubes, which display the NH_3 concentration by the color change of a reactant. The concentration measured in control plots is considered as background and the background adjusted concentration is then used to calculate NH_3 fluxes (*Pacholski* et al., 2006). Due to the chamber system, the original setup did not consider wind speed effects on NH_3 emissions. Therefore, NH_3 “raw fluxes” were calibrated with the IHF method while also taking into consideration the wind speed at the time of measurement. Those wind speed corrected NH_3 fluxes are cumulated by linear interpolation between measurements (*Pacholski* et al., 2006; *Pacholski* et al., 2008; *Pacholski*, 2016). One general problem of all chamber systems is that NH_3 is highly reactive and readily soluble in water. This makes it likely to be retained at chamber walls or air pipes or solved in condensed water anywhere in the system (*Denmead*, 1983). Therefore, the chamber system is cleaned with paper towels and flushed with ambient air between measurements (*Pacholski*, 2016).

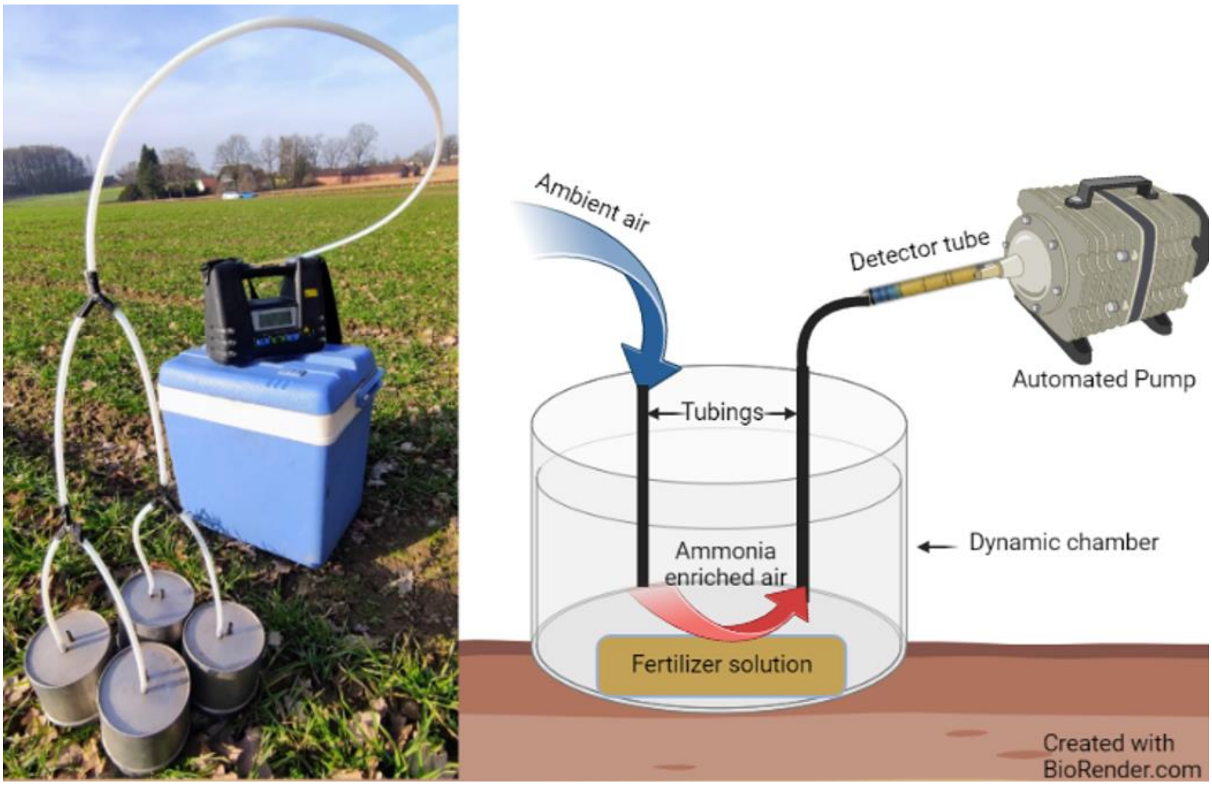

Figure 5: The dynamic tube method. Left site: Photo of chamber system, tubings and automated pump. Right site: Schematic illustration, where only one of the four chambers is displayed.

Standard comparison method

Another comparatively easy approach to measure NH_3 emissions is the standard comparison method (Figure 6). For this method, NH_3 collected by acid traps on plots with slurry application is compared with NH_3 collected on standard plots, where a tubing system releases defined rates of NH_3. Furthermore, plots without NH_3 release were implemented to assess background NH_3 concentrations. To validate the system, NH_3 losses were also determined by slurry analyzes (*Vandré* and *Kaupenjohann*, 1998). However, the gas exposition system to release defined rates of NH_3 was developed for small plots of 2x2 m. Thus it is not feasible for larger plots required for simultaneous agronomic investigation that involves subsequent harvesting of the crop or liquid manure application by larger machinery (*Gericke* et al., 2011). An additional problem of the standard comparison method is that the NH_3 background concentration varied in plots without NH_3 release. *Vandre* and *Kaupenjohann* (1998) attributed this to dense vegetation. Obviously, the NH_3 background might therefore also vary in fertilized plots, potentially masking emissions due to N fertilization.

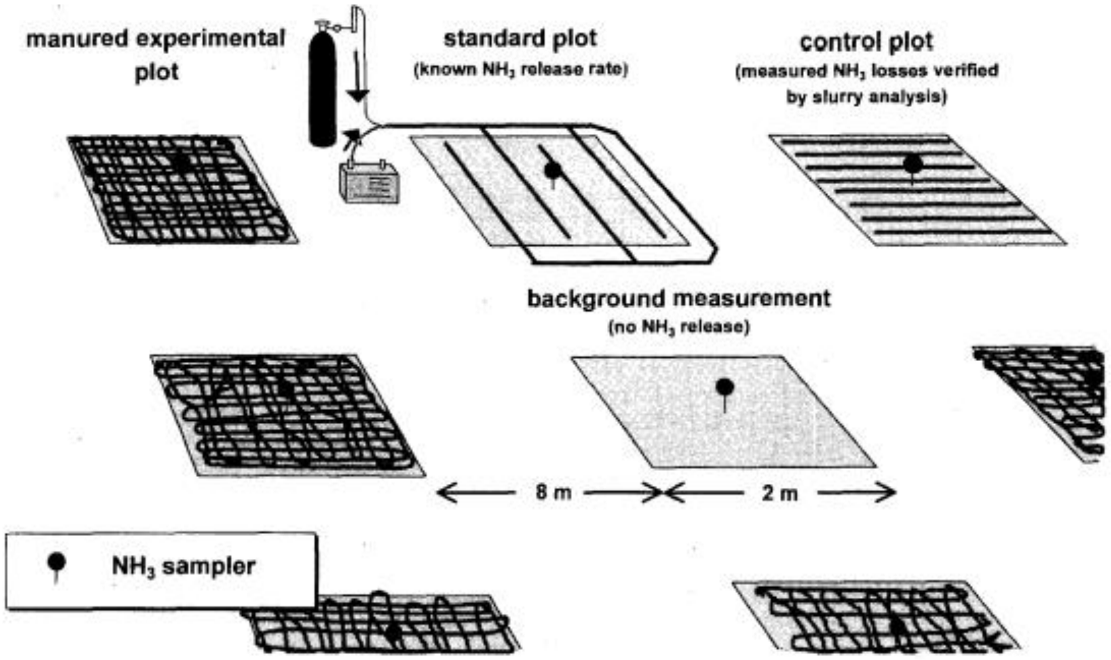

Figure 6: The standard comparison method (*Vandré* and *Kaupenjohann*, 1998)

Calibrated passive sampling

Calibrated passive sampling combines the standard comparison method and DTM (*Gericke* et al., 2011). Passive samplers filled with a sulfuric acid (H_2SO_4) solution are placed in the middle of each plot to collect emitted NH_3 (Figure 7), which enables a relative comparison of NH_3 emissions on different plots. DTM measurements are performed on a few selected plots (Figure 8) with putatively high NH_3 emissions in order to scale those relative differences (*Pacholski*, 2016). This approach allows bigger plot sizes than the standard comparison method, which enables simultaneous agronomic investigation (*Nyameasem* et al., 2022; *ten Huf* et al., 2023). Theoretically, other methods (e.g. wind tunnels) could also be used to quantify emissions in combination with passive samplers (*Pacholski*, 2016).

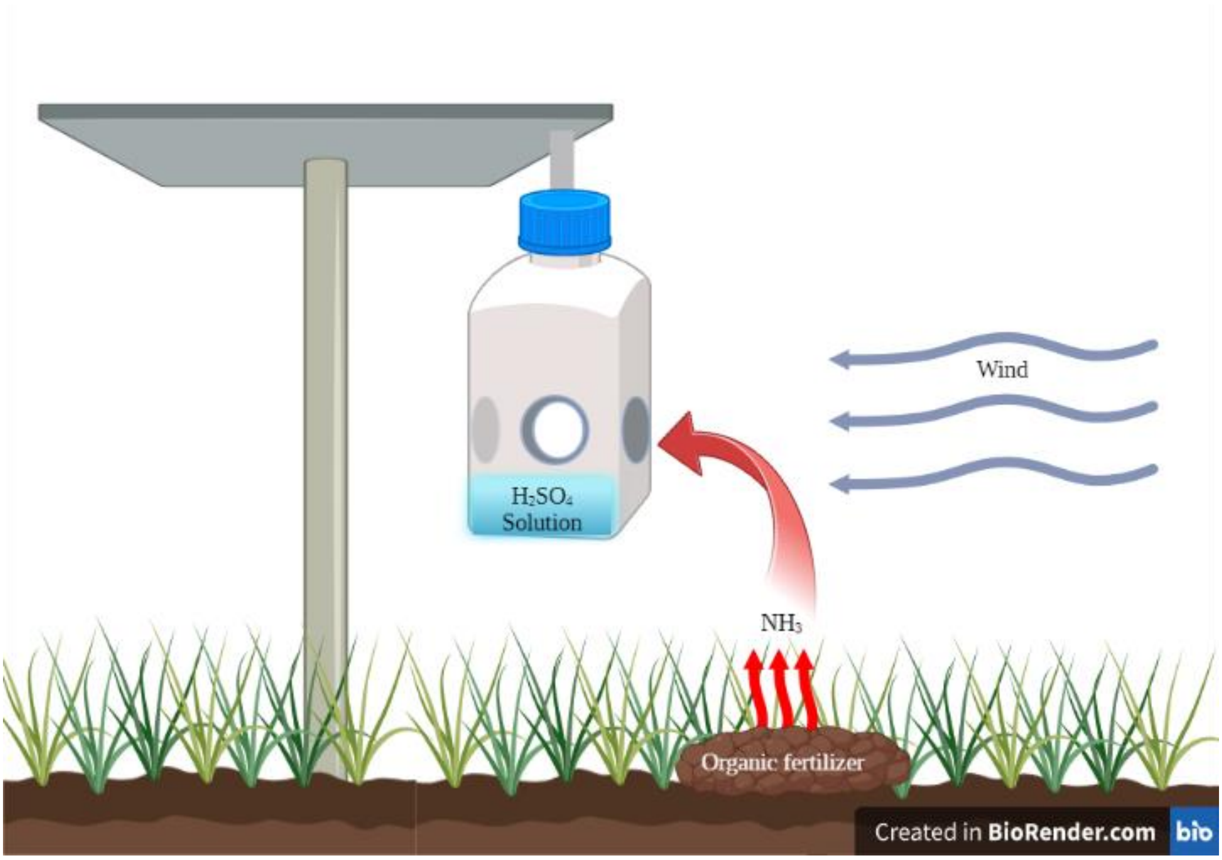

Figure 7: Schematic illustration of a passive sampler placed in the middle of a plot.

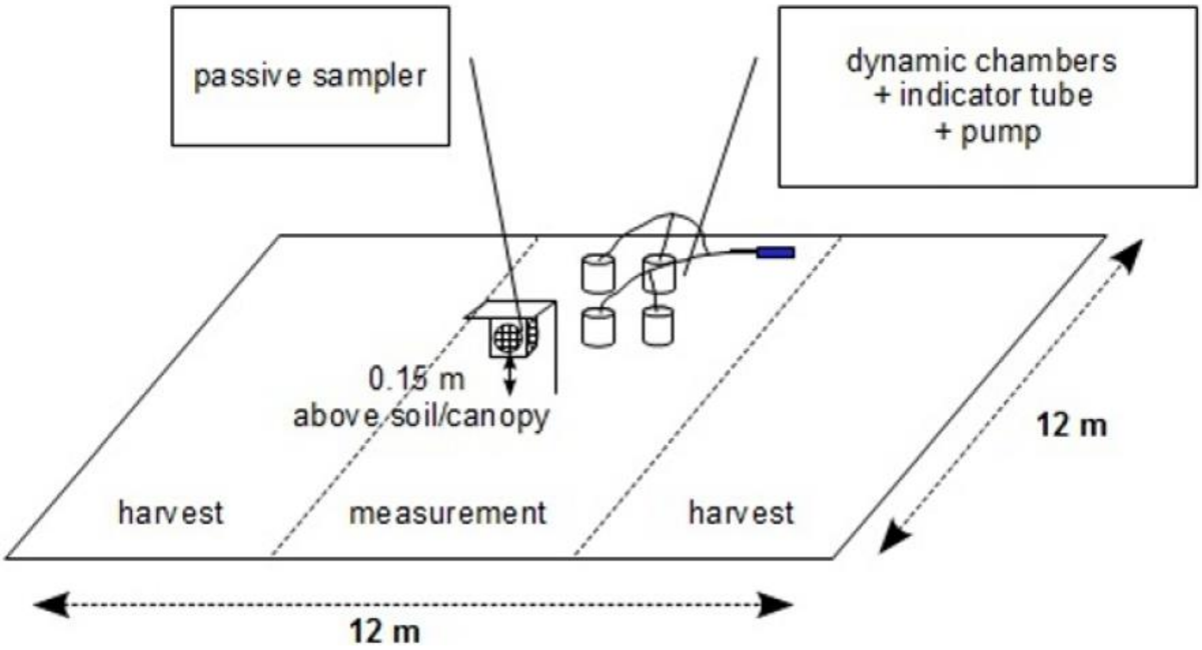

Figure 8: Simultaneous measurement by passive samplers and dynamic tube method (*Pacholski*, 2016).

Ammonia emissions following liquid manure application

After liquid manure application, NH_3 emission depend on the various pathways between fertilizer solution, air and soil (Figure 9).

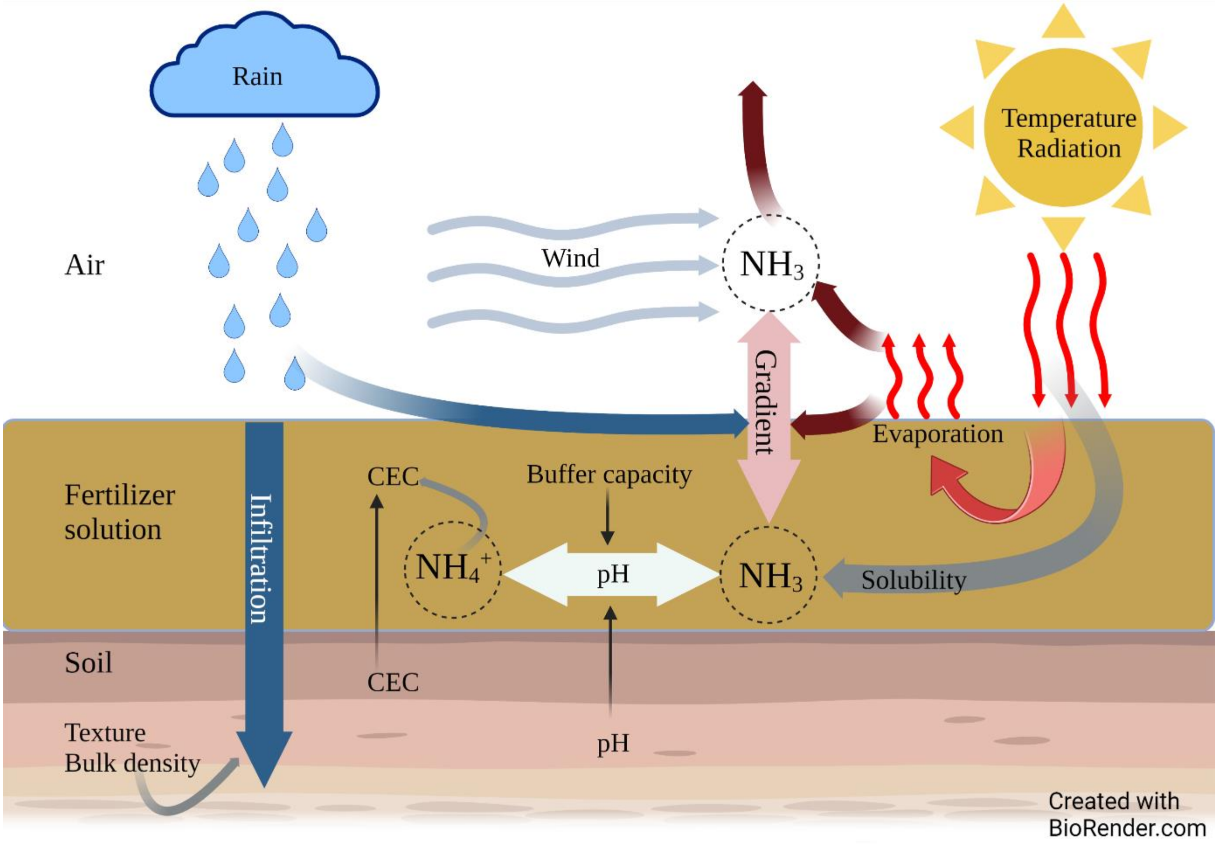

Figure 9: Pathways of ammonia following liquid manure application.

The NH_3 gradient between liquid phase and air governs emission. Diffusion, convection or wind transport fresh air with low ammonia concentration to the surface of the fertilizer solution increasing emissions (*Freney* et al., 1983). Rain dilutes the fertilizer solution and evaporation increases the NH_3 concentration affecting the gradient. Evaporation rates are governed by temperature, radiation, humidity and wind (*Penman*, 1956). Furthermore, the temperature of the fertilizer solution influences the solubility of NH_3, which affects emissions (*Hales* and *Drewes*, 1979).

The properties of the applied liquid manure also affect NH_3 emissions. The NH_4-N concentration in combination with the pH value of the fertilizer solution determine the NH_3 concentration (*Freney* et al., 1983). The inherent buffer capacity of the applied fertilizer solution stabilizes its pH value (*Sommer* and *Husted*, 1995) decreasing the effect of external factors (e.g. soil pH), but might potentially reduce the effect of acidification. Furthermore, the dry matter content affects infiltration rates (*Vadas*, 2006). Finally, binding of NH_4^+ to cation exchange sites within the fertilizer solution might also reduce emissions (*Sommer* et al., 2003).

Infiltration into the soil reduces the contact to the atmosphere decreasing NH_3 emissions (*Sommer* and *Hutchings*, 2001). Infiltration rates are governed by soil texture and bulk density as well as precipitation (*Herrada* et al., 2014). Within the soil, NH_4^+ might be adsorbed to cation exchange sites, further reducing NH_3 emissions (*Sommer* et al., 2003).

Acidification

One obvious way to reduce NH_3 emissions is acidification. Decreasing the pH shifts the NH_4^+/NH_3 ratio towards NH_4^+ (Figure 10), reducing emissions (*Fangueiro* et al., 2017; *Nyord* et al., 2013).

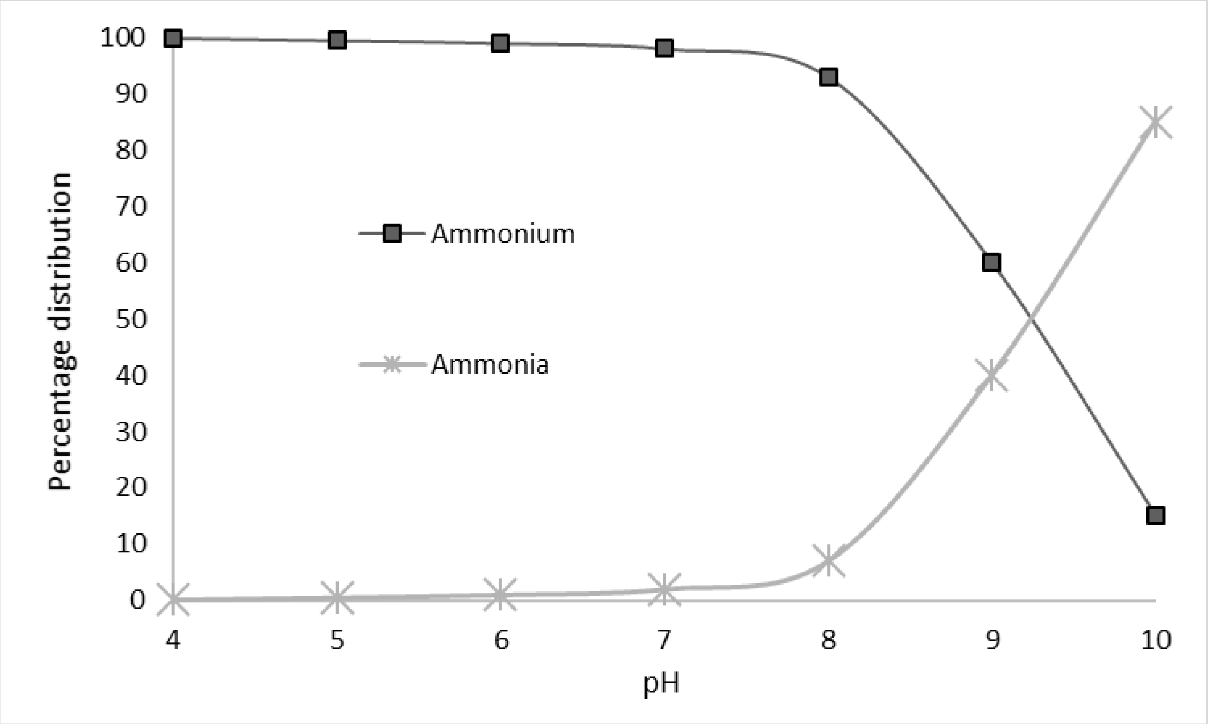

Figure 10: Effect of the pH on the distribution of ammonia and ammonium (*Freney* et al., 1983).

Most commonly, sulfuric acid is used for acidification due to its comparatively low price and high availability. Other strong acids like hydrochloric acid and nitric acid were also tested for this purpose (*Fangueiro* et al., 2015). General drawbacks of acidification are corrosiveness and potential hazards to the human health (*Rotz*, 2004). Effectiveness of acidification was proven in many experiments. Field acidification of pig slurry reduced ammonia emissions by 40 to 80 %. For cattle slurry, 15 to 80 % reduction was observed. For those experiments, the target pH was between 4.5 and 6.8 (*Fangueiro* et al., 2015). Nowadays commercial systems to acidify liquid manure are available. One example is the SyreN system, which is widely used in Denmark. According to *Toft* and *Madsen* (2019) the SyreN system reduces NH_3 emissions by 49 % for cattle slurry and by 40 % for pig slurry. For those commercial systems, acid is added immediately before soil application by using a static mixer installed in the output line of the slurry tanker (*Fangueiro* et al., 2015).

