



## RESEARCH ARTICLE

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

Martin ten Huf<sup>1</sup> | Thorsten Reinsch<sup>2</sup> | Christof Kluß<sup>2</sup> | Christoph Essich<sup>3</sup> |  
 Reiner Ruser<sup>3</sup> | Caroline Buchen-Tschiskale<sup>4</sup> | Andreas Pacholski<sup>4</sup> |  
 Heinz Flessa<sup>4</sup> | Hans-Werner Olf<sup>1</sup>

<sup>1</sup>Plant Nutrition and Crop Production, Faculty of Agricultural Sciences and Landscape Architecture, University of Applied Sciences Osnabrück, Osnabrück, Germany

<sup>2</sup>Institute of Crop Science and Plant Breeding, Grass and Forage Science/Organic Agriculture, Christian-Albrechts-University Kiel, Kiel, Germany

<sup>3</sup>Department Fertilization and Soil Matter Dynamics, Institute of Crop Science, University of Hohenheim, Stuttgart, Germany

<sup>4</sup>Thünen Institute of Climate-Smart Agriculture, Federal Research Institute for Rural Areas, Forestry and Fisheries, Braunschweig, Germany

## Correspondence

Martin ten Huf, University of Applied Sciences Osnabrück, Am Krümpel 31, 49090 Osnabrück, Germany.  
 Email: [martin.ten-huf@hs-osnabrueck.de](mailto:martin.ten-huf@hs-osnabrueck.de)

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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 the 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.

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**Conclusion:** For a robust application of calibrated passive sampling, we recommend calculating the TC 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, slot injection, slurry acidification, standard comparison method, 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, Howard, et al., 2011; Sutton, Oenema, et al., 2011). One important pathway for N losses from agricultural systems is the emission of ammonia (NH<sub>3</sub>) due to the field application of liquid organic fertilizers (Emmerling et al., 2020; Erisman et al., 2008; Wulf et al., 2002). This loss of NH<sub>3</sub> 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<sub>3</sub> 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, the abatement of NH<sub>3</sub> emissions following the 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<sub>3</sub> 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<sup>2</sup> (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<sub>3</sub> 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<sub>3</sub> losses in multi-plot experiments (Gericke et al., 2011), which combines two methodological approaches: the standard comparison method (Vandré & Kaupenjohann, 1998) and the dynamic tube method (DTM; Pacholski et al., 2006).

Applying the standard comparison method, simple passive samplers (PSs) absorb NH<sub>3</sub> volatilized from experimental plots by means of an acid solution. In order to compare NH<sub>3</sub> 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 & Kaupenjohann, 1998). Subsequently, the background-adjusted NH<sub>3</sub> uptake of the PS enables a relative comparison between plots. In the initial setup by Vandré and Kaupenjohann (1998), NH<sub>3</sub> sampled in plots with unknown NH<sub>3</sub> emissions were related to NH<sub>3</sub>

sampled in plots with known NH<sub>3</sub> emissions in order to scale results. Release of NH<sub>3</sub> from a standard gas bottle through a tubing system installed on the standard plots was used to establish a known NH<sub>3</sub> emission source. Subsequently, Möller and Stinner (2009) as well as Wulf et al. (2002) successfully applied this approach to determine NH<sub>3</sub> emissions on comparatively small plots (2 m × 2 m). However, the NH<sub>3</sub> 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<sub>3</sub> 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<sub>3</sub> volatilizing from the applied fertilizer and led through PTFE (polytetrafluoroethylene) tubings to an NH<sub>3</sub>-sensitive gas analysis detector tube. The reading of the detector tube is then corrected for the background NH<sub>3</sub> 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<sub>3</sub> fluxes are generally underestimated (Pacholski et al., 2006). Therefore, the DTM was calibrated with the IHF method in order to adjust the NH<sub>3</sub> 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<sub>3</sub> 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, 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 (backward 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 the total cumulative NH<sub>3</sub>-N loss determined by wind speed corrected DTM by the total amount of NH<sub>3</sub>-N collected by PSs (Gericke

et al., 2011; Pacholski, 2016). To quantify  $\text{NH}_3$  emissions, cumulative PS data are multiplied by the TC. However, the  $\text{NH}_3$  trapping efficiency of PSs is influenced by meteorological conditions and vegetation properties during the sampling period (Vandré & 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  $\text{NH}_3$  fluxes for all treatments (Vandré & Kaupenjohann, 1998).

Originally, it was suggested to derive the TC from the 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 the 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  $\text{NH}_3$  background values that have to be deducted from treatment data (Pacholski, 2016; Vandré & Kaupenjohann, 1998). The background concentration of  $\text{NH}_3$  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. PSs and DTM are both affected by background  $\text{NH}_3$  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  $\text{NH}_3$  emissions, as in treatments with low emissions the ubiquitous  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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 | MATERIALS 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.

