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Evaluation of the Dynamic Tube Method for Measuring Ammonia Emissions after Liquid Manure Application

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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

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1. Introduction

Nitrogen contained in liquid manure is an essential plant nutrient [1]. However, ammonium (NH_4^+) can be easily converted to gaseous ammonia (NH_3) following liquid manure application [2]. The emitted NH_3 is either deposited locally or transported over long distances, where it increases airborne deposition of reactive nitrogen [1,3,4]. Besides detrimental effects on human health [5,6] and nonagrarian ecosystems [7], the nitrogen use efficiency of the applied liquid manure is also reduced [8]. Thus, abatement of NH_3 emissions following liquid manure application is a priority for many countries worldwide [9,10]. For example, the European Union defined limits for maximum NH_3 emissions [11], 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 [12]. Standard micrometeorological methods such as the integrated horizontal flux method [13,14] or wind tunnels [15] for quantifying NH_3 emissions require large experimental plots, expensive equipment, or an in-field electric power supply [12]. Thus, applying standard methods in multi-plot field trials is hardly possible [16].

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 [17], and later, it was adapted for assessing NH_3 fluxes following nitrogen fertilization [16,18]. 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 [12,19,20]. 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 [21,22]). 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 [12]. This approach was used in a wide range of experiments in Germany [4,23–27] and Denmark [28].

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 [12,19]. 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 [12].

Between measurements, the chamber system is cleaned with paper towels and flushed with ambient air to minimize contamination with NH_3 [12]. 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 [12,16]. 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 [29,30], but the chamber system inhibits those effects [19]. Two empirical formulas were developed for different canopy heights [19]. 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.

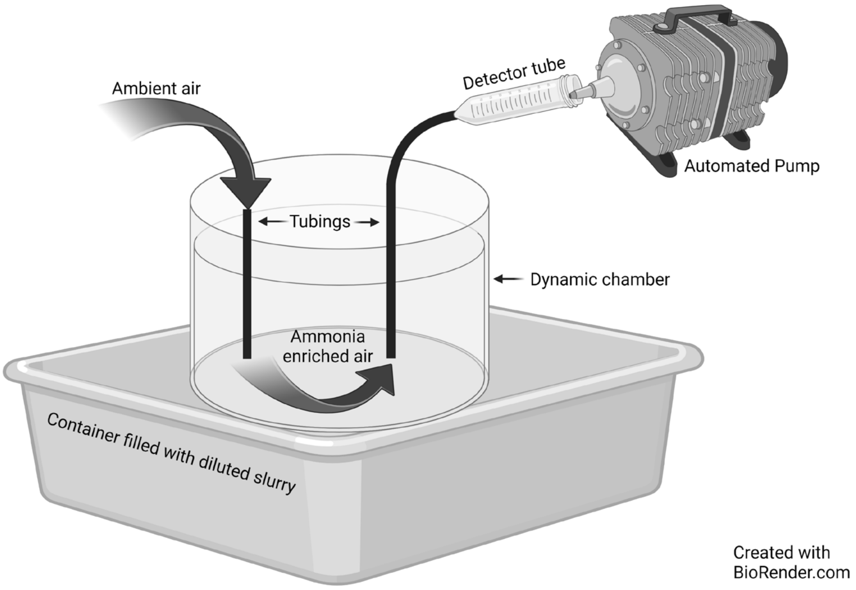

Figure 1. Schematic illustration of the laboratory experiment (only one of the four chambers within the four slurry-filled containers is displayed).

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

ppm = parts per million, s = second.

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. [24]. 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 [12] 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 [12] 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. [19]:

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

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. [19]:

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

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.

Furthermore, we calculated the cumulated NH_3 emissions based on three different approaches:

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.