Liquid manure application techniques for growing crops

The mode of application influences the various environmental pathways of NH_3 originating from liquid manure application (*Misselbrook* et al., 2002; *Sommer*, 2000; *Webb* et al., 2005). However, not all application methods are feasible for growing crops. Broadcast application with a splash plate used to be the standard mode of application, but maximizes contact of liquid manure and atmosphere, risking high NH_3 losses (*Webb* et al., 2010). Application by trailing hose, trailing shoe or open slot injection (Figure 11) aims to reduce contact of fertilizer and atmosphere. Using the trailing hose, liquid manure is applied in narrow bands on the surface, while trailing shoe application additionally slightly opens the soil during application. For open slot injection, a disc cuts the soil in a V-shape and the liquid manure is placed in approximately 5 cm depth (*Webb* et al., 2005). Figure 11 illustrates optimized application techniques suitable for growing crops and Table 1 summarizes the potential reduction of NH_3 emission for those techniques compared to broadcast application on arable land.

Figure 11: Application by trailing hose (left), trailing shoe (middle) and open slot injection (right).

Table 1: Summary of results of experiments measuring the NH_3 abatement efficiency of optimized application techniques compared to broadcast application on arable land (*Webb* et al., 2010).

Mode of application	Papers	Experiments	Mean % reduction	Range (%)
Trailing hose	7	16	37	0 - 75
Trailing shoe	2	2	64	38 - 90
Slot injection	5	9	70	23 - 94

However, feasibility of injection methods depends on soil texture and soil compaction (*Petersen* et al., 2003). Furthermore, it needs to be considered that injection might damage growing crops, when conditions are suboptimal (*Nyord* et al., 2012). Injection of liquid manure is often combined with adding a nitrification inhibitor (NI). The addition of a NI delays the conversion of NH_4^+ to NO_3^- in order to reduce nitrate leaching and the formation of the greenhouse gas N_2O (*Dittert* et al., 2001; *Ruser* and *Schulz*, 2015). However, stabilizing NH_4^+ might increase NH_3 emission. But since NH_3 emissions occur shortly after application (*Hafner* et al., 2018; *Søgaard* et al., 2002), this effect might be negligible.

Part 2

Publications

Paper 1: Evaluation of calibrated passive sampling for quantifying ammonia emissions in multi-plot field trials with slurry application

Journal of Plant Nutrition and Soil Science (2023)
Accepted: 17. May 2023

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Abstract

Background: There is a great need for simple and inexpensive methods to quantify ammonia emissions in multi-plot field trials. However, methods that meet these criteria, have to be thoroughly validated. In the calibrated passive sampling approach, acid traps placed in the center of quadratic plots absorb ammonia, enabling relative comparisons between plots. To quantify ammonia emissions, these acid trap samplings are scaled by means of a transfer coefficient (TC) obtained from simultaneous measurements with the dynamic tube method (DTM). However, dynamic tube measurements are also comparatively costly and time-consuming.

Aims: Our objective was to assess the best practice for using calibrated passive sampling in multi-plot field trials. One particular challenge in such experiments is to evaluate the influence of ammonia drift between plots.

Methods: In a series of eight multi-plot field trials, acid traps and DTM were used simultaneously on all plots to measure ammonia emissions caused by different slurry application techniques. Data obtained by both methods were correlated and the influence of the ubiquitous ammonia background on both methods was evaluated by comparing net values including subtraction of the background with gross values (no background subtraction). Finally, we provide recommendations for calculating a TC for calibrating relative differences between plots, based on simultaneous acid trap and dynamic tube measurements on selected plots.

Results: Treatment mean values obtained by both methods correlated well. For most field trials, R^2 values between 0.6 and 0.8 were obtained. Ammonia background concentrations affected both methods. Drift between plots contributed to the background for the acid traps, whereas the contamination of the chamber system might have caused the background for the DTM. Treatments with low emissions were comparatively more affected by that background.

Conclusion: For a robust application of calibrated passive sampling, we recommend calculating the transfer coefficient based on a treatment with high ammonia emissions, reducing the relative influence of the ubiquitous ammonia background.

Keywords: Acid traps, ammonia background concentration, dynamic tube method, standard comparison method, slot injection, slurry acidification, transfer coefficient

1. Introduction

Although historically a limiting factor for agricultural production, excess nitrogen (N) is nowadays causing tremendous damage. The cost for the European Union is estimated with 70 – 320 billion € annually (*Sutton* et al., 2011a; *Sutton* et al., 2011b). One important pathway for N losses from agricultural systems is the emission of ammonia (NH_3) due to field application of liquid organic fertilizers (*Emmerling* et al., 2020; *Erisman* et al., 2008; *Wulf* et al., 2002). This loss of NH_3 affects air quality through the formation of particulate matter, which impairs human health and life expectancy (*Bauer* et al., 2016; *Lelieveld* et al., 2015; *van Damme* et al., 2018). Additionally, the excess of NH_3 contributes to acidification and eutrophication of natural ecosystems (*Bobbink* et al., 2010; *Galloway* et al., 2003; *Hertel* et al., 2013; *Paerl* et al., 2014; *van Damme* et al., 2018), as well as to climate change (*Shindell* et al., 2009). Therefore, abatement of NH_3 emissions following application of organic fertilizers is a priority for national and international policies (*Webb* et al., 2005), leading to the implementation of new application techniques (*Webb* et al., 2010).

For the assessment of NH_3 emission mitigation technologies under field conditions, standard measurement protocols based on micrometeorological integrated horizontal flux (IHF) methods have been developed (*VERA*, 2009; *Vilms Pedersen* et al., 2018). However, those methods require large field areas of at least 2000 m^2 (Wilson et al., 1983), expensive equipment or in-field electrical power supply (*Pacholski*, 2016). Therefore, the use of these techniques in replicated field trials is very difficult or even impossible (*Roelcke* et al., 2002). However, in order to statistically evaluate the effects of a wider range of application techniques, NH_3 emissions need to be quantified in multi-plot field trials with replicated treatments (*Pacholski*, 2016).

Calibrated passive sampling is a simple procedure to quantify NH_3 losses in multi-plot experiments (*Gericke* et al., 2011), which combines two methodological approaches: the standard comparison method (*Vandré* and *Kaupenjohann*, 1998) and the dynamic tube method (DTM; (*Pacholski* et al., 2006).

Applying the standard comparison method, simple passive samplers (PS) absorb NH_3 volatilized from experimental plots by means of an acid solution. In order to compare NH_3 emissions of treated plots, the background N concentration measured in unfertilized control plots is subtracted from the N concentration measured in the treated plots (*Vandré* and *Kaupenjohann*, 1998). Subsequently, the background-adjusted NH_3 uptake of the PSs enables a relative comparison between plots. In the initial set up by Vandré and Kaupenjohann (1998), NH_3 sampled in plots with unknown NH_3 emissions were related to NH_3 sampled in plots with known NH_3 emissions in order to scale results. Release of NH_3 from a standard gas bottle through a tubing system installed on the standard plots was used to establish a known NH_3 emission source. Subsequently, Möller and Stinner (2009), as well as Wulf et al. (2002) successfully applied this approach to determine NH_3 emissions on comparatively small plots (2 m x 2 m). However, the NH_3 gas exposition system developed for the small plots proved not to be feasible for larger plots also required for agronomic investigation involving combined harvesting or application of larger slurry application machinery (*Gericke* et al., 2011). It turned out, that it was difficult to establish a constant and homogeneous NH_3 flow in the standard plots. Therefore, Gericke et al. (2011) used the DTM (*Pacholski* et al., 2006) for scaling relative differences obtained from the samplers to quantify emissions, leading to the development of calibrated passive sampling.

For DTM measurements, ambient air is sucked through four circular chambers placed on the soil. The air is enriched with NH_3 volatilizing from the applied fertilizer and led through PTFE (polytetrafluoroethylene) tubings to an NH_3 sensitive gas analysis detector tube. The reading of the detector tube is then corrected for the background NH_3 concentration, as well as for meteorological conditions (*Pacholski* et al., 2006; *Roelcke* et al., 2002). Due to the low air exchange rate in the chamber system, the NH_3 fluxes are generally underestimated (*Pacholski* et al., 2006). Therefore, the DTM was calibrated with the IHF method in order to adjust the NH_3 fluxes for the wind speed (*Pacholski* et al., 2006; *Pacholski* et al., 2008).

The DTM is relatively versatile, independent of power supply and easy to translocate, but has also several downsides as being time-consuming and expensive by manual operation and the need to use expensive NH_3 indicator tubes. Therefore, the calibrated passive sampling approach uses DTM measurements only on a few selected plots to scale relative differences obtained by PSs (*Gericke* et al., 2011). This method was tested in a wide range of experiments in Germany (*Gericke* et al., 2011; *Ni* et al., 2014; *Ni* et al., 2015; *Quakernack* et al., 2012; *Seidel* et al., 2017) and Denmark (*Wagner* et al., 2021). In a validated trial by Gericke et al. (2011), the combination of PSs and DTM correlated very well ($R^2 = 0.99$) with simultaneous emission measurements with a micrometeorological method (backwards Lagrangian stochastic dispersion method (*Sommer* et al., 2005)). This result was further supported by additional comparisons presented by Quakernack et al. (2012) and Ni et al. (2015).

The central point of calibrated passive sampling is the derivation of a transfer coefficient (TC) to scale PS data. The TC is derived from dividing total cumulative NH_3-N loss determined by wind speed corrected DTM by the total amount of NH_3-N collected by PSs (*Gericke* et al., 2011; *Pacholski*, 2016). To quantify NH_3 emissions, cumulative PS data are multiplied by the TC. However, NH_3 trapping efficiency of PSs is influenced by meteorological conditions and vegetation properties during the sampling period (*Vandré* and *Kaupenjohann*, 1998). Thus, individual TCs have to be determined for multi-plot experiments conducted at different sites or in different periods (*Gericke* et al., 2011; *Pacholski*, 2016). The TC approach generally assumes that all treatments of a multi-plot experiment are exposed to the same meteorological conditions during the uniform experimental period and that one uniform TC can be used to calculate NH_3 fluxes for all treatments (*Vandré* and *Kaupenjohann*, 1998).

Originally, it was suggested to derive the TC from aggregation of repeated simultaneous measurements with DTM and PSs on high emitting and unfertilized plots to obtain robust signals (*Pacholski*, 2016). However, this recommendation was obtained from reasoning rather than from experimental testing and the appropriate approach to determine TCs may also vary, depending on emission dynamics of the treatments tested and, on the approach, used to aggregate the TC values for the entire experiment.

One important requirement of both methods is the determination of NH_3 background values, that have to be deducted from treatment data (*Pacholski*, 2016; *Vandré* and *Kaupenjohann*, 1998). The background concentration of NH_3 might play a vital role in multi-plot field experiments due to possible cross contamination between plots.

On the background of existing knowledge gaps with regard to calibrated passive sampling, we aimed at testing the following hypothesis:

1. A close correlation between data obtained from PSs and DTM on single plots and averaged across treatments results in the possibility to derive robust and valid TCs.
2. PS and DTM are both affected by background NH_3 concentrations. Treatments with low emissions are comparatively more influenced by that background than treatments with high emissions.
3. TCs should be derived from a treatment with high NH_3 emissions, as in treatments with low emissions the ubiquitous NH_3 background might lead to biased results.
4. The TC value derived for a whole experimental campaign depends on the level of data aggregation used for its calculation.

To test these hypotheses, we set up eight multi-plot experiments with NH_3 flux measurements in different treatments (control, mineral fertilization and four different slurry application techniques) accompanied by DTM and PS measurements in all plots. The effect of the background NH_3 concentration was assessed for both methods by comparing net values with background subtraction to gross values without subtraction. Concerning the third hypothesis, crucial points for the derivation of TCs are summarized to provide general recommendations and guidance for TC determination in future multi-plot calibrated passive studies. Furthermore, we compared TCs based on different levels of data aggregation. This included TCs based on individual plots and treatment mean values, as well as TCs based on data obtained from a whole experimental campaign.

2. Material and methods

2.1 Experimental sites and design

In 2019, we carried out a series of eight multi-plot field experiments in Germany. Weather conditions and soil properties for each individual experiment are summarized in table 1. Four sites were located in North-Germany (close to Kiel in Schleswig-Holstein (SH)), two sites in West-Germany (close to Osnabrück in Lower Saxony (LS)) and two sites in Southwest-Germany (close to Stuttgart in Baden-Württemberg (BW)). Winter wheat (WW) was cultivated on half of the sites, whereas the other half of the experiments was placed on permanent grassland (GL). With regard to the aforementioned abbreviations for crops and locations, the eight sites were named BW:GL, BW:WW, LS:GL, LS:WW, SH:Gla, SH:GLb, SH:WWa and SH:WWb.

Table 1: Soil characteristics, weather conditions and slurry application.

		Soil characteristics				Weather within 48 h after app.			Slurry app.	
		Sand	Silt	Clay	pH	Temp.	Wind	Precip.	NH_4^+-N	pH*
Site	Campaign	%	%	%		°C	$m\ s^{-1}$	mm	$kg\ ha^{-1}$	
BW:GL	1	12	67	21	6.5	5.9	0.7	0.0	42	6.8
BW:GL	2					15.1	0.5	0.0	38	6.7
BW:WW	1	2	64	34	6.8	10.0	0.8	6.6	31	6.8
BW:WW	2					7.9	1.7	0.0	47	6.7
LS:GL	1	68	20	12	5.0	9.0	1.3	0.0	47	7.0
LS:GL	2					14.7	0.7	1.4	34	6.8
LS:WW	1	69	20	11	6.0	5.2	0.8	4.0	38	6.9
LS:WW	2					16.0	2.2	2.2	45	7.1
SH:GLa	1	56	33	11	5.9	8.0	3.2	0.4	56	7.7
SH:GLa	2					10.7	3.2	0.0	39	8.2
SH:GLb	1	59	30	11	5.4	5.9	5.2	0.0	56	7.3
SH:GLb	2					14.9	4.3	29.9	41	8.1
SH:WWa	1	65	25	10	6.8	7.0	2.5	6.0	48	8.0
SH:WWa	2					14.0	4.8	0.2	44	8.0
SH:WWb	1	56	33	11	6.4	4.3	3.8	1.0	48	7.3
SH:WWb	2					7.0	4.0	1.3	47	7.8

*pH value refers to the pH of the raw untreated slurry. GL = Grassland, WW = Winter wheat, BW = Baden-Wuerttemberg, LS = Lower Saxony, SH = Schleswig Holstein, Temp. = Average temperature at 1 m height, Wind = Average wind speed at 2 m height, Precip. = Cumulated precipitation, app. = Application.

At each site, six treatments (Table 2) were set up in a one-factorial randomized complete block design with four replicates.

Table 2: Treatment description for winter wheat (WW) and grassland (GL) sites.

Treatments WW		**Treatments GL**	
N0	Control without N fertilization	N0	Control without N fertilization
CAN	Calcium ammonium nitrate	CAN	Calcium ammonium nitrate
TH	Slurry by trailing hose	TS	Slurry by trailing shoe
TH+A	Slurry + H_2SO_4 by trailing hose	TS+A	Slurry + H_2SO_4 by trailing shoe
SI	1st app. Slurry slot injection 2nd app. Slurry by trailing shoe	SI	Slurry slot injection (both app.)
SI+NI	1st app.: Slurry + NI slot injection 2nd app.: Slurry by trailing shoe	SI+NI	Slurry + NI slot injection (both app.)

App = application; NI = Nitrification inhibitor, H_2SO_4 = sulfuric acid.

The plot size was 9 x 9 m for the experimental sites in LS and BW, whereas the plot size in SH was 9 x 6 m due to limited field areas. Plots were surrounded by unfertilized interspaces of a dimension of 9 m in LS and BW, and 6 m in SH to minimize cross contamination by NH_3 drift (Figure 1).

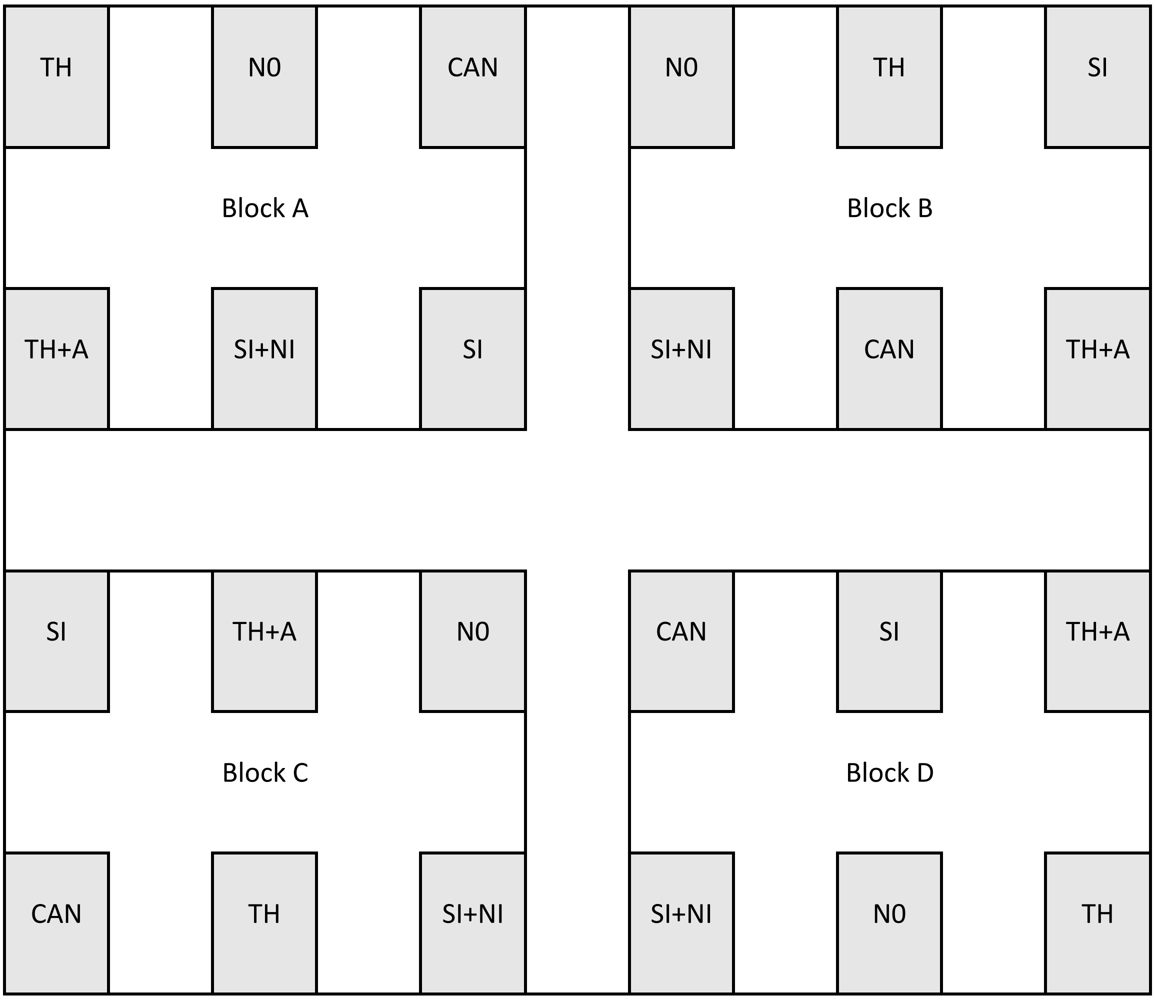

Figure 1: Schematic sketch of the randomized experimental layout. The grey areas represent the quadratic plots (9 m x 9 m). All plots are surrounded by 9 m interspaces to minimize NH_3 cross-contamination. N0 = No nitrogen fertilization, CAN = Calcium ammonium nitrate, TH = Trailing hose, A = Acidification, SI = Slot injection, NI =Nitrification inhibitor.

For the WW sites, the treatments (Table 2) were (1) a control without nitrogen fertilization (N0), (2) broadcast application of calcium ammonium nitrate (CAN), (3) trailing hose application of cattle slurry (TH), (4) trailing shoe using acidified cattle slurry (TH+A), (5) slot injection of cattle slurry (SI), and (6) cattle slurry + nitrification inhibitor (SI+NI). For the GL sites (Table 2), application by trailing hose in treatments (3) and (4) was replaced by trailing shoe application of cattle slurry (TS) and acidified cattle slurry (TS+A). Each site was fertilized twice a year, resulting in 16 fertilization campaigns. The WW sites were fertilized at the end of March/start of April (end of tillering) and at the end of April (sprouting). The GL sites were fertilized approx. six weeks before the first cut (end of March/start of April) and within two weeks after the first cut (middle of May).

For both crops, the target application rate was 170 kg total N ha^{-1}, split up into two equal dressings of 85 kg N ha^{-1} for the WW sites, whereas for the GL sites 100 kg N ha^{-1} were applied before and 70 kg N ha^{-1} after the first silage cut. The NH_4-N application rates varied slightly (Table 1), because the slurry was derived from different farms close to each experimental site. In the treatments with slurry acidification, the target pH was set to 6.0 by adding sulfuric acid (H_2SO_4) to a tank (1m³) filled with slurry before application. The slurry was thoroughly mixed during the process. In treatment SI+NI, the nitrification inhibitor Entec Fl (EuroChem Agro, Mannheim, Germany) with the active ingredient 3,4-dimethylpyrazole phosphate (DMPP) was mixed into the slurry following the recommended application rate of 6 L ha^{-1}. In winter wheat, the NI was applied only for the first application, while for the grassland it was applied for both applications. A custom-made slurry spreader suitable for plot trials based on application tools from Samson Agro A/S (Viborg, Denmark) was used to apply the slurry with the different application implements (see Table 2). For all treatments, the distance between the slurry bands was set to 25 cm.

2.2 Measurement of ammonia emissions

After fertilization, NH_3 emissions were immediately measured by calibrated passive sampling according to Pacholski (2016). Within the first 10 min after fertilizer application, the PSs (250 mL PVC bottles with four circular openings) were filled with 20 mL of 0.05 mol H_2SO_4 solution to absorb emitted NH_3. These containers were fixed to metal rods and placed in the middle of each plot with the bottom 0.15 m above canopy. The H_2SO_4 solution was changed up to five times at the day of fertilizer application. In the following days, the interval between changing sampler solutions was extended, and finally it was changed only once per day. The number of PS samplings varied slightly between sites. However, PS measurement campaigns lasted at all sites for at least 7 days. Sampler solutions were frozen to -18°C until analysis. Ammonium concentration in the sampler solutions were analyzed using well established standard procedures for NH_4^+ measurements (either by UV/Vis spectrophotometer or continuous flow analyzer) and were corrected by the water loss due to evaporation in each container. Subsequently, data were cumulated plot-wise and the cumulated NH_4^+-N content of N0 plots within the same block was subtracted as background.