At each site, six treatments (Table 2) were set up in a one-factorial randomized complete block design with four replicates. The plot size was  $9 \times 9 \text{ m}^2$  for the experimental sites in LS and BW, whereas the plot size in SH was  $9 \times 6 \text{ m}^2$  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  $\text{NH}_3$  drift (Figure 1).

For the WW sites, the treatments (Table 2) were (1) a control without nitrogen fertilization (NO), (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. 6 weeks before the first cut (end of March/start of April) and within 2 weeks after the first cut (middle of May).

For both crops, the target application rate was  $170 \text{ kg total N ha}^{-1}$ , split up into two equal dressings of  $85 \text{ kg N ha}^{-1}$  for the WW sites, whereas for the GL, sites  $100 \text{ kg N ha}^{-1}$  were applied before and  $70 \text{ kg N ha}^{-1}$  after the first silage cut. The  $\text{NH}_4\text{-N}$  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 ( $\text{H}_2\text{SO}_4$ ) to a tank ( $1 \text{ m}^3$ ) filled with slurry before application. The slurry was thoroughly mixed during the process. In treatment SI + NI, the nitrification inhibitor Entec FI (EuroChem Agro, Mannheim, Germany) with the active ingredient 3,4-dimethylpyrazole phosphate (DMPP) was mixed into the slurry following the recommended application rate of  $6 \text{ L ha}^{-1}$ . In WW, the NI was applied only for the first application, whereas for the GL, 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.

**TABLE 1** Soil characteristics, weather conditions, and slurry application.

Site	Campaign	Soil characteristics				Weather within 48 h after app.			Slurry app.	
		Sand (%)	Silt (%)	Clay (%)	pH	Temp. (°C)	Wind (m s <sup>-1</sup> )	Precip. (mm)	NH <sub>4</sub> <sup>+</sup> -N (kg ha <sup>-1</sup> )	pH <sup>a</sup>
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

Abbreviations: app., application; BW, Baden-Württemberg; GL, grassland; LS, Lower Saxony; precip., cumulated precipitation; SH, Schleswig Holstein; temp., average temperature at 1 m height; wind, average wind speed at 2 m height; WW, winter wheat.

<sup>a</sup>pH value refers to the pH of the raw untreated slurry.

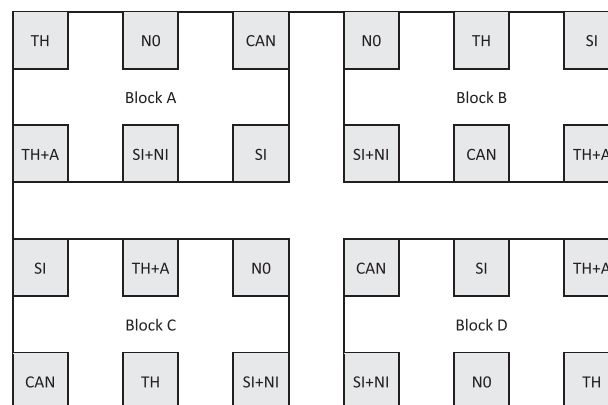
**TABLE 2** Treatment description for winter wheat (WW) and grassland (GL) sites.

Treatments WW		Treatments GL	
NO	Control without N fertilization	NO	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 <sub>2</sub> SO <sub>4</sub> by trailing hose	TS + A	Slurry + H <sub>2</sub> SO <sub>4</sub> 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.)

Abbreviations: app., application; H<sub>2</sub>SO<sub>4</sub>, sulfuric acid; NI, nitrification inhibitor.

## 2.2 | Measurement of ammonia emissions

After fertilization, NH<sub>3</sub> 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 bot-



**FIGURE 1** Schematic sketch of the randomized experimental layout. The grey areas represent the quadratic plots (9 m × 9 m). All plots are surrounded by 9 m interspaces to minimize NH<sub>3</sub> cross contamination. A, acidification; CAN, calcium ammonium nitrate; NO, no nitrogen fertilization; NI, nitrification inhibitor; SI, slot injection; TH, trailing hose.

tles with four circular openings) were filled with 20 mL of 0.05 mol H<sub>2</sub>SO<sub>4</sub> solution to absorb emitted NH<sub>3</sub>. 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<sub>2</sub>SO<sub>4</sub> solution was changed up to five times on 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  $-18^{\circ}\text{C}$  until analysis. Ammonium concentrations in the sampler solutions were analyzed using well-established standard procedures for  $\text{NH}_4^+$  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  $\text{NH}_4^+$ -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 the chamber system and pump to display the  $\text{NH}_3$  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  $\text{NH}_3$  from previous measurements was minimized.  $\text{NH}_3$  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. (2006). 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 on 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  $\text{NH}_3$  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  $\text{NH}_3$  emissions. As treatments SI and SI + NI were identical regarding the second application 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 PS and DTM, the mean cumulated  $\text{NH}_3$ -N emissions of the high emitting TH or TS treatments of each fertilization campaign were defined as 100%. Cumulated  $\text{NH}_3$  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  $\text{NH}_3$  emissions obtained by DTM and  $\text{NH}_3$ -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  $\text{NH}_3$ -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  $\times$  site,” and the random factor “block” (within sites). Subsequently, significant differences regarding the treatment means were analyzed by using the Tukey test ( $p \leq 0.05$ ).