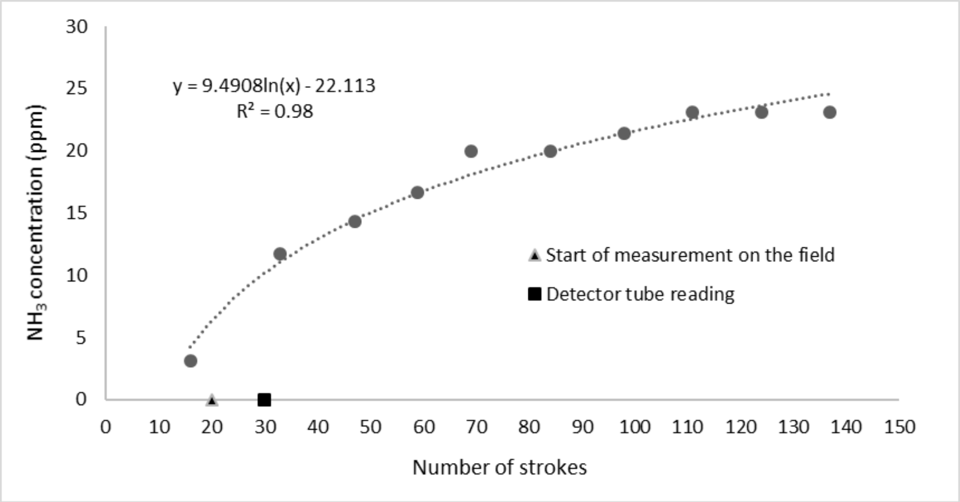

Figure 2. Increase in the NH_3 concentration in the chamber system following ongoing measurements on a surface covered with pig slurry. The slope of the equation is highly significant ($p < 0.001$). R^2 = coefficient of determination, ln = natural logarithm.

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).

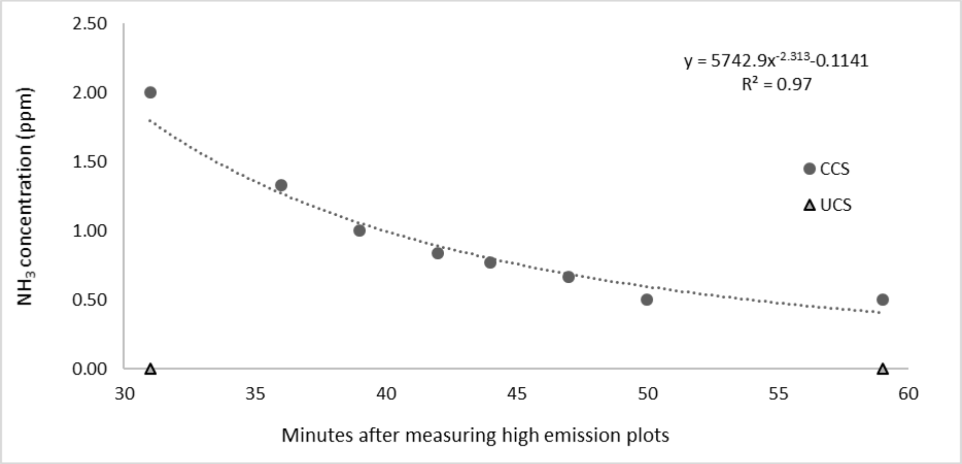

Figure 3. Decrease in the NH_3 concentration within a contaminated chamber system induced by consecutive measurements on unfertilized plots. The slope of the equation is highly significant ($p < 0.001$); R^2 = coefficient of determination, CCS = contaminated chamber system, and UCS = uncontaminated chamber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