For the DTM, ambient air is sucked through four circular stainless steel chambers placed on the soil using a Dräger X-act 5000 pump (Drägerwerk AG, Lübeck, Germany). A detector tube is inserted between chamber system and pump to display the NH_3 concentration. Concerning the CAN treatment, a representative amount of fertilizer was put into four soil rings adapted to the size of the chamber system, whereas for the organically fertilized treatments, the chamber system was centered on the slurry band. The proportion of the area covered by the chambers to the total area between two slurry bands was considered by using the factor 0.46 to obtain the emission from total plot area. The chamber systems cover 11.5 cm of the 25 cm distance between neighboring slurry bands and it was assumed, that no emissions occurred in the unfertilized area between slurry bands. Between measurements on different plots, the chambers were cleaned with paper towel and flushed with ambient air, so that the carryover of NH_3 from previous measurements was minimized. NH_3 raw fluxes were calculated based on the equation (Supporting Information 1) according to Pacholski (2016). The raw fluxes were adjusted to absolute fluxes by considering wind speed effects on emissions by an empirical formula (Supporting Information 2) developed by Pacholski et al. (2016). All data presented in the result and discussion section include the wind speed correction. In case cup anemometers detected no wind at the time of measurement, half of the detection limit of the anemometer was used in the formula as default value for wind speed. If the calculated raw flux was zero or below zero (i.e. the background concentration is higher or equal to the measurement in the treated plot), the absolute flux was set to zero (the logarithmic function does not work with negative values).

Up to five measuring times adapted to the diurnal temperature curve were applied at the day of fertilizer application. On the following days, fewer measurement times adapted to the temperature curve were chosen. Due to soil surface disruption by DTM chamber placement, no measurement was carried out at exactly the same spot within a plot, except for the CAN treatment. Cumulated NH_3 emissions were calculated by linear interpolation between measurement timings within the same plot. The number of measurement cycles differed between sites and fertilizer application dates, depending on actually measured NH_3 emissions. As treatments SI and SI + NI were identical regarding the second applications at the WW sites (Table 2), no DTM measurement was conducted in treatment SI + NI during the second application at each site.

2.3 Data analysis

To compare PSs and DTM, the mean cumulated NH_3-N emissions of the high emitting TH or TS treatments of each fertilization campaign were defined as 100 %. Cumulated NH_3 emissions of other treatments are given as relative values compared to treatment TH (for WW) or TS (for GL) and the N0 treatment is by definition 0 % for both methods. Concentrations detected at those plots have to be considered originating from background concentrations and eventual drift between plots.

To compare treatment effects obtained from both methods, cumulated NH_3 emissions obtained by DTM and NH_3-N absorbed by PSs were analyzed by an analysis of variance ($p \leq 0.05$). GL and WW sites were analyzed separately, because GL and WW treatments were slightly different (Table 2). In the first step, the mean cumulated NH_3-N content of the two fertilization campaigns at each site was calculated for each treatment in each block. As there was no DTM measurement for treatment SI + NI regarding the second application at the WW sites as injection techniques are not performable at high plant heights, those missing values were substituted by the values obtained from treatment SI as these two treatments were identical (Table 2). The model was defined by the fixed factors “treatment”, “site” and “treatment x site”, and the random factor “block” (within sites). Subsequently significant differences regarding the treatment means were analyzed by using the Tuckey Test ($p \leq 0.05$).

To evaluate the correlation between DTM and PSs regarding the cumulated emissions evaluated by DTM and cumulated NH_4^+-N collected by PSs, regression functions and coefficients of determination (R^2) were calculated. The regression included single plot data (DTM given as kg NH_3-N ha^{-1}; PS given as mg N L^{-1}) of all 16 fertilization campaigns. For the regression function, the p-value was calculated for slope and y-intercept. Additionally, R^2 and the significance of the slope were computed for each individual fertilization campaign by comparing single plot data and treatment means. Since PSs and DTM both assess NH_3 within the same plots, R^2 values < 0.4 were therefore indicated as a weak correlation between methods. Values between 0.4 and <0.7, 0.7 - 0.9 and > 0.9 were indicated as moderate, good and excellent correlation. For the second campaign at the WW sites, treatment SI+NI was excluded for calculating correlations, because no DTM measurements were performed.

Differing from the original publication of the method described above, “gross” NH_3 emissions (without subtraction of background values) were compared to “net” NH_3 emissions (with subtraction of background values) to evaluate the relevance of background noise. For the PSs, the subtraction of background values is defined as the subtraction of the cumulated NH_4^+-N collected in the control treatment within the same block. For the DTM, the subtraction of background values for each measurement time is defined as the subtraction of the background concentration in the same block, which was measured closest in time (see Supporting Information 1). Calculations of the cumulative NH_3 emission by linear interpolation were done with and without subtraction of this background noise. The "gross" values were exclusively used to describe the influence of background noise, for all other issues discussed in this paper, the "net" values were used as the calibration of passive sampling was performed using net values.

According to Pacholski (2016) the TC is defined as the cumulative NH_3 emissions calculated by the DTM divided by the cumulative NH_4^+-N adsorbed by PSs for a whole sampling campaign. Cumulated PS values (mg N L^{-1}) can be transformed into absolute values (kg N ha^{-1}) by multiplication with the TC. Three approaches for calculating TC factors were investigated.

$TC_{individual}$ (Equation 1): For each fertilization campaign, the TC values were calculated for each individual plot:

$$TC_{individual} = \left(\frac{DTM\ cumulated\ (kg\ N\ ha^{-1})}{PS\ cumulated\ (mg\ N\ L^{-1})}\right) \quad (1)$$

Subsequently, the mean and standard deviation (SD) of the four $TC_{individual}$ belonging to the same treatment were calculated. Negative numerical PS results after background subtraction of individual plots were considered an exclusion criterion for recommending that treatment for TC calculation.

TC_{mean} (Equation. 2): Alternatively, calculation of the treatment mean of the four replications was done before TC calculation for DTM and PSs. Treatment mean of cumulated DTM samplings (kg N ha^{-1}) was then divided by treatment mean of cumulated PS samplings (mg N L^{-1}):

$$TC_{mean} = \left(\frac{treatment\ mean\ DTM\ cumulated\ (kg\ N\ ha^{-1})}{treatment\ mean\ PS\ cumulated\ (mg\ N\ L^{-1})}\right) \quad (2)$$

TC_{total} (Equation 3): Thirdly, a single TC for each fertilization campaign was calculated by determining mean cumulated DTM samplings (kg N ha^{-1}) and mean cumulated PS samplings (mg N L^{-1}) including data of all plots. DTM mean was then divided by PS mean:

$$TC_{total} = \left(\frac{mean\ DTM\ cumulated\ (kg\ N\ ha^{-1})}{mean\ PS\ cumulated\ (mg\ N\ L^{-1})}\right) \quad (3)$$

3. Results and Discussion

3.1 Comparison of relative cumulated emissions obtained by PSs and DTM

PS and DTM provided cumulative NH_3 emissions in different units and required normalization for further processing. The mean of treatment TH for the WW sites or treatment TS for the GL sites (Table 3) was defined as 100 % for each fertilization campaign for both approaches. Cumulated NH_3 emissions of other treatments are normalized as relative values compared to the TH or TS treatment. Both methods detected the significantly lowest emissions in the CAN treatment (Figure 2). Low NH_3 losses following CAN application were found by many previous studies (*Forrestal* et al., 2016; *Sommer* and *Jensen*, 1994; *Velthof* et al., 1990). Based on PS data even numerically negative values after control subtraction were observed in some cases (Table 3). This means the background value sampled in an unfertilized plot was higher than the value sampled in its respective treatment plot. In opposition to the original publication (*Pacholski*, 2016) we allowed numerically negative values for further calculations. In some cases, contamination due to adjacent plots might be higher in the N0 plot than in its respective treatment plot and vice versa. Including only values ≥ 0 for the calculation of treatment means might therefore lead to biased results when NH_3 emissions are low.

In treatments where the liquid organic manure was acidified, emissions were also comparatively low according to both methods (Figure 2), corresponding with previous studies (*Fangueiro* et al., 2015). For the second fertilization in SH:GLa (Table 3), numerical negative PS values were calculated for the treatment with acidified slurry. In individual plots, negative values were also calculated for other fertilization campaigns (Table 3).

According to the PSs (Fig 2), emissions in the SI treatments with and without NI were lower than in the TH or TS treatments. For the SI+NI treatment, those differences were not significant. Based on the DTM results no differences between SI (with and without NI) and TH treatments were detected for the GL sites, whereas for the WW sites a significant difference was found between SI and TH treatment (Figure 2).

Overall, results of both methods are in accordance with literature (*Fangueiro* et al., 2015; *Forrestal* et al., 2016; *Freney* et al., 1983; *Sommer* and *Jensen*, 1994; *Velthof* et al., 1990; *Webb* et al., 2010). However, differences between treatment means are more pronounced, when using PSs compared to the DTM (Figure 2). When using the PSs, the difference between lowest (CAN) and highest (TH in WW or TS in GL) treatment mean was about 100 %, whereas for the DTM, the difference between lowest (CAN) and highest (TH in WW or TS in GL) treatment mean was only about 70 %. However, the variance of results is higher for the PSs (Table 3). The cumulative NH_3 emissions measured with the DTM showed, with only two exceptions (sites LS:GL and LS:WW; Table 3), a lower SD.

Table 3: Comparison of relative passive sampler (PS) and dynamic tube method (DTM) data.

		100%	CAN		TH/TS		TH/TS+A		SI		SI+NI	
Site/Campaign		kg/ha N	PS	DTM	PS	DTM	PS	DTM	PS	DTM	PS	DTM
BW:GL	1	9.9	18 ± 6	30 ± 9	100 ± 18	100 ± 6	58 ± 7	24 ± 13	63 ± 15	68 ± 11	62 ± 31	77 ± 7
BW:GL	2	7.3	**1 ± 7**	9 ± 5	100 ± 29	100 ± 22	33 ± 21	80 ± 9	76 ± 15	83 ± 5	94 ± 27	46 ± 19
BW:WW	1	3.8	**-10 ± 23**	34 ± 10	100 ± 71	100 ± 24	54 ± 19	58 ± 17	**43 ± 65**	57 ± 24	**59 ± 63**	83 ± 41
BW:WW	2	7.7	**-12 ± 8**	14 ± 1	100 ± 97	100 ± 8	**55 ± 78**	64 ± 5	80 ± 35	63 ± 12	**38 ± 70**	63 ± 12
LS:GL	1	5.6	**8 ± 22**	37 ± 36	100 ± 19	100 ± 27	**16 ± 21**	57 ± 33	73 ± 28	63 ± 31	90 ± 8	82 ± 33
LS:GL	2	1.3	**-17 ± 33**	156 ± 59	100 ± 55	100 ± 46	81 ± 38	127 ± 51	64 ± 39	88 ± 32	99 ± 35	139 ± 62
LS:WW	1	5.2	**-4 ± 23**	21 ± 16	100 ± 13	100 ± 33	**14 ± 18**	82 ± 20	42 ± 23	108 ± 19	49 ± 41	119 ± 23
LS:WW	2	5.1	**0 ± 10**	31 ± 37	100 ± 42	100 ± 59	**5 ± 65**	29 ± 17	**40 ± 34**	69 ± 27	31 ± 33	69 ± 27
SH:GLa	1	18.5	**-8 ± 26**	6 ± 4	100 ± 41	100 ± 11	65 ± 51	56 ± 6	65 ± 45	127 ± 27	75 ± 19	113 ± 4
SH:GLa	2	17.7	**9 ± 37**	8 ± 4	100 ± 44	100 ± 14	**-3 ± 39**	75 ± 28	67 ± 82	87 ± 15	106 ± 43	108 ± 18
SH:GLb	1	10.3	**3 ± 12**	15 ± 1	100 ± 43	100 ± 20	**22 ± 21**	5 ± 3	92 ± 20	171 ± 23	90 ± 18	198 ± 11
SH:GLb	2	17.6	**8 ± 18**	28 ± 9	100 ± 25	100 ± 10	50 ± 16	67 ± 10	92 ± 25	110 ± 13	88 ± 18	111 ± 19
SH:WWa	1	5.1	**-21 ± 13**	48 ± 14	100 ± 36	100 ± 11	**29 ± 39**	67 ± 4	74 ± 20	126 ± 19	108 ± 50	149 ± 17
SH:WWa	2	12.9	**-16 ± 21**	9 ± 6	100 ± 27	100 ± 12	**53 ± 57**	73 ± 10	88 ± 49	92 ± 9	104 ± 68	92 ± 9
SH:WWb	1	9.0	**2 ± 12**	40 ± 8	100 ± 22	100 ± 7	53 ± 33	99 ± 3	50 ± 17	91 ± 8	77 ± 16	111 ± 10
SH:WWb	2	12.4	**2 ± 43**	25 ± 5	100 ± 65	100 ± 12	39 ± 24	27 ± 5	60 ± 34	86 ± 9	91 ± 40	86 ± 9

The mean of the TH or TS treatment were defined as 100 %. Column “100 %” shows the NH_3 emissions (kg N ha^{-1}) in treatment TH/TS according to the DTM. ± indicates the standard deviation of the treatment mean. Numbers in bold print indicate that at least one relative value was below 0.

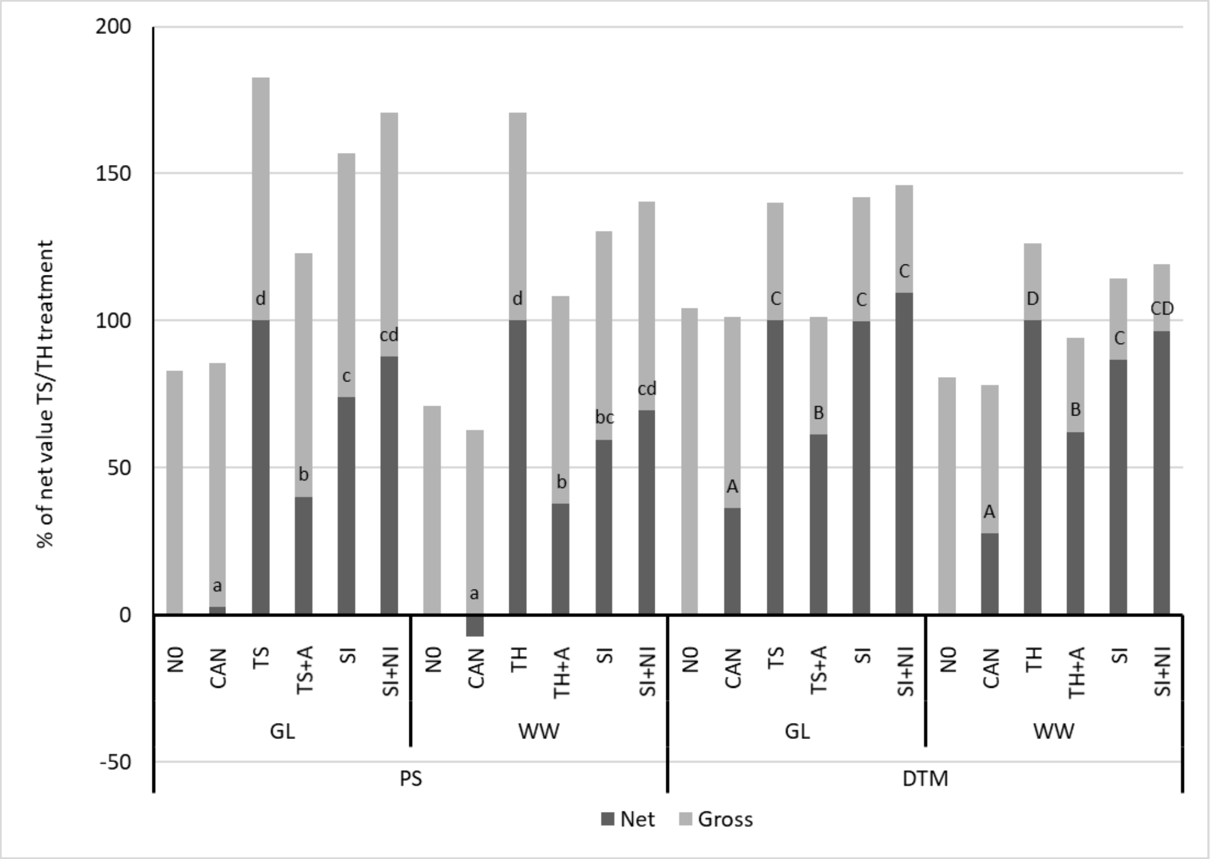

Figure 2: Comparison of gross- and net cumulated ammonia emissions across sites calculated based on data measured by passive samplers (PS; left side) and the dynamic tube method (DTM, right side). The net ammonia emissions of the TS or TH treatment of each individual site and campaign were defined as 100 % for both methods. Depicted are the mean cumulated ammonia emissions across all sites. The gross value represents the relative cumulated ammonia emissions without control subtraction. The net value represents the relative cumulated ammonia emission including the control subtraction. Different lower case letters (left side) indicate significant differences (Tuckey test; $p \leq 0.05$) between net values of different treatments regarding the PSs. GL and WW sites were analyzed separately. Different capital letters (right side) indicate significant differences (Tuckey test; $p \leq 0.05$) between net values of different treatments regarding the DTM. GL and WW sites were analyzed separately. N0 = No Nitrogen fertilization, TH = Trailing hose, TS = Trailing shoe, A = Acidification, SI = Slot injection, NI =Nitrification inhibitor, GL = Grassland, WW = Winter wheat

When comparing the different sites, the highest emissions according to the DTM occurred, when the wind speed was high within the first 48 h after fertilization (Table 1; Table 3). High wind speed leads to an increased air exchange rate. Therefore, the NH_3 concentration in the air layer close to the applied nitrogen fertilizer is comparatively low (*Freney* et al., 1983), leading to a higher concentration gradient between fertilizer solution and ambient air, increasing NH_3 volatilization (*Freney* et al., 1983). It is important to note that the DTM 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 (*Pacholski*, 2016). Instead, the raw fluxes (Supporting Information 1) have to be adjusted for the wind speed (Supporting Information 2; *Pacholski*, 2016). However, it has to be kept in mind that this calibration included only wind speeds up to 4 m s^{-1} (*Gericke* et al., 2011; *Ni* et al., 2015; *Pacholski*, 2016). Especially the experiments conducted in SH exceeded this limit (Table 1), possibly reducing the validity of the data obtained by the DTM at these sites.

When comparing PSs and DTM across fertilization campaigns and all treatments (Figure 3), correlation between these two methods was rather moderate ($R^2 = 0.44$). This could be expected due to varying environmental conditions (temperature, wind speed, surface roughness) affecting NH_3 uptake efficiency of PSs (*Pacholski*, 2016; *Vandré* and *Kaupenjohann*, 1998). However, when comparing PS and DTM data of individual plots within fertilization campaigns, R^2 values also indicated oftentimes only weak or moderate correlation between methods (Table 4). Cumulative NH_3 emissions obtained by the PSs show a high SD (Table 3), impairing the correlation between PSs and DTM when comparing individual plots. The initial hypothesis, that a good correlation between methods is expected, is therefore only partially validated. When comparing treatment means within fertilization campaigns (Table 4), correlation between methods generally increases, because treatment means are less affected by extreme values of single plots. However, as those correlations are only based on five values compared to 20 values for the correlation of individual plots, the increased R^2 values oftentimes do not coincide with increased statistical significance. The second important aspect regarding the regression analysis is the comparison of intercepts. Zero NH_3 emissions according to the PSs should equal zero emissions according to the DTM. However, this was not validated (Figure 3). On average, zero NH_3 emissions according to the PSs equaled 3.6 kg N ha^{-1} NH_3 emissions according to the DTM.

Table 4: R^2 values for the correlation between passive sampler and dynamic tube method data for each site and fertilization campaign.

Site→	BW:GL		BW:WW		LS:GL		LS:WW		SH:GLa		SH:GLb		SH:WWa		SH:WWb	
Campaign↓	R^2_i	R^2_m	R^2_i	R^2_m	R^2_i	R^2_m	R^2_i	R^2_m	R^2_i	R^2_m	R^2_i	R^2_m	R^2_i	R^2_m	R^2_i	R^2_m
1	0.50*	0.62	0.37*	0.90*	0.14	0.85*	0.20*	0.38	0.46*	0.67	0.67*	0.77*	0.53*	0.79*	0.57*	0.78*
2	0.27	0.40	0.43*	0.92*	0.05	0.26	0.60*	0.95*	0.25*	0.70	0.73*	0.94*	0.69*	0.98*	0.41*	0.80*

*significant slope ($p \leq 0.05$), R^2_i = Coefficient of determination for the correlation of individual plots, R^2_m = Coefficient of determination for the correlation of treatment means, GL = Grassland, WW = Winter wheat, BW = Baden-Wuerttemberg, LS = Lower Saxony, SH = Schleswig Holstein

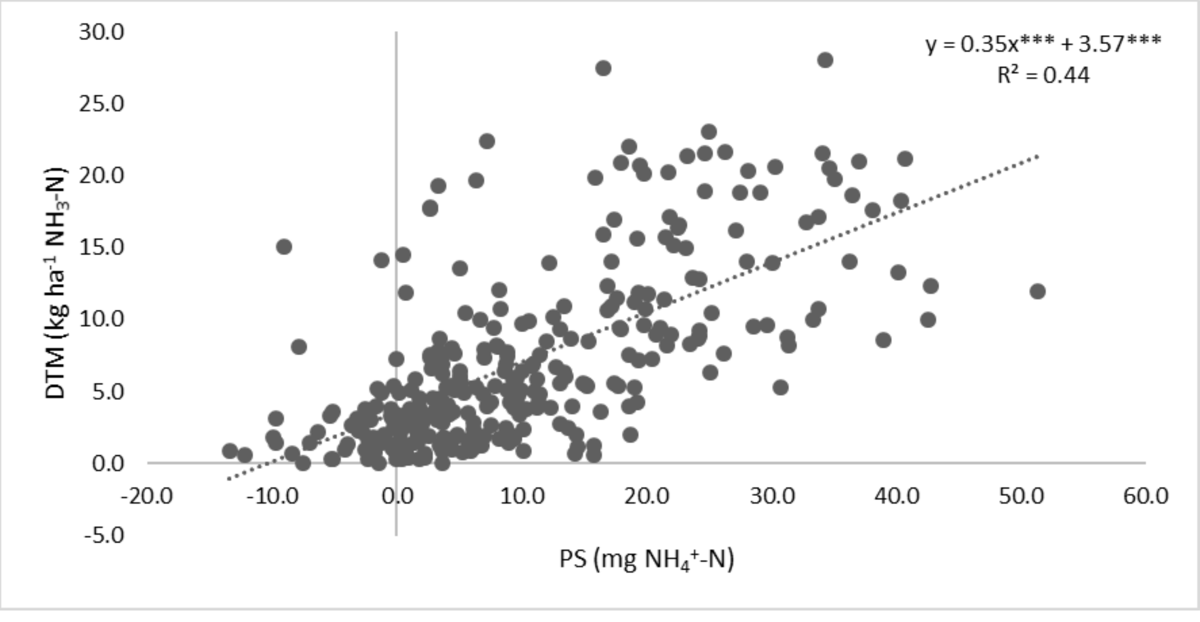

Figure 3: Correlation of ammonia emissions calculated based on passive sampler (PS) and dynamic tube method (DTM) data across fertilization campaigns. *** indicates a highly significant effect ($p \leq 0.001$) of slope or y intercept. R^2 = Coefficient of determination.