To evaluate the correlation between DTM and PSs regarding the cumulated emissions evaluated by DTM and cumulated  $\text{NH}_4^+$ -N collected by PSs, regression functions and coefficients of determination ( $R^2$ ) were calculated. The regression included single plot data (DTM given as  $\text{kg NH}_3\text{-N ha}^{-1}$ ; PS given as  $\text{mg N L}^{-1}$ ) 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. As PS and DTM both assess  $\text{NH}_3$  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 correlations. 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”  $\text{NH}_3$  emissions (without subtraction of background values) were compared to “net”  $\text{NH}_3$  emissions (with subtraction of background values) to evaluate the relevance of background noise. For the PS, the subtraction of background values is defined as the subtraction of the cumulated  $\text{NH}_4^+$ -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  $\text{NH}_3$  emission by linear interpolation were done with and without subtractions 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  $\text{NH}_3$  emissions calculated by the DTM divided by the cumulative  $\text{NH}_4^+$ -N adsorbed by PSs for a whole sampling campaign. Cumulated PS values ( $\text{mg N L}^{-1}$ ) can be transformed into absolute values ( $\text{kg N ha}^{-1}$ ) by multiplication with the TC. Three approaches for calculating TC factors were investigated.

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

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

Subsequently, the mean and standard deviation (SD) of the four  $\text{TC}_{\text{individual}}$  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.

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

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

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

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

### 3 | RESULTS AND DISCUSSIONS

#### 3.1 | Comparison of relative cumulated emissions obtained by PSs and DTM

PSs and DTM provided cumulative  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  losses following CAN application were found by many previous studies (Forrestal et al., 2016; Sommer & Jensen, 1994; Velthof et al., 1990). Based on PS data, even numerically neg-

ative 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  $\geq 0$  for the calculation of treatment means might therefore lead to biased results when  $\text{NH}_3$  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 (Figure 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 treatments (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 & 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 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  $\text{NH}_3$  emissions measured with the DTM showed, with only two exceptions (sites LS:GL and LS:WW; Table 3), a lower SD.

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 (Tables 1 and 3). High wind speed leads to an increased air exchange rate. Therefore, the  $\text{NH}_3$  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  $\text{NH}_3$  volatilization (Freney et al., 1983). It is important to note that the DTM does not directly measure increased  $\text{NH}_3$  emissions induced by high air exchange rates, because the air exchange rate in the chamber system is not influenced by the actual wind speed (Pacholski et al., 2006). Instead, the raw fluxes (Supporting Information 1) have to be adjusted for the wind speed (Supporting Information 2; Pacholski et al., 2006). However, it has to be kept in mind that this calibration included only wind speeds up to  $4 \text{ m s}^{-1}$  (Gericke et al., 2011; Ni et al., 2015; Pacholski et al., 2006). 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.

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

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

Note: The means of the TH or TS treatment were defined as 100%. Column "100%" shows the NH<sub>3</sub> emissions (kg N ha<sup>-1</sup>) 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.