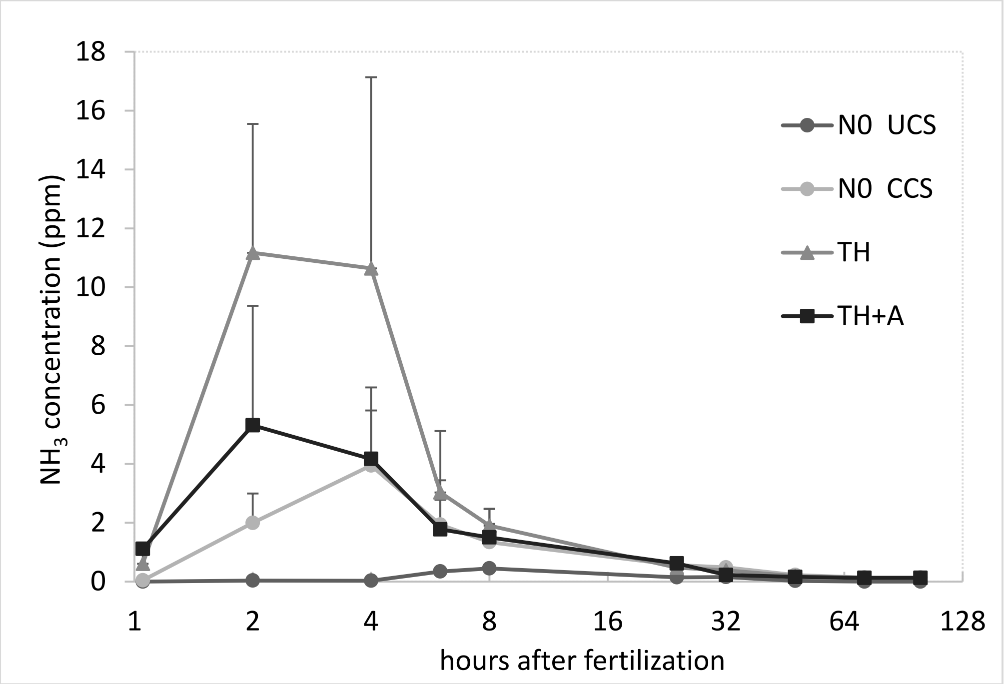

Figure 4. Mean NH_3 concentrations within the chamber system for different treatments and unfertilized control plots following slurry application in a winter wheat field experiment. Logarithmic transformation of the x-axis was used to highlight the first day after application when the NH_3 concentration 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".

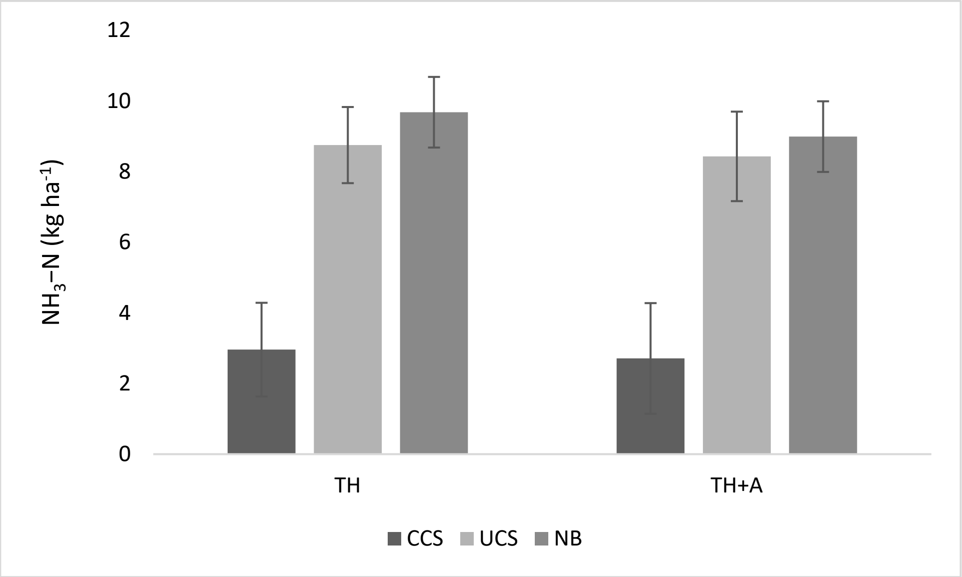

Figure 5. Cumulated NH_3 emissions for three approaches to subtract background values for calculating NH_3 emissions following two slurry application techniques in a winter wheat field experiment. The error bars represent the standard deviation (n = 4). TH = trailing hose application of slurry, TH+A = 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, and 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 [12]. However, that means that linear conversion between the alternating number of pump strokes as required for Equation (1) [16,19] 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" [16,19] 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) [12,16,19] 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. [19] 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 [19], 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 [12,21]. 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 [31]. 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.

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