3.2 Handling of background subtraction according to PSs and DTM

The comparison of PS and DTM results showed two major differences between the two methods. First, when comparing treatments within a fertilization campaign, variance of cumulated ammonia emissions according to the PSs is generally larger than variance according to the DTM (Table 3). Second based on the applied calculation approach and different from the original publication (*Pacholski*, 2016), negative numerical PS values are possible, whereas the DTM always leads to results ≥ 0. These differences might be explained by the differences in handling the background subtraction for both methods. Per definition, the background represents the ubiquitous atmospheric NH_3 concentration. In such a multi-plot field trial set-up with slurry application, the drift of NH_3 between experimental plots might be the primary source of that background. Furthermore, NH_3 sources outside the experimentation site might also contribute to the background (*Vandré* and *Kaupenjohann*, 1998). Due to the chamber system, wind drift might be a less important factor for the DTM than for the PSs. However, air passing through the DTM system from a relatively low altitude compared to the PSs is probably also affected by emissions from neighboring plots. Furthermore, the contamination of the chamber system with NH_3 adsorbed from previous measurements can be an additional factor contributing to increased background values. To minimize this problem, the chamber systems require thorough cleaning by e.g. paper towel and flushing with ambient air in-between measurements (*Pacholski*, 2016).

In our study, the PS background was defined as the cumulated NH_3 emissions of the N0 plot of the same block. That means that for each fertilization campaign the same background was subtracted for each treatment within the same block, leading to the same average background subtraction for each treatment (Figure 2). Data obtained in our field experiments showed that many plots exhibited numerically negative cumulated NH_3 emissions after control subtraction (Table 3; Figure 3), indicating that the determination of the background in the N0 plot might sometimes not be representative for the background in the treated plots. That also might at least partially explain the high SD of PS results (Table 3). Besides, varying NH_3 emissions due to fertilization, the calculated cumulated N emission of each plot was also affected by varying background NH_3 concentrations. Treatments with high emissions are comparatively less influenced by background noise than treatments with low emissions, which supports our second hypothesis. Regarding the PSs, the “gross” emissions in the TH or TS treatment were on average 80 % higher than the “net” emissions (range: 24 % to 170 % higher without background subtraction; Figure 4) without background subtraction (Figure 2). Obviously, the percentage of background subtraction is even higher in treatments with lower emissions. Therefore, the problem of the inaccurate determination of the background is more pronounced in those treatments. This can be seen in particular for CAN plots where NH_3 emissions were very low during the whole measurement period.

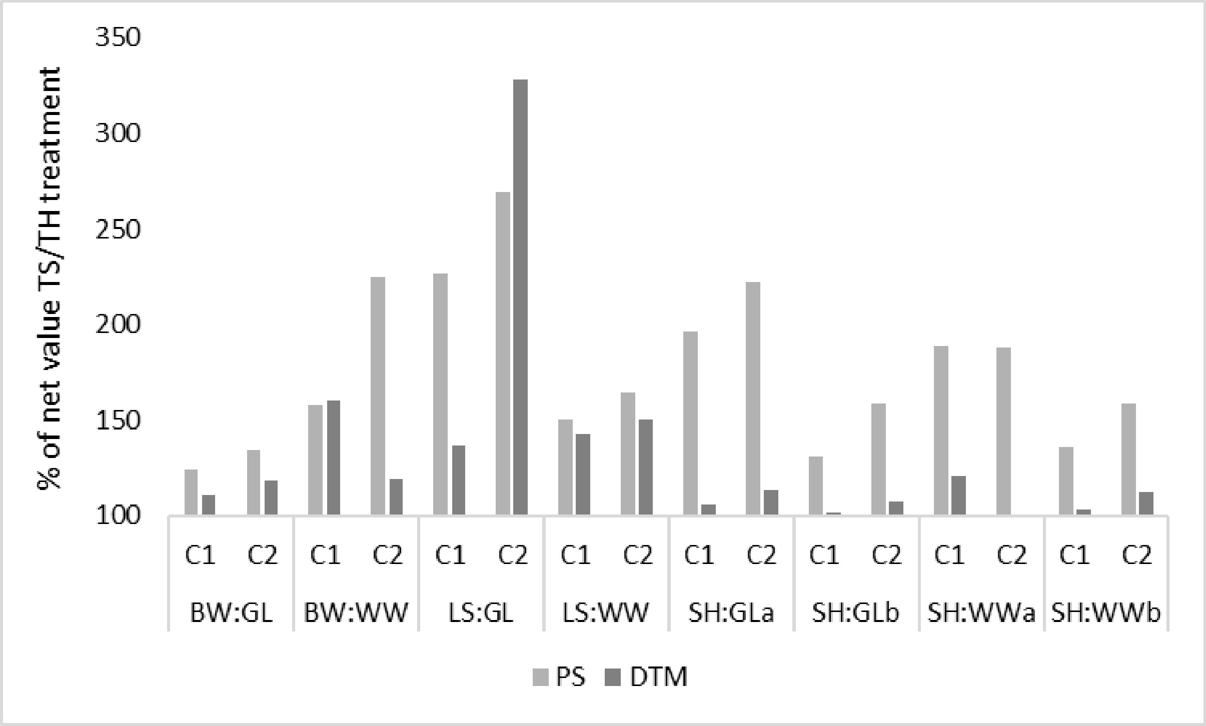

Figure 4: Gross ammonia emissions for passive sampler (PS) and dynamic tube method (DTM) data in the trailing hose (TH) or trailing shoe (TS) treatment for the different sites. The net ammonia emissions of the TH or TS treatment of each individual site and campaign were defined as 100 %. The gross value represents the relative cumulated ammonia emissions without control subtraction. The net value represents the relative cumulated ammonia emission after control subtraction. C = Fertilization campaign, GL = Grassland, WW = Winter wheat, BW = Baden-Wuerttemberg, LS = Lower Saxony, SH = Schleswig Holstein.

For the DTM, the background was subtracted for each individual measurement when applying the raw flux formula (Supporting Information 1). It was defined as the detector tube reading of the N0 plot within the same block, which is closest in time. The result of that calculation can be either numerically positive or negative. Subsequently the raw fluxes are corrected for wind speed (Supporting Information 2). Negative raw fluxes were set to zero absolute fluxes according to Pacholski (2016). Between measurements within the 7-day period after fertilizer application, cumulative NH_3 emissions of each individual plot were calculated by the linear interpolation of absolute fluxes. A general requirement of that procedure is the exact determination of the background. Theoretically, the background should never be higher than the emissions measured in a fertilized plot. In practice however, the background value used for the calculation might often be inaccurate. This is illustrated by the comparison of “gross” and “net” emissions of CAN and N0 treatment. The mean-cumulated NH_3 emissions across sites according to the DTM (Figure 2) show that the ammonia emissions in the CAN treatment reach approximately 30 % of the value reached in the TH or TS treatment. In the N0 treatment, the emissions are by definition at 0 %, as those N0 plots are used to define the background value. However, when cumulating NH_3 without the subtraction of background values (Figure 2), results in N0 and CAN treatment are similar. The reason for that is that the result of the raw flux calculation in the N0 plots is always zero, whereas in the CAN plots it is sometimes slightly above or slightly below zero. For the calculation of the absolute fluxes only positive raw fluxes are taken into consideration.

The average difference between "gross" and "net" values varied also between other treatments (Figure 2). Those differences can be explained by the non-linear wind speed correction following calculation of raw fluxes (Supporting Information 2) and by applying the factor 0.46 (Supporting Information 1) for organically fertilized treatments, where the chambers covered only the slurry bands, but not for the CAN treatment.

For the DTM, the percentage of control subtraction varied substantially between sites. Regarding the TH or TS treatment, the sites in SH had generally the lowest percentage of control subtraction, whereas in LS percentage of control subtraction was relatively high (Figure 4). Especially the second fertilization campaign in LS:GL exhibited high background values according to the DTM. This might be partially explained by the amount of NH_3 emissions. In LS emissions were generally low (Table 3), so the relative influence of background was comparatively high. On the contrary, the comparatively low emissions might also be explained by the high amount of background subtraction.

Further investigation revealed that the handling of DTM measurements in the field differed slightly between sites with a potential impact on background subtraction. In SH and BW, the order of measurement was treatment-wise (e.g. at first all TS plots then all TS+A plots). Moreover, for each measurement cycle, one separate chamber system was used for low emitting plots (mainly N0 and CAN plots) and another chamber system was used for organically fertilized treatments to minimize carry-over effects from low to high emitting treatments. In LS, the order of measurement was block wise and the chamber systems were used for all treatments. Treatment-wise order of measurement and using different chamber systems for high and low emitting treatments means that potentially lower background values are subtracted, as the N0 plots which are used for determining the background are less affected by cross contamination compared to the block-wise order of measurement. Furthermore, in LS cumulative NH_3 emissions scatter more around their respective treatment mean compared to the sites in SH and BW (Table 3), as the measurements of the four plots of the same treatment were influenced by different amounts of cross contamination (one plot might have been measured after a N0 plot, another after a TH plot).

Therefore, the treatment-wise order of measurement should be preferred to compare different treatments. Furthermore, using a separate chamber system for each treatment might be even better to compare different treatments. However, contamination of the chamber system due to previous measurements within the same treatment remains and must be minimized by carefully cleaning and purging all DTM measurement devices before sampling the next plot.

The purpose of the DTM is to provide area-based NH_3 emissions. In the initial set up by Pacholski et al. (2006) only two high emitting plots involving repeated measurements within the plot and one unfertilized area for determining the background were measured. Each of those three treatments consisted of only one plot. Considering that there were fewer measurements, cross contamination was probably a less important factor than in the experimental set up of this study. As the approach by Pacholski et al. (2006) is based on an empirical formula, small changes of the original set up might finally result in large differences regarding the cumulated NH_3 emissions. In order to be close to initial calibration conditions, it is therefore advisable to limit the number of consecutive measurements from emitting plots.

3.3 Transfer coefficient

The PS measurements enable relative, semi-quantitative comparisons between plots, delivering effect sizes between treatments. To finally transfer the relative differences between PS results to absolute differences, calibrated passive sampling requires the calculation of a TC on the precondition that all factors influencing the TC (wind speed and direction, temperature, plant height and canopy structure) are equal throughout the experimental site (*Vandré* and *Kaupenjohann*, 1998). However, in practice this is probably rarely the case as for example NH_3 drift between plots might affect background NH_3 emissions of each individual plot differently.

The TC (Table 5) was calculated for single plots ($TC_{individual}$; Equation 1), treatment means (TC_{mean}; Equation 2) or a whole multi-plot field experiment (TC_{total}; Equation 3). As it is costly and time consuming to execute DTM measurements in a large number of plots, our aim was to identify characteristics of a well-suited treatment for calculating the TC. We hypothesized that the TC should be calculated based on data obtained from a treatment with high NH_3 emissions. Under those conditions the relative influence of background noise is expected to be low.

Calculation of the $TC_{individual}$ (Table 5) showed that negative PS results after N0 subtraction lead to negative TCs in plots of treatments with low emissions (TH+A, TS+A and CAN treatments). When emissions are higher, the probability of such values was clearly reduced. After background subtraction, the cumulated emissions by PSs can also provide a result very slightly above zero leading to a meaningless large TC. This problem is also more likely to occur in plots with comparatively low emissions. These two factors might explain why the $TC_{individual}$ SD is generally higher for treatments with low emissions (Table 5), confirming our hypothesis that TC calculations should be based on a treatment with high emissions.

When calculating the TC according to the TC_{mean} (Equation 2) approach, no negative results occurred for TH, TS, SI and SI+NI treatment (Table 5). The results according to $TC_{individual}$ and TC_{mean} approach differed remarkably for treatments with low emissions, demonstrating that TC values depend on the level of data aggregation used for their calculation. Even in the TH or TS treatment, the difference between the two approaches ranged from 0 to 48 %. Considering that cumulated NH_3 emissions according to both methods are influenced by background NH_3 emissions and that this background might influence individual plots more than treatment means, calculating TC_{mean} seems more reliable than calculating the mean of four $TC_{individuals}$. Furthermore, the correlation of PS and DTM treatment means is higher than the correlation of individual plots (Table 4), substantiating that treatment means are more reliable than values determined in individual plots.

Comparing the TC_{mean} of the TH or TS treatment with the TC_{total} shows, that the TC_{total} is always higher than the TC_{mean} (Table 5). Zero NH_3 emissions according to the PSs do not equal zero NH_3 emissions according to the DTM (Figure 3). When emissions are low, the DTM might overestimate the cumulated NH_3 emissions. That means that treatments with low emissions add comparatively more N according to the DTM (numerator for calculating the TC) than according to the PSs (denominator for calculating the TC). Therefore, although based on more data, the TC_{total} might be less reliable than calculating the TC_{mean} based on a treatment with high emissions

Table 5: Transfer coefficients calculated from different treatments and for different degrees of data aggregation ($TC_{individual}$, TC_{mean} and TC_{total}).

		$TC_{individual}$					TC_{mean}					TC_{total}
Site	Campaign	CAN	TH/TS	TH/TS+A	SI	SI+NI	CAN	TH/TS	TH/TS+A	SI	SI+NI	
BW:GL	1	2.37 ± 1.36	1.10 ± 0.17	0.53 ± 0.33	1.18 ± 0.1	1.88 ± 0.64	2.03	1.08	0.49	1.16	1.64	1.15
BW:GL	2	**-0.88 ± 3.55**	0.52 ± 0.18	1.70 ± 1.51	0.54 ± 0.11	0.26 ± 0.14	0.96	0.49	1.13	0.53	0.24	0.50
BW:WW	1	**-0.38 ± 1.02**	0.85 ± 0.59	0.76 ± 0.46	**-4.03 ± 5.06**	**0.14 ± 1.42**	**-1.59**	0.57	0.66	0.81	0.83	0.81
BW:WW	2	**-2.08 ± 11.05**	2.11 ± 1	**0.13 ± 2.87**	1.28 ± 0.44	n.m.	12.79	1.48	1.65	1.14	n.m.	1.48
LS:GL	1	**0.24 ± 2.19**	0.56 ± 0.21	**-5.38 ± 13.3**	0.54 ± 0.38	0.51 ± 0.21	1.53	0.54	1.52	0.48	0.51	0.63
LS:GL	2	**1.6 ± 3.48**	0.15 ± 0.11	0.23 ± 0.13	0.39 ± 0.48	0.19 ± 0.11	**-1.02**	0.11	0.19	0.17	0.17	0.22
LS:WW	1	**-0.13 ± 0.53**	0.41 ± 0.17	**1.36 ± 3.45**	1.27 ± 0.51	7.08 ± 11.99	**-4.95**	0.40	3.97	1.09	1.09	0.91
LS:WW	2	**-1.79 ± 4.58**	0.33 ± 0.1	**-0.27 ± 0.41**	**-0.02 ± 0.95**	n.m.	**-0.84**	0.35	2.36	0.64	n.m.	0.62
SH:GLa	1	**0.31 ± 0.74**	0.7 ± 0.12	4.63 ± 8.38	2.58 ± 2.81	1 ± 0.22	**-0.84**	0.67	0.58	1.29	0.97	0.89
SH:GLa	2	**-0.24 ± 0.53**	1.48 ± 1.12	**-1.17 ± 7.6**	9.5 ± 13.16	1.49 ± 1.08	**-0.50**	1.13	**-13.32**	1.66	1.19	1.80
SH:GLb	1	**0.78 ± 2.8**	0.34 ± 0.18	**-0.06 ± 0.17**	0.57 ± 0.11	0.68 ± 0.14	**-0.48**	0.30	**-0.13**	0.56	0.66	0.56
SH:GLb	2	**-21.88 ± 44.07**	0.58 ± 0.11	0.87 ± 0.43	0.7 ± 0.21	0.75 ± 0.18	2.41	0.56	0.84	0.67	0.73	0.70
SH:WWa	1	**-0.8 ± 0.49**	0.26 ± 0.08	**-12.84 ± 21.01**	0.44 ± 0.14	0.44 ± 0.29	**-0.59**	0.25	0.63	0.41	0.35	0.42
SH:WWa	2	**-1.57 ± 1.5**	0.48 ± 0.07	**0.09 ± 0.76**	0.59 ± 0.24	n.m.	**-0.29**	0.47	0.65	0.50	n.m.	0.57
SH:WWb	1	**0.07 ± 1.36**	0.29 ± 0.06	0.98 ± 1.05	0.6 ± 0.3	0.41 ± 0.1	**-18.40**	0.28	0.54	0.52	0.40	0.44
SH:WWb	2	**0.04 ± 0.79**	0.74 ± 0.34	0.58 ± 0.32	1.14 ± 0.67	n.m.	258.00	0.60	0.44	0.88	n.m.	0.73

Table 5: The section $TC_{individual}$ (Equation 1) shows mean and standard deviation of the four $TC_{individuals}$ belonging to the same campaign and treatment. Bold numbers indicate that at least one of those four respective $TC_{individuals}$ were negative. TC_{mean} was calculated according to Equation 2. TC_{total} was calculated according to Equation 3 for each site. n.m. = No measurement conducted, GL = Grassland, WW = Winter wheat, BW = Baden-Wuerttemberg, LS = Lower Saxony, SH = Schleswig Holstein, N = Nitrogen, N0 = No N fertilization, TH = Trailing hose, TS = Trailing shoe, A = Acidification, SI = Slot injection, NI =Nitrification inhibitor.

4. Conclusion

Determining NH_3 emission in multi-plot field trials with several fertilized treatments is challenging and requires detailed methodological considerations. Our aim was to assess the best practice for using calibrated passive sampling under such conditions. The key point of this approach is calculating a TC for scaling relative differences between plots obtained by PSs with simultaneous dynamic tube measurements. The main problem in our experimental set-up was cross-contamination between plots, masking NH_3 emissions of treatments with comparatively low emissions. Treatments with high NH_3 emissions were therefore identified to deliver the most robust TCs. This confirms the procedure advocated in the initial publication (*Pacholski*, 2016): the chamber system used for scaling PS results should only be used in unfertilized control and one treatment with high NH_3 emissions. This reduces time and costs for dynamic tube measurements and minimizes chamber system cross contamination between treatments. PS results of multi-plot field experiments with slurry application may also differ from the initial set-up due to increased NH_3 drift between plots. We demonstrated that calculating TCs based on treatment averages is more robust when compared to the calculation of TCS for single plots, because treatment means are less influenced by changing NH_3 background concentrations than individual plots. In perspective, the highly empirical calibrated passive sampling approach can be applied with some confidence, when all procedures are covered appropriately. However, there is a need for a more direct quantitative method for multi-plot field trials. Such a method could be based on more precise NH_3 concentration measurements in higher resolution in time and inverse flux modeling, which has been tested in recent studies but requires further development.

Supplement

Supporting Information 1: Raw flux calculation

$$F_{Ng} = vol.* conc * \frac{1013(hPa)}{pact} * \left(\frac{696.1\ \left(\frac{mg}{L}\right) * 298.15K}{(273.15 + Tact)K}\right) * 10^{-6} * \frac{14\ \left(\frac{g}{mol}\right)}{17\ \left(\frac{g}{mol}\right)} * \frac{10000(cm^2/m^2)}{415(cm^2)} * \frac{3600\left(\frac{s}{h}\right)}{dur(s)} * 0.46$$

F_{Ng}	Ammonia flux (mg N m^{-2} h^{-1})
Vol	Volume of air passed through the system (l).
Conc	Reading of the detector tube minus background concentration (ppm). The background concentration is defined as the detector tube reading of the N0 plot within the same block which is closest in time
Pact	Actual air pressure (hPa)
Tact	Air temperature at measurement (°C)
14/17	Conversion from NH_3 to N by their atomic weight
415	Area covered by chambers (cm²)
Dur	Duration of measurement (s).
0.46	Adjustment for the area covered by the chambers (only for plots with slurry application)

Supporting Information 2: Wind speed correction

$$\ln(absolute\ flux) = 0.444 * \ln(raw\ flux) + 0.59 * \ln(V_{wind})$$

absolute flux	Ammonia flux (kg N ha^{-1} h^{-1})
raw flux	Ammonia flux (kg N ha^{-1} h^{-1}) calculated by supp. 1
V_{wind}	Wind speed (m s^{-1}) at 2 m height during the measurement

Paper 2: Evaluation of the dynamic tube method for measuring ammonia emissions following liquid manure application

Agriculture (2023), Volume 13, 1217

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Author Contributions: Conceptualization, M.t.H. and H.-W.O.; methodology, M.t.H.; software, M.t.H.; validation, H.-W.O.; formal analysis, M.t.H.; investigation, M.t.H.; resources, H.-W.O.; data curation, M.t.H.; writing—original draft preparation, M.t.H.; writing—review and editing, H.-W.O.; visualization, M.t.H.; supervision, H.-W.O.; project administration, H.-W.O.; funding acquisition, H.-W.O. All authors have read and agreed to the published version of the manuscript

Abstract:

Easy and inexpensive methods for measuring ammonia emissions in multi-plot field trials allow the comparison of several treatments with liquid manure application. One approach that might be suitable under these conditions is the dynamic tube method (DTM). Applying the DTM, a mobile chamber system is placed on the soil surface, and the air volume within is exchanged at a constant rate for approx. 90 s. with an automated pump. This procedure is assumed to achieve an equilibrium ammonia concentration within the system. Subsequently, a measurement is performed using an ammonia-sensitive detector tube. Ammonia fluxes are calculated based on an empirical model that also takes into account the background ammonia concentration measured on unfertilized control plots. Between measurements on different plots, the chamber system is flushed with ambient air and cleaned with paper towels to minimize contamination with ammonia. The aim of this study was to determine important prerequisites and boundary conditions for the application of the DTM. We conducted a laboratory experiment to test if the ammonia concentration remains stable while performing a measurement. Furthermore, we investigated the cleaning procedure and the effect of potential ammonia carryover on cumulated emissions under field conditions following liquid manure application. The laboratory experiment indicated that the premeasurement phase to ensure a constant ammonia concentration is not sufficient. The concentration only stabilized after performing more than 100 pump strokes, with 20 pump strokes (lasting approximately 90 s) being the recommendation. However, the duration of performing a measurement can vary substantially, and linear conversion accounts for those differences, so a stable concentration is mandatory. Further experiments showed that the cleaning procedure is not sufficient under field conditions. Thirty minutes after performing measurements on high emitting plots, which resulted in an ammonia concentration of approx. 10 ppm in the chamber, we detected a residual concentration of 2 ppm. This contamination may affect measurements on plots with liquid manure application as well as on untreated control plots. In a field experiment with trailing hose application of liquid manure, we subsequently demonstrated that the calculation of cumulative ammonia emissions can vary by a factor of three, depending on the degree of chamber system contamination when measuring control plots. When the ammonia background values were determined by an uncontaminated chamber system that was used to measure only control plots, cumulative ammonia emissions were approximately 9 kg NH_3-N ha^{-1}. However, when ammonia background values were determined using the contaminated chamber system that was also used to measure on plots with liquid manure application, the calculation of cumulative ammonia losses indicated approximately 3 kg NH_3-N ha^{-1}. Based on these results, it can be concluded that a new empirical DTM calibration is needed for multi-plot field experiments with high-emitting treatments.

Keywords: Ammonia background concentration; chamber system contamination; multi-plot field trials

1. Introduction

Nitrogen contained in liquid manure is an essential plant nutrient (*Sutton* et al., 2011b). However, ammonium (NH_4^+) can be easily converted to gaseous ammonia (NH_3) following liquid manure application (*Sommer* et al., 2003). The emitted NH_3 is either deposited locally or transported over long distances, where it increases airborne deposition of reactive nitrogen (*Asman* et al., 1998; *Ni* et al., 2015; *Sutton* et al., 2011b). Besides detrimental effects on human health (*Lelieveld* et al., 2015; *van Damme* et al., 2018) and nonagrarian ecosystems (*Emmerling* et al., 2020), the nitrogen use efficiency of the applied liquid manure is also reduced (*Liu* et al., 2022). Thus, abatement of NH_3 emissions following liquid manure application is a priority for many countries worldwide (*Webb* et al., 2005; *Webb* et al., 2010). For example, the European Union defined limits for maximum NH_3 emissions (*European Environment Agency*, 2016), forcing member states to reduce emissions. Hence, optimized techniques to apply liquid manures are mandatory. However, to assess the effects of different application techniques, NH_3 emissions need to be quantified in multi-plot field trials (*Pacholski*, 2016). Standard micrometeorological methods such as the integrated horizontal flux method (*Leuning* et al., 1985; *Sherlock* et al., 1989) or wind tunnels (*Sommer* and *Misselbrook*, 2016) for quantifying NH_3

emissions require large experimental plots, expensive equipment, or an in-field electric power supply (*Pacholski*, 2016). Thus, applying standard methods in multi-plot field trials is hardly possible (*Roelcke* et al., 2002).

An alternative, which might be feasible for multi-plot field trials, is the dynamic tube method (DTM). Originally the DTM was developed for evaluating CO_2 formation in soils (*Richter*, 1972), and later, it was adapted for assessing NH_3 fluxes following nitrogen fertilization (*Roelcke*, 1994; *Roelcke* et al., 2002). This original setup did not consider wind speed effects on NH_3 emissions. Therefore, DTM NH_3 "raw fluxes" were calibrated with the so-called "Integrated Horizontal Flux" method, taking into consideration the wind speed at the time of measurement (*Pacholski*, 2016; *Pacholski* et al., 2006; *Pacholski* et al., 2008). Nowadays, the wind speed corrected DTM is used in combination with so-called "passive samplers" (i.e., plastic bottles with small openings for air exchange that are filled with an acid solution(*Gericke* et al., 2011; *Vandré* and *Kaupenjohann*, 1998). These acid traps are placed in each plot of a field experiment to collect NH_3 to assess relative differences between plots, while the wind speed corrected DTM is used on a few selected plots to scale those relative differences (*Pacholski*, 2016). This approach was used in a wide range of experiments in Germany (*Ni* et al., 2015; *Ni* et al., 2014; *Nyameasem* et al., 2022; *Quakernack* et al., 2012; *Seidel* et al., 2017; *ten Huf* et al., 2023) and Denmark (*Wagner* et al., 2021).

For DTM measurements, a stainless steel chamber system, including four individual circular chambers with 11.5 cm diameter and small openings for air exchange, is placed on the soil surface where N fertilizer was applied (*Pacholski*, 2016; *Pacholski* et al., 2006). Tubings connect the chambers with an automated pump. Before starting the measurement, 20 pump strokes are performed in 90 s to flush the volume of the chamber system while already placed on the soil surface where the measurement is planned. This procedure is assumed to ensure a "steady" NH_3 concentration when the measurement is carried out. Subsequently, an NH_3 detector tube is inserted, which displays the NH_3 concentration after a defined number of pump strokes by the color change in a reactant, reaching one of the calibration marks on the transparent glass tube. If no mark is reached after performing the specified number of pump strokes, the measurement is continued. Depending on the expected NH_3 concentration, different detector tubes with a varying default number of strokes are used. Different numbers of pump strokes are taken into consideration by linear conversion to the default number of strokes of the respective detector tube (*Pacholski*, 2016).

Between measurements, the chamber system is cleaned with paper towels and flushed with ambient air to minimize contamination with NH_3 (*Pacholski*, 2016). When measurements are conducted under field conditions, the NH_3 concentration of unfertilized plots is considered as background and subtracted from the concentration measured in fertilized plots (*Pacholski*, 2016; *Roelcke* et al., 2002). This background-adjusted NH_3 concentration is then used to calculate NH_3-N raw fluxes. Subsequently, the raw flux is adjusted for the wind speed at the time of measurement by an empirical formula since the wind would affect actual in-field NH_3 emissions (*Freney* et al., 1983; *Sommer*, 2000), but the chamber system inhibits those effects (*Pacholski* et al., 2006). Two empirical formulas were developed for different canopy heights (*Pacholski* et al., 2006). Finally, NH_3 emissions are cumulated by linear interpolation of wind speed-adjusted fluxes between measurements.

The overall aim of this study was to propose an improved approach to use the DTM. Therefore, we formulated several subordinate objectives. The first was to determine whether the NH_3 concentration remains stable during the actual measurement period to allow the comparison of deviating numbers of pump strokes and/or the use of different detector tubes. The second objective was to evaluate the on-site cleaning procedure with paper towels and the flushing of the chamber system with ambient air. Possible NH_3 carryover could affect both the measured NH_3 concentration in the treated plots and in the unfertilized control, which is considered as background. Finally, we examined how different ways of accounting for background NH_3 levels affect the calculated values for cumulative NH_3 emissions.

2. Materials and Methods

2.1. Constancy of the NH_3 concentration within the chamber system

In a laboratory experiment (Figure 1), we filled four squared aluminum trays (12 × 12 cm) with 25 mL pig slurry and 25 mL distilled water so that the bottom of those trays was completely covered. The slurry NH_4-N content was 1.4 kg m^3, the pH was 8.4, and it contained 1.3% dry matter. The temperature in the laboratory was set to 13.5 °C. Sixty minutes after preparing the trays, the background NH_3 concentration within the laboratory was checked using a 0.25a detector tube (Drägerwerk AG, Lübeck, Germany; Table 1) with a detection range of 0.25–3 ppm. Subsequently, each of the four chambers of the DTM measuring system was placed into one of the four aluminum trays, a 5a detector tube (Drägerwerk AG, Lübeck, Germany; Table 1) was inserted, and a measurement was started (Figure 1). After performing the default number of strokes (in case no calibration mark was reached, the measurement was continued), the NH_3 concentration was noted, a new 5a detector tube was inserted, and the next measurement was started immediately. Overall, ten consecutive measurements were carried out, and the NH_3 concentration, as well as the required pump strokes of each measurement, were noted.

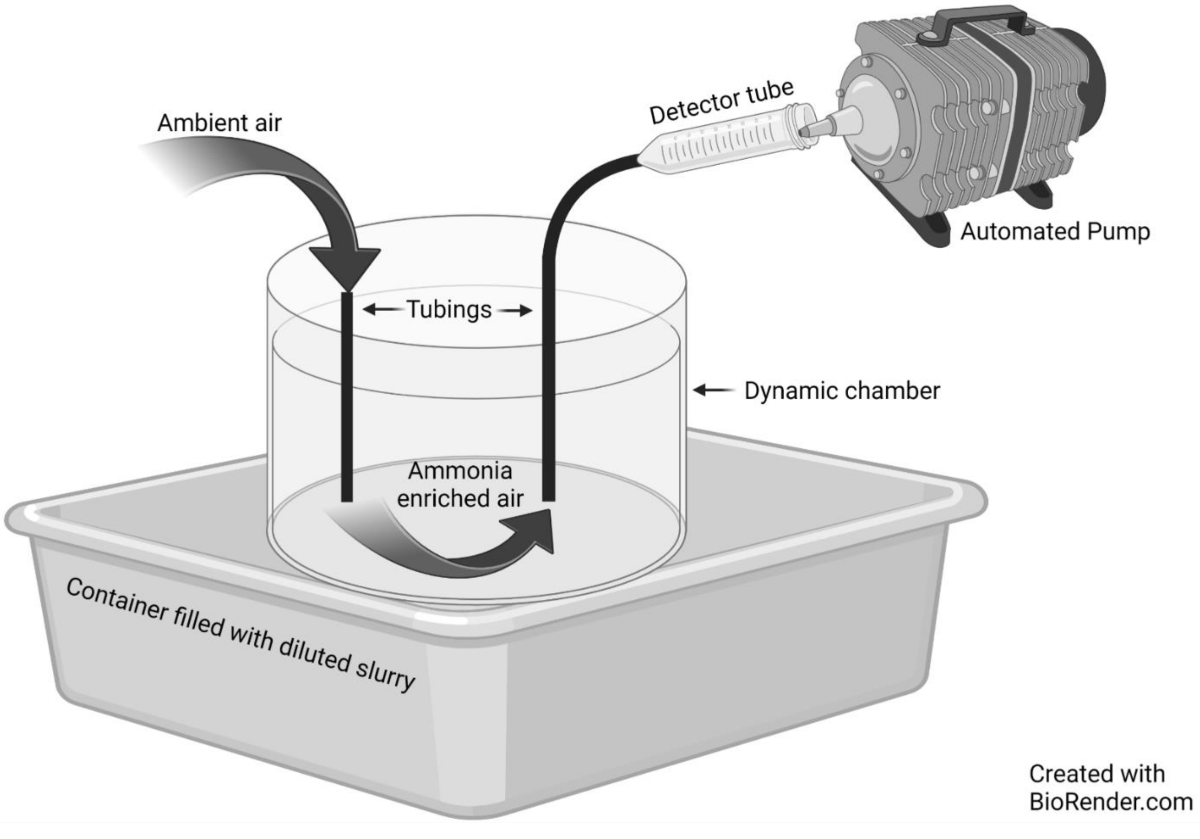

Figure 1. Schematic illustration of the laboratory experiment (only one of the four chambers within the four slurry-filled containers is displayed).

Table 1. Ammonia detector tubes (Drägerwerk AG, Lübeck, Germany).

Detector Tube	Detection Range (ppm)	Default Stroke Number	Time per Stroke (s)
0.25a	0.25–3	10	4.5
2a	2–30	5	6.5
5a	5–70	10	4.5

2.2. Assessment of the in-field chamber system cleaning procedure

On 23 June 2020, we conducted a grassland experiment on a farm close to Osnabrück in northwest Germany. The experiment included four different slurry application techniques and unfertilized control plots in a randomized block design with four replicates. More detailed information on that grassland experiment (site Osnabrück 2020) is published in Nyameasem et al. (2022). Immediately after slurry application, the chamber system was placed on the slurry-covered soil surface, and a DTM measurement was performed. After each measurement, the chamber system was thoroughly cleaned with paper towels and flushed with ambient air as described by Pacholski *(2016)* and subsequently moved to another plot to carry out the next measurement. Within the next 100 min, all 16 plots with slurry application were measured once. The final measurement in this series indicated an NH_3 concentration of 10 ppm within the chamber system. Thirty minutes after measuring the last plot with slurry application, we started a series of eight consecutive measurements on unfertilized control plots using this contaminated chamber system (CCS). The control plots were measured in blockwise order, and we performed two measurement cycles so that each of the four control plots was measured twice. Immediately before and directly after these eight measurements, a so-called "uncontaminated chamber system" (UCC; i.e., not used for previous measurements on fertilized plots) was also used to measure the NH_3 concentrations in unfertilized control plots.

2.3. Winter wheat field trial to estimate the influence of ubiquitous NH_3 concentration and chamber system contamination

Further tests were conducted in a winter wheat (*Triticum aestivum* L.) field trial carried out close to Osnabrück in Lower Saxony between 28 April and 2 May 2020 on a loamy soil (41% sand, 51% silt, and 8% clay; pH 6.1). During this 5-day period, air temperature (11.1 °C on average at 1 m height), wind speed (1.5 m s^{-1} on average at 2 m height), and rainfall (total 12.8 mm) were detected by a nearby weather station. Slurry and acidified slurry were applied by trailing hose technique using a custom-made slurry spreader based on an applicator system from Samson Agro A/S (Viborg, Denmark). Distance between slurry bands was 25 cm. Overall, 26.6 m^3 slurry ha^{-1} with an NH_4-N content of 2.3 kg m^3 was applied, leading to an NH_4-N application rate of 61 kg ha^{-1}. The slurry dry matter content was 8.0%, and the slurry pH was 7.8 for the nontreated slurry and 6.1 for the acidified slurry. Acidification was performed by adding sulfuric acid to a 1-m^3 tank filled with slurry until the target pH was reached while the substrate was thoroughly mixed. Additional control plots without N fertilization were also implemented to assess the background NH_3 concentration. All treatments were setup in a randomized block design with four replicates. The plot size was 9 × 9 m, and additional unfertilized interspaces of 9 m minimized cross-contamination by NH_3 drift between individual plots.

DTM measurements started immediately after slurry application in each individual plot using an NH_3-sensitive detector tube adapted to the expected concentration (Table 1). For treatments with slurry application, the chamber system was centered on the slurry bands, covering 11.5 cm of the 25 cm distance between two slurry bands. Therefore, we adjusted the raw flux calculation (Equation (1)) by applying the factor 0.46. To calculate NH_3 emission rates, we applied the formula for wind speed correction developed by Pacholski *(2016)* for low canopy height (Equation (2)). On the first day, we performed five measurements per plot; on the second day, we carried out two measurement cycles and during the remainder of the 5-day measurement period, only one measurement cycle was carried out each day. We used two separate chamber systems, i.e., one chamber system was used on all plots ("contaminated chamber system" [CCS]), whereas the second chamber system was used exclusively on unfertilized control plots ("uncontaminated chamber system" [UCS]).

Equation (1)—raw flux calculation according to Pacholski et al. (2006):

$$F_{Ng} = vol. * conc * \frac{1013(\mathrm{hPa})}{pact} * \left(\frac{696.1\left(\frac{\mathrm{mg}}{\mathrm{L}}\right) * 298.15\mathrm{K}}{(273.15 + Tact)\mathrm{K}}\right) * 10^{-6} * \frac{14\left(\frac{\mathrm{g}}{\mathrm{mol}}\right)}{17\left(\frac{\mathrm{g}}{\mathrm{mol}}\right)} * \frac{10000(\mathrm{cm}^2/\mathrm{m}^2)}{415(\mathrm{cm}^2)} * \frac{3600\left(\frac{\mathrm{s}}{\mathrm{h}}\right)}{dur(\mathrm{s})} \quad (1)$$

where F_{Ng} = ammonia flux (mg N m^{-2} h^{-1}), *vol.* ^{1} = volume of air passed through the system (l), *conc* ^{1} = detector tube reading minus background concentration (ppm). The background concentration is defined as the detector tube reading on unfertilized control plots. Measurements in treated and control plots should be closely related in space and time; *pact* = actual air pressure (hPa), *Tact* = air temperature at measurement (°C), 14/17 = conversion from NH_3 to N by their atomic weight, 415 = area covered by chambers (cm^2), *dur* ^{1} = duration of measurement (s), and ^{1} = by linear conversion related to the default stroke number of the detector tube used.

Equation (2)—wind speed correction for low canopy height according to *Pacholski* et al. (2006):

$$\ln(absolute\ flux) = 0.444 * \ln(raw\ flux) + 0.59 * \ln(V_{wind)}) \quad (2)$$

where *absolute flux* = ammonia flux (kg N ha^{-1} h^{-1}), *raw flux* = ammonia flux (kg N ha^{-1} h^{-1}) calculated by Equation (1), and V_{wind} = wind speed (m s^{-1}) at 2 m height during the measurement.

2.4. Data analyses

For assessing the constancy of the NH_3 concentration within the chamber system, we plotted the cumulative number of strokes on the x-axis and the measured NH_3 concentration on the y-axis. For calculating the regression function, we used natural logarithmic transformation. Subsequently, we calculated the coefficient of determination (R^2) and the significance of the slope using IBM SPSS statistics 28.

To evaluate the in-field chamber system cleaning procedure, we plotted the time after measuring on high emission plots on the x-axis and the measured NH_3 concentration on the y-axis. For calculating the regression function, we used exponential transformation, and subsequently, the R^2 value and significance of the slope were calculated using IBM SPSS statistics 28.

The influence of ubiquitous NH_3 concentration and chamber system contamination was evaluated by plotting the hours after slurry application on the x-axis and treatment mean NH_3 concentrations on the y-axis. For the unfertilized control, we present treatment mean values measured by the UCS as well as treatment mean values measured by the CCS. We used logarithmic transformation of the x-axis since the majority of emissions occurred within the first eight hours of the five-day experiment.

1. No background subtraction regarding the raw flux calculation;
2. Background subtraction based on UCS data to estimate the influence of the ubiquitous NH_3 concentration;
3. Background subtraction based on CCS data.

Subsequent to raw flux calculation (Equation (1)), the formula for wind speed correction (Equation (2)) was applied, and emissions were cumulated by linear interpolation for all three approaches.

3. Results

3.1 Constancy of the NH_3 concentration within the chamber system

Prior to the start of the experiment, the background NH_3 concentration in the laboratory was 0.25 ppm. After performing 16 strokes with a 5a detector tube inserted while the chamber system was placed on the aluminum trays filled with slurry, the measured NH_3 concentration was 3.1 ppm (Figure 2). For 20 strokes, corresponding to the premeasurement phase to establish a constant NH_3 concentration in the chamber system [12], we calculated a concentration of 6.3 ppm. After 30 strokes (i.e., detector tube reading on the field), the NH_3 concertation increased to 10.2 ppm. Thereafter, the concentration in the chamber system continued to increase until a concentration of 23.1 ppm was reached at 111 strokes. No further increase in concentration was detected thereafter.

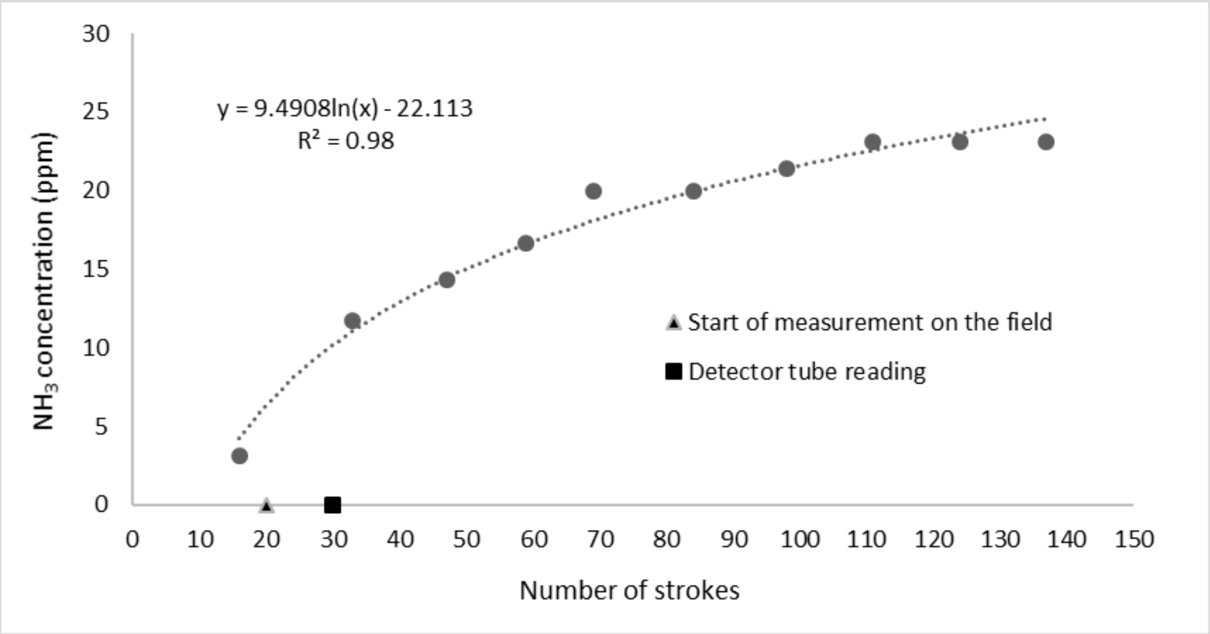

Figure 2. Increase in the NH_3 concentration in the chamber system following ongoing measurements on a surface covered with pig slurry. The slope of the equation is highly significant ($p < 0.001$). R^2 = coefficient of determination, ln = natural logarithm.

3.2 Assessment of the in-field chamber system cleaning procedure

The first measurement on the unfertilized control indicated an NH_3 concentration of 2 ppm, while for the second measurement, the concentration decreased to 1.33 ppm (Figure 3). Thereafter, the decrease in the NH_3 concentration in the chamber system slowed down and leveled off at the seventh consecutive measurement (0.5 ppm). Approximately one hour after measuring the last plot with slurry application, we performed the eighth measurement on the unfertilized control, where the NH_3 concentration was still 0.5 ppm. No NH_3 was detected during simultaneous measurements with a chamber system not used for previous measurements on plots with slurry application (Figure 3).

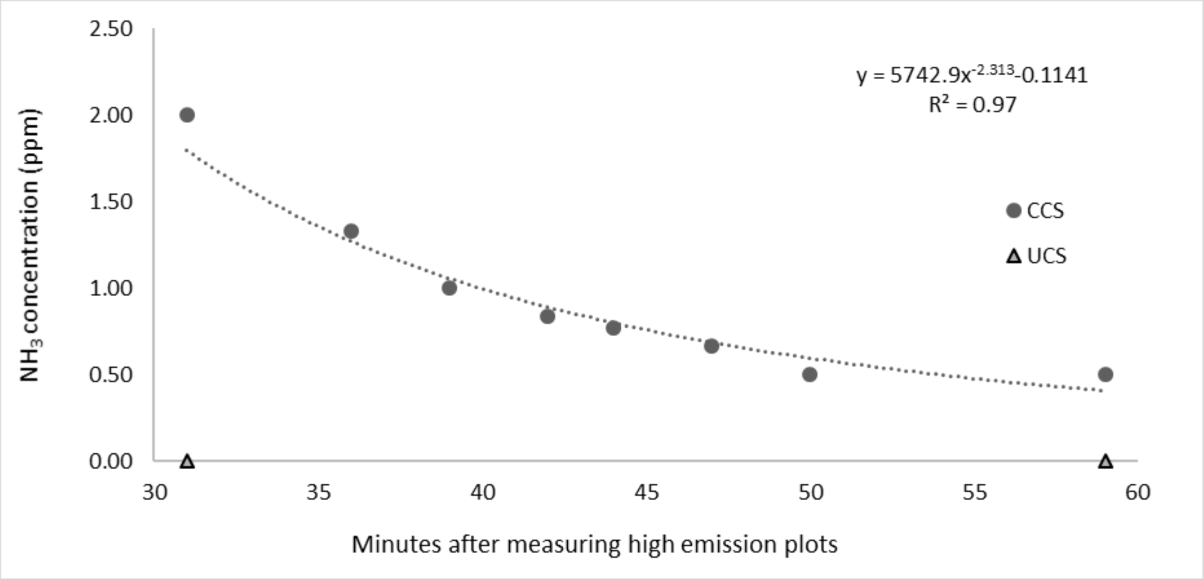

Figure 3. Decrease in the NH_3 concentration within a contaminated chamber system induced by consecutive measurements on unfertilized plots. The slope of the equation is highly significant (p < 0.001); R^2 = coefficient of determination, CCS = contaminated chamber system, and UCS = uncontaminated chamber system.

3.3 Influence of ubiquitous NH_3 concentration and chamber system contamination

Figure 4 shows the NH_3 concentration within the chamber system for two treatments with slurry application and for unfertilized control plots in a winter wheat field experiment. Two separate chamber systems were used for the measurements on the control plots. One chamber system was exclusively used for control plots (UCS), whereas the other was also used for plots with slurry application (CCS). Within the first four hours after application, the NH_3 concentration measured for trailing hose application of slurry increased to approximately 11.2 ppm, while for trailing hose application of acidified slurry, the NH_3 concentration reached only 5.3 ppm (Figure 4). Four hours after the start of the experiment, the CCS indicated an NH_3 concentration of 3.9 ppm for the control plots, while the UCS did not indicate any NH_3. Within eight hours after application, the NH_3 concentration in the trailing hose treatment without acidification decreased to approximately 2 ppm. For the trailing hose treatment with acidification and the control treatment measured by the CCS, the NH_3 concentration was approximately 1.5 ppm. The NH_3 concentration in the control measured by the UCS increased to 0.5 ppm. Thereafter, the NH_3 concentration gradually decreased until no NH_3 was measured 72 h after the slurry application started. Plots with slurry application and control plots measured with the CCS exhibited a similar pattern for the period 24 to 96 h after application: 24 h after application, the concentration was approximately 0.5 ppm, and thereafter, it declined to 0.1 ppm 96 h after application.

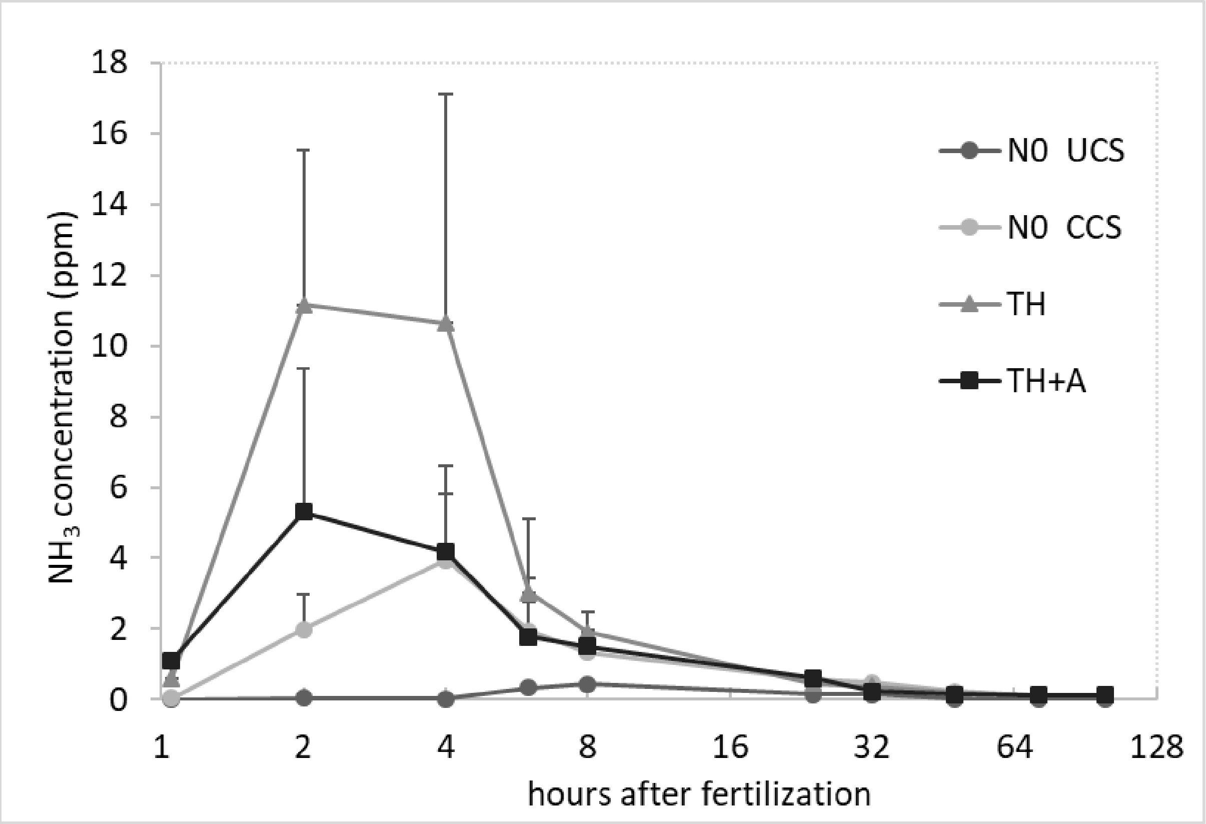

Figure 4. Mean NH$_3$ concentrations within the chamber system for different treatments and unfertilized control plots following slurry application in a winter wheat field experiment. Logarithmic transformation of the x-axis was used to highlight the first day after application when the NH$_3$ concentration was highest. Error bars represent the standard deviation (to minimize overlapping, only the positive standard deviation is shown). N0 UCS = control plots without slurry application measured with an uncontaminated chamber system exclusively used for measuring control plots, N0 CCS = control plots without slurry application measured with a contaminated chamber system also used for measuring plots with slurry application, TH = trailing hose application of slurry, and TH+A = trailing hose application of acidified slurry.

Figure 5 shows cumulated NH$_3$ emissions for two treatments with slurry application for the 5-day measuring period in the winter wheat field experiment. We used three different approaches for calculating cumulative NH$_3$ emissions: (1) no background subtraction, (2) background subtraction based on UCS data, and (3) background subtraction based on CCS data. When applying no background subtraction, NH$_3$-N emissions sum up to 9.7 kg ha^{-1} following slurry application by trailing hose. Background subtraction based on UCS data resulted in NH$_3$-N emissions of 8.8 kg ha^{-1}, and when background subtraction was based on CCS data, we calculated NH$_3$-N emissions of only 3.0 kg ha^{-1}. Slightly lower emissions were found for the trailing hose treatment with slurry acidification for these three approaches. The standard deviation of the four replicates for the approaches "no background subtraction" and "background subtraction based on UCS data" overlaps for both treatments with slurry application. However, when looking at individual plots, "no background subtraction" always leads to higher NH$_3$-N emissions than "background subtraction based on UCS data".

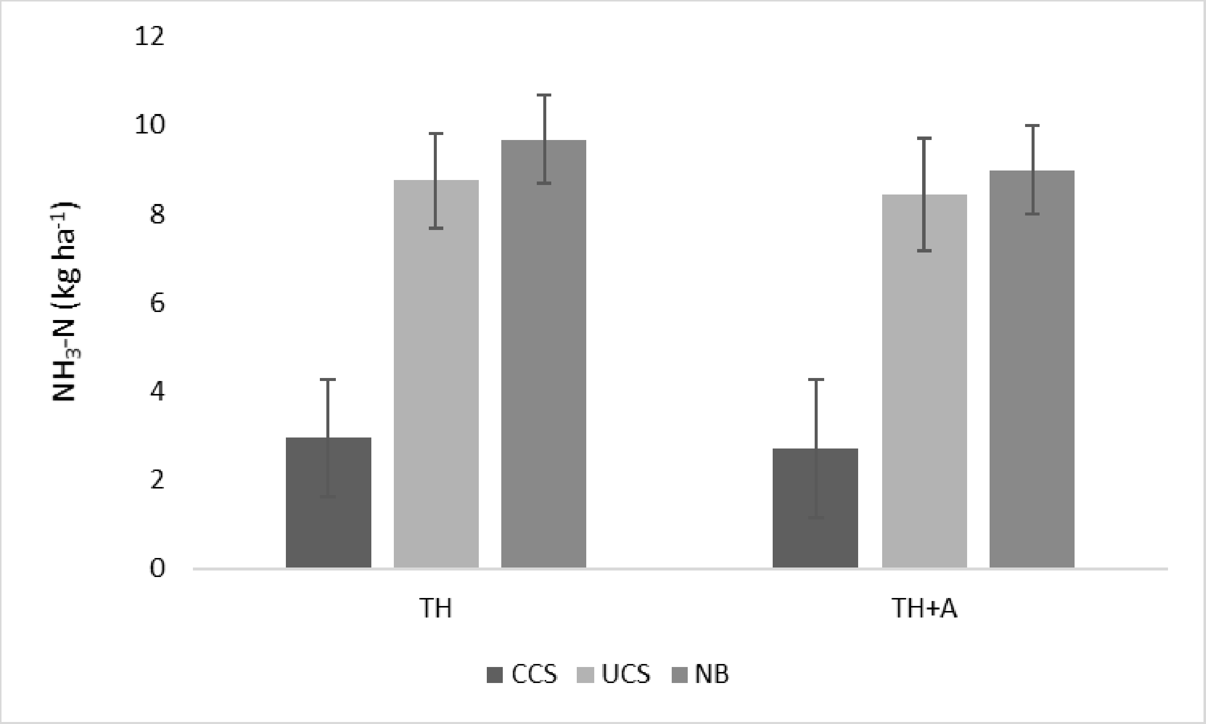

Figure 5. Cumulated NH_3 emissions for three approaches to subtract background values for calculating NH_3 emissions following two slurry application techniques in a winter wheat field experiment. The error bars represent the standard deviation. TH = trailing hose application of slurry, TH+A = trailing hose application of acidified slurry, CCS= background subtraction based on data obtained from a contaminated chamber system also used for measuring plots with slurry application, UCS= background subtraction based on data obtained from an uncontaminated chamber exclusively used for measuring unfertilized control plots, NB = no background subtraction applied.

4. Discussion

4.1 Constancy of the NH_3 concentration within the chamber system

For the laboratory test, the relevant experimental conditions (i.e., temperature and NH_3 concentration) were chosen to be comparable to conditions typical for a field experiment on the first day after slurry application. Obviously, the NH_3 concentration in the chamber system is not stable after performing 20 pump strokes (Figure 2). Different detector tubes with varying standard stroke numbers can be used for the DTM, and if no calibration mark is reached after performing the standard stroke number of the respective detector tube, the measurement should be extended (*Pacholski*, 2016). However, that means that linear conversion between the alternating number of pump strokes as required for Equation 1 (*Pacholski* et al., 2006; *Roelcke* et al., 2002) is problematic since the NH_3 concentration within the chamber system is not stable. Furthermore, changing the number of initial pump strokes prior to the actual measurement would affect raw flux calculation and the subsequent result of the empirical wind speed correction. Therefore, the “raw flux” (*Pacholski* et al., 2006; *Roelcke* et al., 2002) cannot be regarded as a flux and should be viewed as an empirical factor based on the NH_3 concentration within the chamber system.

4.2 Assessment of the in-field chamber system cleaning procedure

Our data (Figure 3) revealed that the in-field cleaning procedure is not sufficient to reduce chamber system contamination. Cleaning by using paper towels removes dirt sticking to the chamber system but might not affect NH_3 retained at chamber walls or tubings or solved in condensed water anywhere in the system. Flushing by ambient air addresses this problem, but it might take too long to reduce contamination under field conditions. Thirty minutes after measuring on high emission plots, the NH_3

concentration in the CCS was still as high as 2 ppm, while simultaneous measurements with a UCS did not indicate any NH_3. Even one hour after measuring on high emission plots, the concentration was still 0.5 ppm. In that period, eight consecutive measurements were performed so that the chamber system was constantly flushed with ambient air. The inadequacy of the cleaning procedure for the chamber system under field conditions means that the calculation of NH_3 emissions is affected by ubiquitous NH_3 but also by chamber system contamination.

4.3 Influence of ubiquitous NH_3 concentration and chamber system contamination

In our multi-plot field trial, the NH_3 background in the control plots was much more influenced by chamber system contamination than by ubiquitous NH_3. Measurements with the UCS did not result in NH_3 concentrations above 0.5 ppm, whereas for the CCS concentrations, up to 3.9 ppm in unfertilized control plots on the day of slurry application were detected (Figure 4). Obviously, in fertilized plots, the chamber system was contaminated with similar amounts of residual NH_3 from previous measurements. Moreover, the background value within the chamber system might vary depending on the emissions in the previously measured plot. This might explain the high standard deviation on the day of slurry application (Figure 4).

Furthermore, the so-called background NH_3 concentration required for the calculations according to Equation (1) (*Pacholski*, 2016; *Pacholski* et al., 2006; *Roelcke* et al., 2002) is not exactly specified. We showed that cumulated NH_3 emissions differ depending on its definition (Figure 5). When background subtraction was solely based on the ubiquitous NH_3 concentration measured by a UCS, cumulated NH_3 emissions were approximately threefold higher compared to calculations using background values measured with a CCS. Furthermore, it needs to be considered that the NH_3 background of the chamber system and actual NH_3 emissions caused by fertilization might not be additive (i.e., the NH_3 concentration measured in a treated plot increases by the amount of the NH_3 background concentration). The laboratory experiment (Figure 2) revealed that after 30 strokes, corresponding to the timing of reading the detector tube in the field, the NH_3 concentration was 10.2 ppm. The measured background was 0.25 ppm leading to a background-adjusted concentration according to the recommendations from Pacholski et al. (2006) of 9.95 ppm. However, when considering the NH_3 concentration after 30 strokes (10.2 ppm) as background for the measurement after 60 strokes (16.7 ppm), the value of the background adjusted NH_3 concentration would only be 6.5 ppm. This illustrates that, at least for very high chamber system NH_3 concentrations, background and emissions caused by fertilization are not additive. Thus, simply subtracting background values is problematic.

It has to be kept in mind that DTM raw flux calibration was performed in only two fertilized plots and one unfertilized area (*Pacholski* et al., 2006), so the relevance of chamber system contamination was probably much lower than in our multi-plot field experiment (Figure 4). Currently, the DTM is frequently used to quantify relative differences in NH_3 emission between treatments (e.g., different techniques for slurry application) as determined by acid traps placed in the center of each plot (*Pacholski*, 2016; *Gericke* et al., 2011). For this purpose, DTM measurements are only performed in one or a few selected plots so that the conditions are closer to the initial calibration setup. When applied with great care regarding chamber system contamination, this approach might still be the best alternative for estimating NH_3 emissions in multi-plot field trials. To reduce the risk of nonrepresentative background values due to chamber system contamination, we suggest using at least two chamber systems. One chamber system is used for treated plots as well as for control plots, whereas another chamber system measures exclusively on control plots to determine the ubiquitous NH_3 concentration. Subsequently, the results of both chamber systems are compared. If a discrepancy between the chamber systems occurs regarding the measurement on the control plots, the chamber system used for treated plots should be thoroughly cleaned, or another chamber system should be used.

5. Conclusions

Our objective was to test important prerequisites and boundary conditions for the application of the DTM technique in order to propose an improved approach. We showed that (1) the NH_3 concentration in the chamber is not stable and that (2) the cleaning procedure with paper towels and flushing with ambient air is not sufficient under field conditions. Therefore, NH_3 carryover affects the measurements in both the treated plots and the unfertilized control plots. This affects the calculation of NH_3 emissions.

Ultimately, the DTM approach requires a new empirical calibration that considers these problems. Instead of using analog detector tubes with calibration marks, the use of a digital NH_3 detector would allow for performing measurements after exchanging a specified air volume in a specified time. Furthermore, we advise using separate chamber systems for each individual plot so that cross-contamination is prevented. Overall, the new empirical model should be based on the factors (1) NH_3 concentration measured in the fertilized plot, (2) NH_3 concentration measured in a control plot using the CCS as well as (3) a UCS and (4) wind speed. For the current empirical model, the wind speed at the time of measurement is used. However, the wind speed at the time of measurement is then used to extrapolate emissions until the next measurement is performed. Therefore, we suggest including the average wind speed between the two measurements in the new model.

Moreover, it has to be considered that contamination might not only affect DTM measurements. It might be a common problem for all chamber systems and wind tunnels since NH_3 is highly reactive and readily soluble in water, which makes it likely to be retained anywhere in those systems (*Denmead*, 1983). Therefore, we suggest that all systems currently used to estimate NH_3 emissions should be tested for contamination. Otherwise, it needs to be considered that NH_3 emissions, estimated by those systems, are not only caused by the effect(s) of interest (e.g. N fertilization) but also by the system's specific NH_3 release after it was initially exposed to an NH_3 source.

Paper 3: Effects of liquid manure application techniques on ammonia emission and winter wheat yield

Agronomy (2023), Volume 13, 472

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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

1. Introduction

Due to the growing human population, it is expected that animal husbandry will be doubled within this century (*Emmerling* et al., 2020; *Petersen* and *Sommer*, 2011) leading to increased ammonia (NH_3) emissions at the different stages of the manure management chain (*Aneja* et al., 2020). Besides animal housing and manure storage, spreading of liquid organic fertilizers is an important NH_3 emission pathway (*Emmerling* et al., 2020; *Erisman* et al., 2008; *Wulf* et al., 2002) . Ammonia emissions lead to the formation of particulate matter, which affects air quality and impairs human health (*Bauer* et al., 2016; *Lelieveld* et al., 2015; *van Damme* et al., 2018). Furthermore, NH_3 contributes to climate change (*Shindell* et al., 2009), 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 (*Arp* and *Stein*, 2003; *Ruser* and *Schulz*, 2015; *Saggar* et al., 2013). Acidification as well as eutrophication are additional problems associated with NH_3 emissions, especially when emitted NH_3 enters non-agricultural ecosystems (*Bobbink* et al., 2010; *Galloway* et al., 2003; *Hertel* et al., 2013; *van Damme* et al., 2018). 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 (*European Environment Agency*, 2016). Thus, the development of improved application techniques for liquid manures is mandatory (*Webb* et al., 2005; *Webb* et al., 2010). Digestate from anaerobic fermentation, which has become increasingly popular over the last three decades due to rising global energy consumption (*Herrmann* et al., 2017), is associated with a high risk of NH_3 emission because pH and NH_4-N levels increase during the digestion process (*Möller* and *Müller*, 2012), leading to increased NH_3 emissions (*Freney* et al., 1983).

Ammonia emissions are only one aspect worth consideration when applying liquid manures. Crop yield (*Chen* et al., 2018), nutrient leaching (*Eriksen* et al., 1999; *Huang* et al., 2017) and the emission of greenhouse gases (*Ruser* and *Schulz*, 2015) 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 (*DÜV*, 2020). 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 (*Webb* et al., 2010). 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 (*Fangueiro* et al., 2015) or on reducing the contact area of the applied organic fertilizer with the atmosphere. The application by trailing shoe (*Misselbrook* et al., 2002; *Sommer*, 2000) or direct injection into the soil (*Nyord* et al., 2008) 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 (*Ruser* and *Schulz*, 2015), as well as nitrate leaching (*Subbarao* et al., 2006). 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:

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

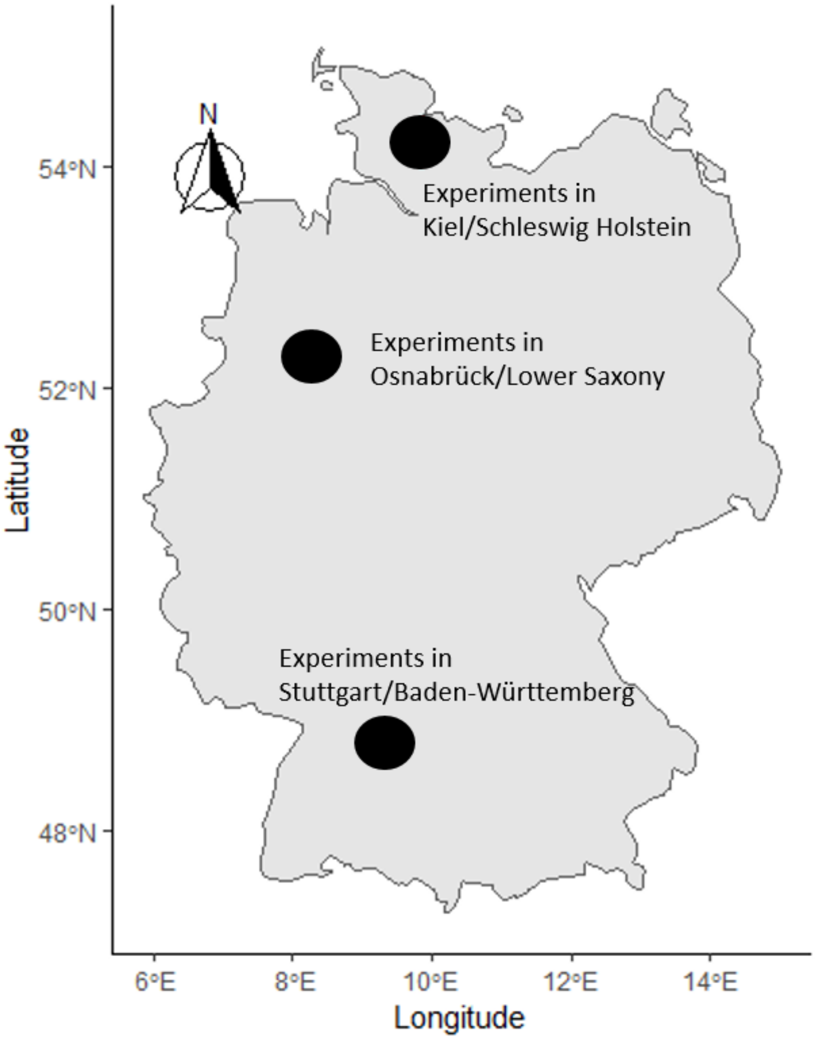

Figure 1. The three experimental regions across Germany.

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 (*DIN*, 1997) and soil texture analysis (*DIN*, 2018). Organic carbon and N content of the soil samples were analyzed by dry combustion (*Yeomans* and *Bremner*, 1991). 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 (*WRB*, 2015). Table 1 shows the results from the initial soil analyses.

Table 1. Soil characteristics and weather conditions.

		Soil Characteristics									Weather Conditions	
Site	**Year**	**Soil Type**	**Sand**	**Silt**	**Clay**	**pH**	**Bulk Density**	**CEC**	**C_{org}**	**N_{total}**	**Precip.**	**Temp.**
			%	%	%		g cm^{-3}	mmolc kg^{-1}	g kg^{-1}	g kg^{-1}	mm	°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.

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 (*DÜV*, 2020), 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). 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).

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**				
		Precip.	**Temp.**	**Wind**	**NH_4-N**	**DM**	**pH**	**pH Acid**	**Acid**	**NH_4-N**	**DM**	**pH**	**pH Acid**	**Acid**
Site	**App.**	**mm**	**°C**	**ms^{-1}**	**kg ha^{-1}**	**%**			**l m^{-3}**	**kg ha^{-1}**	**%**			**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.

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 (app. 1.) 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 (app. 1.) 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 (*Pacholski*, 2016).

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* (2016) 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)):

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

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. (2010):

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

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 (*Nyameasem* et al., 2022):

$$Mitigation\ potential\ (\%) = \frac{(mean\ NH_3\ in\ TH\ treatment) - (NH_3\ in\ treated\ plot)}{(mean\ NH_3\ in\ TH\ treatment)} * 100 \tag{3}$$

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 (*Freney* et al., 1983). 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 (*Nyord* et al., 2012), 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 (*Webb* et al., 2010). BD application by trailing hose led to significantly higher NH_3 emissions than CS application (Tab 4). 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 (*Möller* and *Müller*, 2012), which might explain the increased NH_3 emissions (*Freney* et al., 1983). 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 (*Sommer* et al., 2003) 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.

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	−0.20
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	−0.30	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.

NH_3 emissions following TH application varied between sites (Table 6; Table 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 (*Fangueiro* et al., 2015). 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 (*Emmerling* et al., 2020; *Fangueiro* et al., 2017). 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 (*Sommer* et al., 2003), 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).

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 (*Hales* and *Drewes*, 1979) leading to increased NH_3 emissions. Additionally, more water evaporates due to higher temperature, increasing the NH_3 concentration in the liquid phase (*Freney* et al., 1983). 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 (*Pacholski* et al., 2006), which decreases the NH_3 concentration in the air layer close to the applied organic fertilizer (*Freney* et al., 1983). 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 (*Freney* et al., 1983). 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 (*Pacholski* et al., 2006). Instead, the measured NH_3 emissions are adjusted for wind speed using an empirical formula (*Pacholski* et al., 2006). 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. (2004) 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				

				CS				BD			
Site	**App.**	**N0**	**CAN**	**TH**	**TH+A**	**SI/TS**	**SI+NI/TS**	**TH**	**TH+A**	**SI/TS**	**SI+NI/TS**
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.

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 (*Fangueiro* et al., 2015; *Kai* et al., 2008). 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).

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).

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.

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 (*Husted* et al., 1991; *Sommer* and *Hutchings*, 2001). 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 (*Toft* and *Madsen*, 2019) , acid is added immediately before soil application using a static mixer installed in the output line of the slurry tanker (*Fangueiro* et al., 2015). 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 (*Toft* and *Madsen*, 2019), 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. (2003) 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 (*Subbarao* et al., 2006), 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 (*Hafner* et al., 2018; *Søgaard* et al., 2002), 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 (*Huijsmans*, 2003), 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 (*Petersen* et al., 2003). 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 (*Freney* et al., 1983). 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 (*Misselbrook* et al., 2004). *Sanz-Cobena* et al. (2019) 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 (*Chadwick* et al., 2000). 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 (*Forrestal* et al., 2016; *Sommer* and *Jensen*, 1994; *Velthof* et al., 1990), 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.

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	**N Uptake Grain**	**N Uptake Total**	**aNUE Grain**	**aNUE Total**
	t ha^{-1}	**kg N ha^{-1}**	**kg N ha^{-1}**	**%**	**%**
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.

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. (2007) 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.

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 (*Nyord* et al., 2012). 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 (*Subbarao* et al., 2006), 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* (2012) 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 (*Gutser* et al., 2005). Therefore, the C:N ratio declines remarkably, decreasing the risk of bacterial N immobilization (*Boer*, 2008), which might explain the significantly improved yield, N uptake and aNUE (Table 8) in our experiments.

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.

4. Conclusion

Our results show that a reduction in 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.

Appendix

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

Table A1: 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.

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.

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.

Part 3

General Discussion

The overall aim of this study was to propose the best way to apply slurry and biogas digestate in growing winter wheat. The focus was on reducing NH_3 emissions, while simultaneously also assessing yield and N uptake. In order to evaluate optimized application techniques, NH_3 emissions were estimated using calibrated passive sampling. However, this thesis highlighted some problems when applying calibrated passive sampling. Those problems need to be considered for the evaluation of optimized strategies to apply liquid manure in growing winter wheat. Thus, the first part of this discussion deals with the evaluation of calibrated passive sampling and its constituent methods (dynamic tube method (DTM) and passive samplers) regarding the measurement of NH_3 emissions in multi plot field trials with liquid manure application. In the second part, optimized techniques to apply liquid manure were evaluated.

Ammonia emission measurement in multi plot field experiments with liquid manure application: Challenges and opportunities

Passive samplers

The main problem when using passive samplers for multi-plot field experiments is the determination of the NH_3 background (Paper 1; Section 3.2). Each plot might be affected differently (*Vandré* and *Kaupenjohann*, 1998). Thus, control plots without N fertilization are only an approximation for the background in fertilized plots. Therefore, cumulated emission values of each individual plot depend not only on the NH_3 emission of the respective plot, but also on its specific background. Hence, many replications are necessary to obtain valid treatment mean values and those means exhibit high standard deviations (Paper 1; Table 3). This made it difficult to obtain statistically significant differences of liquid manure application techniques in individual experiments (Paper 3; Table 6). However, there was no evidence that passive sampler results are generally biased. Therefore, they might be an easy way to compare treatment means. However, they are less suited to provide emission curves, since they collect NH_3-N over an extended period of time.

Dynamic tube method

Several problems occurred regarding the DTM measurements. The NH_3 concentration within the chamber system was not stable when taking a measurement (Paper 2; Figure 2). Different detector tubes are used for different NH_3 concentrations (Paper 2; Table 1) and measurements are prolonged when no calibration mark is reached after the default stroke number of the respective tube was performed. However, linear interpolation is used to account for alternating stroke numbers (*Pacholski*, 2016), which requires a stable concentration. Moreover, the biggest problem regarding the DTM is chamber system contamination, which affects background NH_3 levels. This background is not specified and might or might not include chamber system contamination, so that estimation of NH_3 emissions following liquid manure application might differ drastically depending on the approach chosen by the respective research group (Paper 1; Section 3.2). Unfortunately, it is not possible to clean the system adequately using paper towels under field conditions (Paper 2; Figure 3). This procedure removes dirt sticking to chamber walls, but might not affect NH_3 retained anywhere in the system (*Denmead*, 1983). Therefore, each measurement is influenced by previous measurements, affecting the calculation process to cumulate emissions (Paper 2, Figures 4 and 5). Furthermore, the formula for wind speed correction (*Pacholski* et al., 2006) in combination with chamber system contamination might lead to overestimated values when NH_3 emissions are low (Paper 1; Figure 2). The background in the chamber system might not be the same when measuring unfertilized control plots and treated plots. Thus, the background adjusted NH_3 concentration is sometimes numerically negative. Subsequently, the wind speed correction formula (Paper 2; Equation 2; *Pacholski* et al., 2006) sets those negative values to zero, which might lead to biased results for treatments with low emissions where those numerically negative values occur more often. Considering the importance of chamber system contamination, each plot should be measured by a separate chamber system and the background in the chamber system should be constantly checked on unfertilized control plots. Ultimately, the DTM requires a new calibration that accounts for the described problems. However, every empirical model that includes weather parameters (e.g. wind speed) faces the problem, that studies using this approach cannot analyze the effect of the respective parameter on NH_3 emissions. Unfortunately, it might be necessary to include several parameters. Wind for example might lead to surface cooling at days with intense radiation, which might even reduce emissions under those circumstances (*Sommer* et al., 2003). However, the chamber system might be less affected by surface cooling induced by high wind speed and a calibration solely based on the wind speed would not include this effect. Moreover, alternating weather conditions might also influence the potential for chamber system contamination.

Calibrated passive sampling

The problems regarding the DTM indicate that the calculated height of NH_3 emissions is somewhat speculative, while the relative difference between treatment means obtained by passive samplers seems to be valid. Therefore, passive samplers should be calibrated either by another method or by an adjusted DTM. However, when comparing relative values and treatment means scaled by DTM measurements in a treatment with high emission (cattle slurry application by trailing hose), results are comparable (Figure 1 and 2).

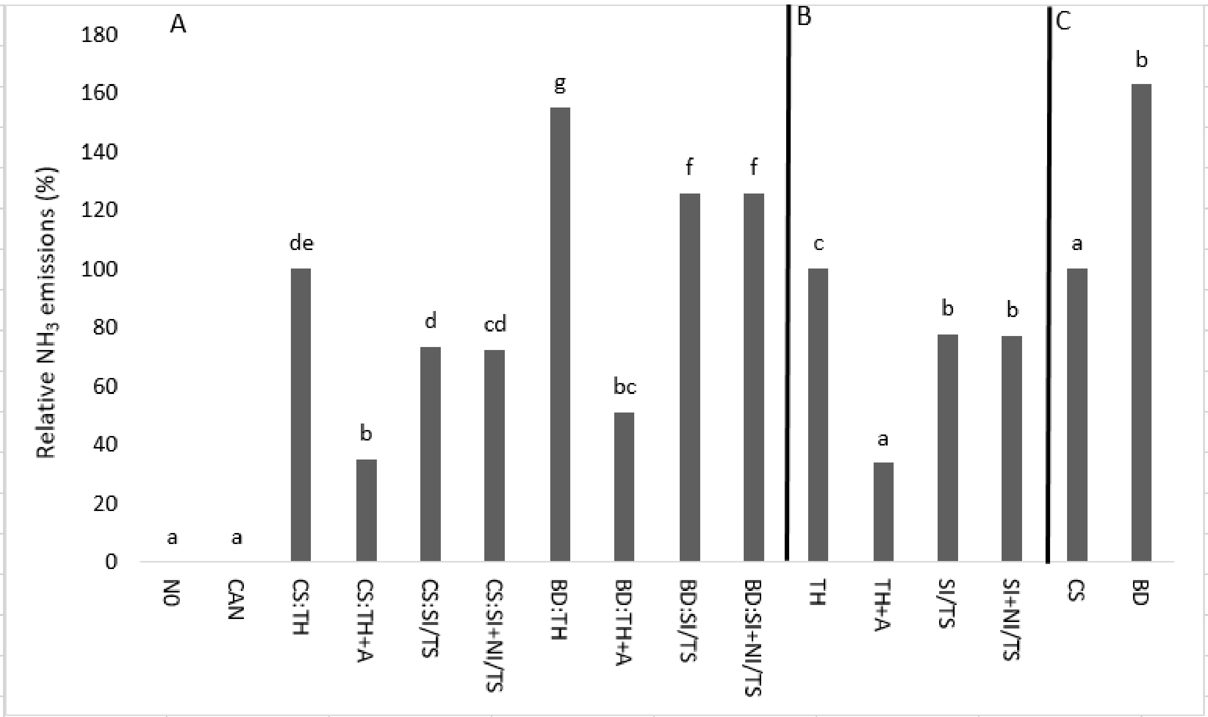

Figure 1: Relative NH_3 emissions across sites. A = Comparison of treatments (Paper 3; ANOVA model 1 in Table A1), B = Comparison of application techniques averaged by manure type (Paper 3; ANOVA model 2 in Table A1), C = Comparison of manure types averaged by application technique (Paper 3; ANOVA model 2 in Table A1). Different lower case letters indicate significant differences (Tuckey Test $p \leq 0.05$) between groups. CAN = Calcium ammonium nitrate, CS = Cattle slurry, BD = Biogas digestate, TH = Trailing hose, +A = Acidification, SI = Slot injection, TS = Trailing shoe, NI = Nitrification inhibitor.

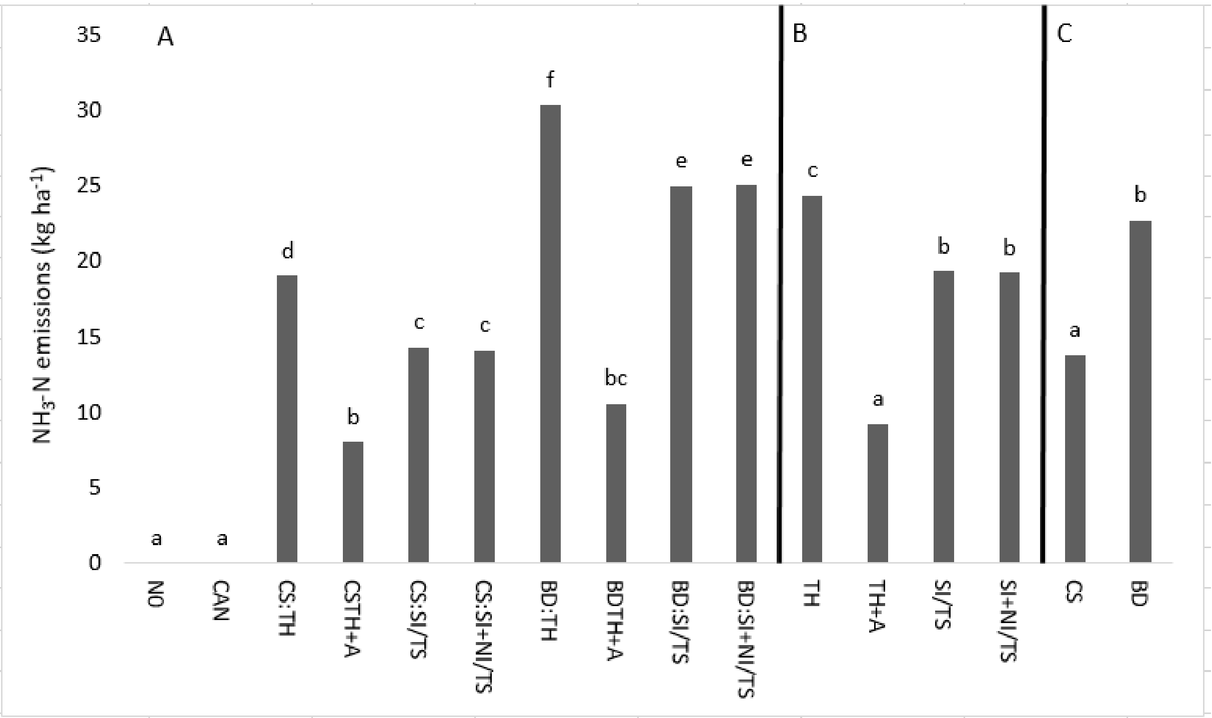

Figure 2: Qualitative NH_3 emissions across sites. A = Comparison of treatments, B = Comparison of application techniques averaged by manure type, B = Comparison of manure types averaged by application technique. Different lower case letters indicate significant differences (Tuckey Test $p \leq 0.05$) between groups. Data and statistics were obtained from Paper 3; Table 4. CAN = Calcium ammonium nitrate, CS = Cattle slurry, BD = Biogas digestate, TH = Trailing hose, +A = Acidification, SI = Slot injection, TS = Trailing shoe, NI = Nitrification inhibitor.

Furthermore, this thesis shows that regardless of the calibration method, one plot is not sufficient for scaling relative emissions obtained by passive samplers. Passive sampler results are scaled by a transfer coefficient (TC) obtained from simultaneous measurements by passive samplers and a qualitative method on plots with putatively high emissions (*Pacholski*, 2016). The TC is calculated based on dividing qualitative emissions by the amount of N collected by passive sampler. If the TC is only based on one plot (Paper 1; Equation 1), the effect of the fluctuating NH_3 background has an immense impact. Calculating the mean of several TCs obtained from individual plots, leads to a similar problem since outliers due to the fluctuating background might influence the mean disproportionally (Paper 1; Table 5). Therefore, the best way for deriving the TC is calculating mean values for qualitative method and passive samplers first and subsequently dividing qualitative mean by passive sampler mean (Paper 1; Equation 2). This procedure should reduce the influence of outliers. In summary, scaling of calibrated passive sampling should be performed by an adjusted DTM or another qualitative method based on mean values in a treatment with high NH_3 emissions. Moreover, broadcast fertilizer application in the treatment used for simultaneous measurements with passive samplers and qualitative method should be preferred. For this study, a factor (0.46; Paper 1; Supplement 1) was used to account for the band wise application. However, it was obtained from reasoning rather than experimental testing.

Ammonia measurements in future multi-plot field experiments

Future studies using chamber systems or wind tunnels to estimate NH_3 emissions should consider that NH_3 is highly reactive so that it might be retained anywhere in the system (*Denmead*, 1983). Thus, the potential for contamination should be carefully evaluated for all of those methods currently used to estimate NH_3 emissions, if the literature does not provide sufficient information. In order to do this, each system should be exposed to a NH_3 source similar to the source it would be exposed to under experimental conditions. Subsequently, the NH_3 source is removed and measurements are performed to evaluate the extent to which the system is contaminated. In case the system measures any NH_3 after the NH_3 source was removed, it needs to be considered that emissions calculated by that system are not only influenced by the effect of interest (e.g. N fertilization), but also by the system´s specific NH_3 release after it was initially exposed to a NH_3 source.

Besides of the factors analyzed in this thesis, other parameters might also influence NH_3 emissions and emission measurements in multi-plot field trials with liquid manure application. In those trials, the plot size is comparatively small and plots are surrounded by unfertilized interspaces to minimize cross-contamination between plots. Thus, the NH_3 concentration in the air layer close to the applied liquid manure is probably much lower than it would be under practical conditions where liquid manure is applied on large fields (*Sommer* et al., 2003). This might lead to an increased NH_3 concentration gradient between liquid manure and atmosphere which increases emissions (*Freney* et al., 1983). Moreover, in large fields some of the emitted NH_3 might be reemitted back into the same field, whereas in small plots, emitted NH_3 might leave the experimental area. Therefore, the potential impact of both effects needs to carefully evaluated in future studies. Otherwise, small plot experiments might systematically overestimate NH_3 emissions.

Another challenge is that liquid manure application using practice-oriented techniques is usually performed in treatment wise order, since it is very difficult to constantly modify those techniques. However, conditions might change over the course of the day, affecting emissions of treatments differently. Therefore, application in the early morning should be avoided, because it might increase the temperature gradient when applying liquid manure for different treatments. However, it is nonetheless difficult to equalize other parameters like precipitation or exposure to background NH_3. The treatment were liquid manure is applied first is exposed to all the background NH_3 originating from liquid manure application in other treatments, whereas treatments were liquid manure is applied later, are potentially exposed to less background NH_3.

Overall, many of the described problems (NH_3 drift between plots, scaling of NH_3 emissions derived from small-plot experiments, treatment wise order of application) can be addressed by reducing the number of treatments and increasing the plot size. Thus, future studies aiming to quantify NH_3 emissions should prioritize which treatments they want to include into their experimental set-up. Moreover, the role of the unfertilized interspaces between plots has to be carefully evaluated. On one hand, they minimize drift between plots. On the other hand, they occupy space, which could be used to increase the plot size and they might lead to an increased NH_3 concentration gradient between liquid manure and atmosphere.

Evaluation of techniques to apply liquid manure in growing winter wheat

For this evaluation, it needs to be considered that although relative differences between methods are valid, scaling of NH_3 emissions is somewhat speculative (Paper 2). The second point that has to be taken into account is that although NH_3 emissions differed distinctly between liquid manure application techniques (Paper 3; Table 4) so that putative N availability was higher in treatments with low NH_3 emissions, yield and N uptake where not significantly influenced by the liquid manure application technique (Paper 3; Table 8). This discrepancy might be explained by general overestimation of NH_3 emissions.

Another factor that requires consideration for the assessment of optimized techniques is which type of fertilizer is applied. Averaged by application technique, applying biogas digestate lead to approximately 60 % higher NH_3 emissions than employing cattle slurry (Paper 3; Table. 4). Therefore, the use of optimized techniques is especially important for biogas digestates. One possible explanation for the high emissions is that the digestion process increases pH and NH_4-N content (*Möller* and *Müller*, 2012). However, this increase must be considered in relation to pH and NH_4-N content of the source material. Only for the experiments in Osnabrück, the biogas digestate was based on the cattle slurry that was also applied in the same experiments, while for the other sites, maize was the main constituent. Overall, pH and NH_4-N content of the biogas digestate was only slightly higher compared to cattle slurry (Paper 3; Table 2). Thus, increased pH and NH_4-N levels cannot fully explain high NH_3 emissions following biogas digestate application. Another explanation might be that the pH buffer capacity of biogas digestate was significantly higher compared to cattle slurry, so that the pH of the fertilizer solution remained on a high level for an extended period of time after application (*Sommer* and *Husted*, 1995). In order to reduce the pH of biogas digestate to 6.0, more acid was required in comparison to cattle slurry, substantiating this theory (Paper 3; Table 2).

When comparing techniques, application by trailing hose lead to the highest emissions. Averaged by type of fertilizer, 24 kg NH_3-N ha^{-1} was lost when cumulating both applications per site (Paper 3; Table 4). However, compared to broadcast application, using a trailing hose is already considered a NH_3 mitigation technique (*Webb* et al., 2010) and it was the most economical way to apply liquid manure (*Buchen-Tschiskale* et al., 2022a).

Using the combination of slot injection for the first application and trailing shoe for the second application lead to an overall NH_3 mitigation of 23 % compared to trailing hose application (Paper 3; Table 7). There was no significant difference between slot injection and trailing hose application (Paper 3; Table 7) although slot injection reduced atmospheric contact to a greater extent than the trailing shoe. However, it needs to be considered that due to this study's design, the factors "application date" and "application technique" were mixed. One possible drawback of using slot injection for growing crops, is potential damage to the crop (*Nyord* et al., 2012). However, yield data (Paper 3; Table 8) did not substantiate this concern.

Overall, acidification lead to 64 % NH_3 mitigation compared to trailing hose application without addition of sulfuric acid (Paper 3; Table 7). However, the acidification system used for this study differs slightly from systems used in farm practice (*Fangueiro* et al., 2015; *Toft* and *Madsen*, 2019). Thus, the amount of acid required for acidification as well as the mitigation potential might vary when using those systems.

The question is when should those techniques be used to mitigate NH_3 emissions. The combination of slot injection for the first application and trailing shoe for the second application had no general drawback except for being less economic than trailing hose application (*Buchen-Tschiskale* et al., 2022a). For a full assessment, N_2O emissions and fuel consumption need to be considered as well. Regarding N_2O, *Buchen-Tschiskale* et al. (2022b) did not find significant differences compared to trailing hose application when analyzing datasets obtained from the same experiments. Thus, the combination of slot injection and trailing shoe application seems to be a valid method to reduce NH_3 emissions, without impairing other ecological objectives.

Although having generally a better NH_3 mitigation potential than the combination of slot injection and trailing shoe, acidification has the potential drawback of bringing in excessive amounts of sulfur into the environment. Thus, the general use of acidification to reduce NH_3 emissions is problematic. One possible area of application is the use under sub-optimal conditions (e.g. high wind speed and intense radiation). However, liquid manure should not be applied under those conditions after all. However, there are sub-optimal conditions that cannot be changed. As pointed out previously, biogas digestate application leads to high NH_3 emissions and the combination of slot injection and trailing shoe had a reduced mitigation potential regarding biogas digestate application (Paper 3; Table 7). However, acidifying biogas digestate requires high amounts of acid (Paper 3; Table 2), increasing the problem of surplus sulfur. Similarly, both ways to mitigate NH_3 emissions might have a reduced efficiency when the soil pH is high (Paper 3; Table 5). However, acidification might be a valuable addition when the soil texture is suboptimal for slot injection and/or trailing shoe application, since acidification was not influenced by soil texture (Paper 3; Table 5). However, it needs to be considered that soil texture does not change, so that acidification would be used on the same field over and over again. In summary, acidification should only be used when sulfur fertilization is required in the crop rotation. Under those circumstances it might be a good method to apply sulfur, while simultaneously also reducing NH_3 emissions originating from liquid manure application. Moreover, *Buchen-Tschiskale* et al (2022b) did not find significant differences compared to trailing hose application when analyzing N_2O datasets obtained from the same experiments. Thus, excess sulfur seems to be the only ecological drawback of acidification when fertilizing growing winter wheat.

Conclusion

Everybody using chamber methods or wind tunnels should consider that NH_3 is highly reactive and might stick to the system, influencing measurements. Thus, there is a great need to check all systems currently used to estimate NH_3 emissions in multi-plot field experiments regarding the potential impact of contamination. Only when methods to measure NH_3 emissions in multi-plot field experiments are improved, multiple optimized techniques to apply liquid manure can be tested regarding their qualitative NH_3 mitigation potential while simultaneously evaluating them agronomically. On the other hand, a relative comparison of treatment means is easier to perform by using passive samplers, which absorb NH_3 depending on the source strength in the respective plot. However, NH_3 drift between plots is an important factor that needs to be considered in multi-plot field experiments. Increasing the plot size might reduce the impact of that factor.

According to this study, acidification was the system with the best NH_3 mitigation potential. However, extensive use of sulfuric acid might lead to sulfur surplus and subsequent leaching of sulfate. Furthermore, the costs for acidification might increase drastically, if every farmer uses this technique. Therefore, other systems like slot injection should also be used to reduce NH_3 emissions. However, no farmer should have multiple techniques to apply liquid manure. Therefore, contractors have to apply liquid manure using optimized application techniques. Unfortunately, applying optimized techniques did not increase winter wheat yield in this multi-site two-year study. Therefore, farmers using those techniques should be compensated in order to increase acceptance.

Summary

Ammonia emissions caused by liquid manure application affect human life expectancy and threaten natural ecosystems. However, other associated concerns like greenhouse gas emissions and nitrate leaching are equally relevant. Thus, German legislation severely restricted autumn application of liquid manure, since most crops have low nutrient demand at this development stage, so that much of the applied nitrogen would be lost to the environment. Therefore, liquid manures have to be applied in spring into growing crops. However, immediate incorporation into the soil to minimize ammonia emissions is not possible under these circumstances. Moreover, biogas digestate has become an increasingly popular organic fertilizer over the last three decades, since anaerobic fermentation is a climate friendly energy source. However, it might be associated with increased ammonia emissions due to its comparatively high pH and ammonium content. Therefore, liquid manure should be applied using optimized techniques for growing crops to mitigate ammonia emissions. Those techniques are based either on reducing the contact of fertilizer and atmosphere or on acidifying liquid manure.

To evaluate optimized techniques, ammonia emissions have to be quantified in multi-plot field trials. Unfortunately, standard micrometeorological methods require large field areas and expensive equipment, making them difficult or even impossible to apply. Thus, other approaches adjusted to those specific requirements are used in multi-plot field trials. Calibrated passive sampling uses acid traps placed in the center of each plot to absorb ammonia, which enables a relative comparison of emissions. Subsequently, acid trap samplings are scaled by simultaneous measurements with the dynamic tube method, which uses a mobile chamber system to quantify ammonia emissions.

The first objective of this study was therefore to evaluate calibrated passive sampling in multi-plot field trials with liquid manure application. However, ammonia drift between plots as well as chamber system contamination might be a particular challenge in such an experimental set-up. Therefore, the first step was to analyze the potential influence of the ammonia background on acid trap samplings and dynamic tube measurements. In a second step, the best practice to scale relative differences between plots obtained from acid trap samplings was assessed. In order to reduce costs and to minimize chamber system contamination, dynamic tube measurements are only performed on a few selected plots. Thus, characteristics of a well-suited treatment to perform simultaneous measurements with both methods were evaluated. However, the transfer coefficient (cumulated qualitative emissions divided by cumulated acid trap samplings) required to scale emissions might depend on the level of data aggregation. It can be calculated based on individual plots, treatment means or all plots of a field experiment. Therefore, it was evaluated which amount of data aggregation is sufficient.

The second objective of this study was to evaluate optimized techniques to apply liquid manure in growing winter wheat in a series of field experiments in Germany. Calibrated passive sampling was used to assess ammonia emissions and yield and nitrogen uptake were measured as well to allow an agronomical evaluation of those techniques. Nitrogen fertilizer were applied at a total rate of 170 kg N ha^{-1} split into two equal dressings. Each experiment consisted of several techniques to apply cattle slurry and biogas digestate: i) trailing hose application using untreated and ii) acidified liquid manure, as well as iii) a combination of open slot injection for the first dressing and trailing shoe application for the second dressing. Furthermore, ammonia emissions, yield and nitrogen uptake of organically fertilized treatments were put into perspective by also implementing a treatment with mineral fertilization (broadcast calcium ammonium nitrate) and an unfertilized control.

Furthermore, the unfertilized control was crucial to assess the influence of ammonia drift between plots. Acid trap samplings differed significantly between control plots, indicating that cumulated samplings of each individual plot depend not only on the ammonia emissions of the respective plot,

but also on its specific background. Hence, many replications are necessary to obtain valid treatment means and those mean values show high standard deviations. However, there is no evidence, that passive sampler results are generally biased. Therefore, they are an easy way to obtain relative comparisons between treatment means.

For the dynamic tube method, ammonia drift between plots had only a minor impact. However, we showed that chamber system contamination has a profound effect on calculating cumulated ammonia emissions in multi-plot field trials. The on field cleaning procedure using paper towels was not sufficient to reduce contamination.

The relative influence of background ammonia was higher in treatments with low emissions for both methods. Therefore, scaling of acid trap samplings by simultaneous dynamic tube measurements should be performed in a treatment with high ammonia emissions. Regarding the amount of data aggregation required to scale emissions, this thesis showed that calculating a transfer coefficient based on individual plots is not sufficient, due to the influence of the fluctuating ammonia background. Therefore, acid trap samplings were scaled based on mean values in a treatment with high ammonia emissions.

In this series of winter wheat field trials, the highest ammonia emissions (on average 24 kg N ha^{-1}) occurred following trailing hose application. Applying biogas digestate lead to approximately 60 % higher emissions than cattle slurry application. Overall, acidification reduced emissions by 64 % for both liquid manure types. On average, the combination of slot injection and trailing shoe application resulted in 23% lower ammonia emissions compared to trailing hose application. However, decreasing ammonia emissions did not increase yield and nitrogen uptake. All treatments with liquid manure application led to similar crop yield (approximately 7 t ha^{-1} grain dry matter yield) and aboveground biomass nitrogen uptake (approximately 150 kg ha^{-1}). Yield (8 t ha^{-1}) and nitrogen uptake (approximately 190 kg ha^{-1}) were significantly increased for the minerally fertilized treatment, while for the control, yield (approximately 4.5 t ha^{-1}) and nitrogen uptake (approximately 90 kg ha^{-1}) were significantly reduced.

In summary, our results show that the mitigation of ammonia emissions originating from liquid manure application to growing crops is possible by using optimized application techniques. For this series of field trials, acidification was the technique with the highest ammonia mitigation potential. Future studies using calibrated passive sampling should address the importance of ammonia drift and chamber system contamination. Therefore, the use of separate dynamic tube chamber systems for each plot is recommended. Furthermore, increasing the plot size might reduce ammonia drift.

Zusammenfassung

Die Ausbringung von Wirtschaftsdüngern verursacht Ammoniakemissionen, die die menschliche Gesundheit beeinträchtigen und natürliche Ökosysteme bedrohen. Andere mit der Ausbringung von Wirtschaftsdüngern verbundene Probleme (z.B. Treibhausgasemissionen und Nitratauswaschung) sind jedoch ebenso relevant. Daher schränkt die aktuelle deutsche Düngeverordnung die Düngung im Herbst stark ein. Die meisten Nutzpflanzen weisen in diesem Entwicklungsstadium nur einen geringen Nährstoffbedarf auf, sodass ein Großteil des ausgebrachten Stickstoffs verloren ginge. Deshalb werden Wirtschaftsdünger im Frühjahr in wachsende Kulturen ausgebracht, wo jedoch eine sofortige Einarbeitung in den Boden zur Minimierung von Ammoniakemissionen nicht möglich ist. Zudem wurden Biogasgärreste in den letzten drei Jahrzehnten zu einer beliebten Wirtschaftsdüngerform, da die anaerobe Fermentation eine klimafreundliche Energiequelle ist. Aufgrund des vergleichsweise hohen pH-Werts und Ammoniumgehalts kann deren Ausbringung jedoch mit erhöhten Ammoniakemissionen verbunden sein. Vor diesem Hintergrund sind optimierte Techniken der Wirtschaftsdüngerausbringung in wachsende Bestände erforderlich, um Ammoniakemissionen zu verringern. Diese Techniken basieren entweder auf der Reduzierung des Kontakts zur Atmosphäre oder auf Absenkung des pH-Werts des Wirtschaftsdüngers.

Zur Bewertung dieser Techniken, müssen Ammoniakemissionen in Parzellenversuchen mit mehreren Wiederholungen quantifiziert werden. Standardmethoden zur Messung dieser Emissionen erfordern jedoch große Feldflächen und/oder teure Ausrüstung, was deren Anwendung erschwert oder sogar unmöglich macht. Daher werden in Parzellenversuchen an die spezifischen Anforderungen angepasste Methoden eingesetzt. Beim „Calibrated Passive Sampling“ werden Säurefallen (sogenannte Passivsammler) in der Mitte jeder Parzelle aufgestellt. Diese absorbieren Ammoniak, was einen relativen Vergleich der Emissionen zwischen den Parzellen ermöglicht. Anschließend werden diese Relativwerte durch gleichzeitige Messungen mit der Dräger-Tube Methode skaliert. Die Dräger-Tube Methode verwendet ein mobiles Kammersystem zur Quantifizierung von Ammoniakemissionen.

Das erste Ziel dieser Dissertation war daher die Bewertung des „Calibrated Passive Samplings“ in Feldversuchen mit Wirtschaftsdüngerausbringung. Ammoniakdrift zwischen den Parzellen sowie die Verunreinigung des Kammersystems könnten bei einem solchen Versuchsaufbau jedoch eine besondere Herausforderung darstellen. Daher wurde in einem ersten Schritt der potenzielle Einfluss des Ammoniak-Hintergrundes auf Passivsammler und Dräger-Tube Methode evaluiert. Im zweiten Schritt wurde der beste Weg zur Quantifizierung der Ammoniak-Absorption durch die Passivsammler bewertet. Um Kosten zu senken und die Verunreinigung des Kammersystems zu minimieren, sollten Dräger-Tube Messungen nur auf wenigen ausgewählten Parzellen durchgeführt werden. Daher wurden Charakteristiken einer gut geeigneten Variante zur simultanen Messung mit beiden Methoden evaluiert. Der Transferkoeffizient (kumulierte qualitative Ammoniak-Emissionen geteilt durch kumulierte Ammoniak-Absorption der Passivsammler), der zur Skalierung der Emissionen erforderlich ist, könnte jedoch vom Grad der Datenaggregation abhängen. Der Koeffizient kann auf Grundlage einzelner Parzellen, der Variantenmittelwerte oder aller Parzellen eines Feldversuchs berechnet werden. Daher wurde untersucht, welcher Umfang der Datenaggregation ausreichend ist.

Das zweite Ziel war die Evaluierung optimierter Techniken für die Ausbringung von Wirtschaftsdüngern in einer Winterweizen-Feldversuchs-Serie in Deutschland. Ammoniakemissionen wurden durch „Calibrated Passive Sampling“ bestimmt und die zusätzliche Erfassung von Ertragsdaten, ermöglichte die agronomische Bewertung dieser Verfahren. Die Stickstoffdüngung erfolgte mit einer Gesamtmenge von 170 kg N ha^{-1}, aufgeteilt in zwei gleiche Gaben. Jeder Versuch beinhaltete mehrere Techniken zur Ausbringung von Rindergülle und Biogasgärresten: i) Ausbringung mit Schleppschlauch unter Verwendung von unbehandeltem und ii) angesäuertem Substrat sowie iii) eine Kombination aus Schlitzinjektion für die erste Gabe und Schleppschuhausbringung für die zweite Gabe. Zudem wurden

die Ammoniakemissionen, der Ertrag und die Stickstoffaufnahme der organisch gedüngten Varianten mit einer Mineraldüngervariante (breitflächige Ausbringung von Kalkammonsalpeter) und einer ungedüngten Kontrolle verglichen.

Darüber hinaus war die ungedüngte Kontrolle entscheidend, um den Einfluss der Ammoniakdrift zwischen den Parzellen zu bewerten. Die Ammoniak-Absorption der Passivsammler unterschied sich signifikant zwischen den Kontrollparzellen. Dies deutet darauf hin, dass die kumulierte Ammoniak-Absorption der Passivsammler nicht nur von den Ammoniakemissionen der jeweiligen Parzelle, sondern auch vom parzellen-spezifischem Ammoniak-Hintergrund abhängt. Daher sind viele Wiederholungen erforderlich, um valide Variantenmittelwerte zu erhalten. Zudem wiesen diese Mittelwerte hohe Standardabweichungen auf. Es gab jedoch keine Hinweise, dass Passivsammler zu generell verzerrten Ergebnissen führen. Passivsammler sind daher ein einfacher Weg, um relative Unterschiede zwischen Variantenmittelwerten zu bestimmen.

Bei der Dräger-Tube Methode hatte die Ammoniakdrift zwischen den Parzellen nur einen geringen Einfluss. Es stellte sich jedoch heraus, dass die Verunreinigung des Kammersystems einen großen Effekt auf die Berechnung der kumulierten Ammoniakemissionen in Feldversuchen mit mehreren Parzellen hat. Die Reinigung mit Papiertüchern reichte nicht aus um diese zu reduzieren.

Der relative Einfluss des Ammoniak-Hintergrundes war in Varianten mit niedrigen Emissionen bei beiden Methoden höher. Daher sollte die Skalierung der relativen Passivsammler-Ammoniak-Absorption durch die Dräger Tube Methode in einer Variante mit hohen Ammoniakemissionen durchgeführt werden. Hinsichtlich des Umfangs der Datenaggregation zeigte sich, dass die Berechnung eines Transferkoeffizienten auf der Grundlage einzelner Parzellen aufgrund des Einflusses des variierenden Ammoniak-Hintergrunds nicht ausreichend ist. Daher wurde die relative Ammoniak-Absorption durch die Passivsammler auf Grundlage von Mittelwerten in einer Variante mit hohen Ammoniakemissionen skaliert.

Die Ausbringung mit dem Schleppschlauch verursachte die höchsten Ammoniakemissionen (im Durchschnitt 24 kg N ha^{-1}). Zudem führte die Applikation von Biogasgärresten zu etwa 60 % höheren Emissionen im Vergleich zu Rindergülle. Insgesamt reduzierte Ansäuerung die Emissionen bei beiden Wirtschaftsdüngerformen um etwa 64 %. Die Kombination aus Schlitzinjektion und Schleppschuh-ausbringung führte im Durchschnitt zu 23 % geringeren Ammoniakemissionen im Vergleich zur Schleppschlauchausbringung. Die Verringerung der Ammoniakemissionen führte jedoch nicht zu einer Erhöhung des Ertrags und der Stickstoffaufnahme. Alle Varianten mit Wirtschaftsdünger-Ausbringung führten zu vergleichbaren Erträgen (ca. 7 t ha^{-1} Korntrockenmasse) und Stickstoffaufnahme der oberirdischen Biomasse (ca. 150 kg ha^{-1}). Ertrag (8 t ha^{-1}) und Stickstoffaufnahme (ca. 190 kg ha^{-1}) waren für die mineralisch gedüngten Variante signifikant erhöht, während für die Kontrolle Ertrag (ca. 4,5 t ha^{-1}) und Stickstoffaufnahme (ca. 90 kg ha^{-1}) signifikant reduziert waren.

Zusammenfassend wurde gezeigt, dass die Minderung von Ammoniakemissionen infolge der Ausbringung von Wirtschaftsdüngern in wachsende Kulturen durch den Einsatz optimierter Techniken möglich ist. In dieser Feldversuchsreihe war die Ansäuerung die Methode mit dem besten Minderungspotenzial. Künftige Studien die „Calibrated Passive Sampling“ zur Quantifizierung von Ammoniakemission nutzen, sollten sich mit der Bedeutung von Ammoniakdrift und der Kontamination des Dräger-Tube Kammersystems befassen. Daher ist die Verwendung von separaten Kammern für jede Parzelle empfehlenswert. Zudem könnte die Vergrößerung der Parzellen ein Weg sein, Ammoniakdrift zu verringern.

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Danksagung

Eine Dissertation ist natürlich immer mit Team-Work verbunden, auch wenn ich gezwungener Maßen die Hauptrolle übernehmen musste. Ohne die Hilfe anderer ist so ein Projekt sicherlich nicht möglich!

An erster Stelle möchte ich mich bei Prof. Dr. Hans-Werner Olfs bedanken. Ich konnte mich während der gesamten Zeit immer an dich wenden und wenn es Probleme gab, hast du deine schützenden Hände ausgebreitet!

Dann möchte ich Prof. Dr. Klaus Dittert für die offizielle Betreuung meiner Promotion an der Georg-August-Universität Göttingen danken. Unterstützung außerhalb des Projektes „GülleBest“ war ein wertvoller Perspektivwechsel, der den Fokus auf die Verständlichkeit der Präsentation gelenkt hat.

Prof. Dr. Heinz Flessa möchte ich dafür danken mein Promotionsprojekt ins Leben gerufen zu haben und bei Projekttreffen mit Rat und Tat zur Seite gestanden zu haben.

Bei Dr. Caroline Buchen-Tschiskale möchte ich mich für die Leitung des Projektes bedanken. Ohne ihre Unterstützung wären wir Doktoranden sicherlich in der Datenflut ertrunken.

Großer Dank gilt dem Bundesministerium für Ernährung und Landwirtschaft für die Finanzierung des Projektes GülleBest.

Am Anfang so einer Promotion hat man ja eigentlich keine Ahnung worauf man sich einlässt. Daher möchte ich mich bei Herbert Pralle für die Unterstützung bei der Anlage der ersten Feldversuche bedanken. Aber auch bei der Aufarbeitung der Datenflut war seine Hilfe für mich unerlässlich!

Im Rahmen des Projektes wurden unzählige Proben gesammelt. Daher möchte ich Elke Nagel für die Unterstützung im Labor und das Anlernen meiner Hilfskräfte danken. Ich selbst habe unter ihrer Regie natürlich auch einiges im Labor gelernt. Am Ende konnte ich alles, außer die Spülmaschine korrekt befüllen.

Maria Vergara wurde für mich zum Herzen des GülleBest-Teams in Osnabrück. Daher möchte ich mich für ihr freundliches Wesen und ihre allgegenwärtige Unterstützung bedanken!

Für die Durchführung des Projektes wurden mir zahlreiche Hilfskräfte zur Seite gestellt. Ich hoffe ihr behaltet mich als guten und kompetenten Chef in Erinnerung. Danke dafür, dass ich ungeliebte Aufgaben auf euch abschieben konnte. Alleine hätte ich das niemals alles geschafft: Vials evakuieren, Proben ziehen, Proben analysieren, Ernten, Daten eingeben, Löcher buddeln … Insbesondere möchte ich hier Tillmann hervorheben, ohne dessen Kernkompetenz, das schwere Heben, das Projekt gnadenlos gescheitert wäre. Dank gilt natürlich auch denjenigen, die für sich entscheiden haben im Konkurrenzprojekt bei Max besser aufgehoben zu sein ;)

Max hat mit mir gemeinsam die Höhen und Tiefen einer Promotion durchlebt. Ohne Leidensgenossen ist das nur schwer zu überstehen. Bei dir möchte ich mich insbesondere dafür bedanken, dass du etwas eher fertig wurdest als ich, sodass ich immer nachfragen konnte welche Dokumente man benötigt.

Natürlich möchte ich auch meiner Familie danken! Vielen Dank dafür, dass ihr so viel Verständnis für etwas so Unverständliches wie eine Promotion aufgebracht habt! Ihr habt dafür gesorgt, dass ich ein Zuhause hatte, wenn es mich in die weite Welt gezogen hat. Und meine angeheiratete Familie hat mit wiederum eine Heimat in der Ferne geboten.

Meiner Frau Giao möchte ich dafür danken, dass du mich schon in der Danksagung deiner Dissertation erwähnt hast, obwohl das damals doch mit erheblichem Risiko verbunden war. Du hast mir immer den Rücken freigehalten und mich motiviert endlich fertig zu werden. Zudem warst du dir nicht zu schade mit mir Gras zu ernten, wenn der Landwirt (Vielen Dank fürs Bereitstellen der Versuchsflächen! Im

Großen und Ganzen hat auch die Kommunikation super geklappt) urplötzlich beschlossen hat, dass es Zeit für den nächsten Grünlandschnitt ist.

Meiner Tochter Leonie Linh möchte ich einfach dafür danken, dass sie gesund und munter ist. Jetzt schon mehr zu erwarten, stößt vermutlich übers Ziel hinaus.

Zu guter Letzt möchte ich meinen Freunden, und wen ich sonst so vergessen haben könnte, danken. Ihr musstet es mit mir als Kommilitonen oder einfach als Freund (oder in Einzelfällen sogar als Mitbewohner) aushalten. Ihr habt mir das (Studenten-)Leben erklärt und seid in Kontakt geblieben, obwohl ich mich dazu entschieden habe zu promovieren!

Vielen Dank!

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Hünxe, den 23.06.2023

Declarations

1. I, hereby, declare that this Ph.D. dissertation has not been presented to any other examining body either in its present or a similar form.

Furthermore, I also affirm that I have not applied for a Ph.D. at any other higher school of education.

2. I, hereby, solemnly declare that this dissertation was undertaken independently and without any unauthorized aid.

Hünxe den 30.06.2023