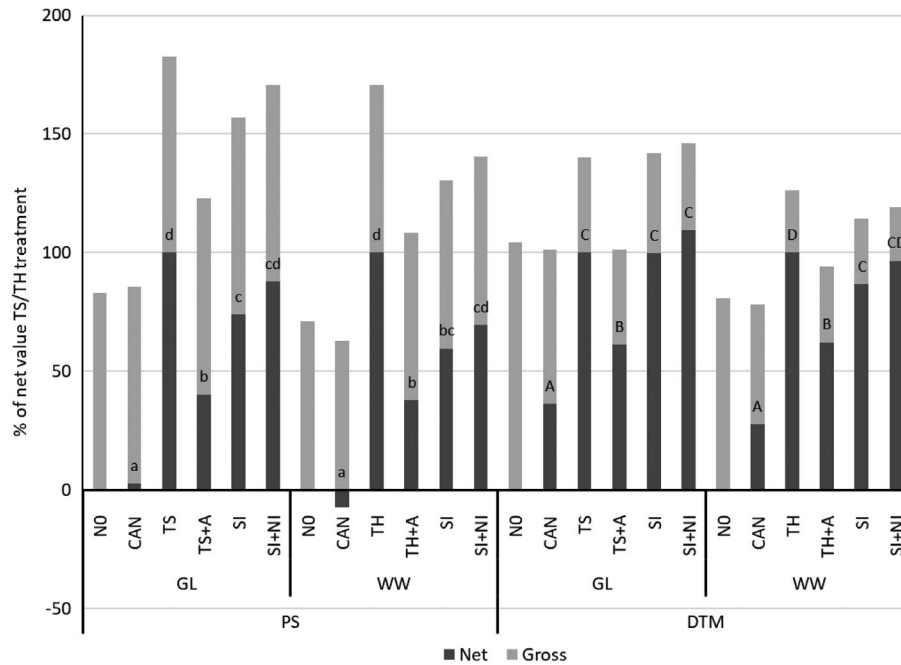
Abbreviations: A, acidification; BW, Baden-Württemberg; CAN, calcium ammonium nitrate; GL, grassland; LS, Lower Saxony; N, nitrogen; NO, no N fertilization; NI, nitrification inhibitor; SH, Schleswig Holstein; SI, slot injection; TH, trailing hose; TS, trailing shoe; WW, winter wheat.

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, and surface roughness) affecting the NH<sub>3</sub> uptake efficiency of PSs (Pacholski, 2016; Vandré & 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<sub>3</sub> emissions obtained by 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 5 values compared to 20 values for the correlation of individual plots, the increased  $R^2$  values oftentimes do not coincide with increased statistical significance.

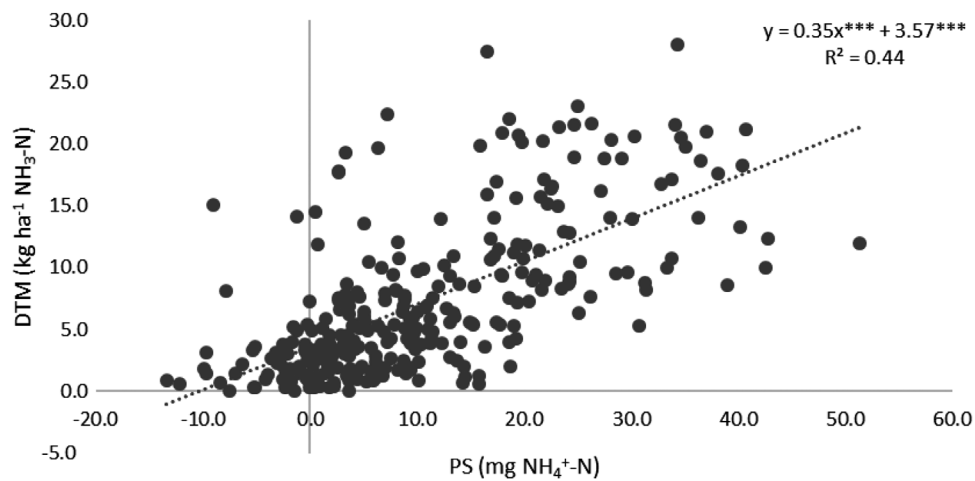
The second important aspect regarding the regression analysis is the comparison of intercepts. Zero NH<sub>3</sub> emissions according to the PS should equal zero emissions according to the DTM. However, this was not validated (Figure 3). On average, zero NH<sub>3</sub> emissions according to the PS equaled 3.6 kg N ha<sup>-1</sup> NH<sub>3</sub> emissions according to the DTM.

### 3.2 | Handling of background subtraction according to PS 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, the 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  $\geq 0$ . 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<sub>3</sub> concentration. In such a multi-plot field trial set-up with slurry application, the drift of NH<sub>3</sub> between experimental plots might be the primary source of that background. Furthermore, NH<sub>3</sub> sources outside the experimentation site might also contribute to the background (Vandré & Kaupenjohann, 1998). Due to the chamber system, wind drift might be a less important factor for the DTM than for the PS. However, air passing through the DTM system from a relatively low altitude compared to PSs is probably also affected by emissions from neighboring plots. Furthermore, the contamination of the chamber system with NH<sub>3</sub> adsorbed from previous measurements can be an additional factor contributing to increased background values. To minimize this



**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 trailing shoe (TS) or trailing hose (TH) treatments 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 lowercase letters (left side) indicate significant differences (Tukey test;  $p \leq 0.05$ ) between net values of different treatments regarding the PS. Grassland (GL) and winter wheat (WW) sites were analyzed separately. Different capital letters (right side) indicate significant differences (Tukey test;  $p \leq 0.05$ ) between net values of different treatments regarding the DTM. GL and WW sites were analyzed separately. A, acidification; NO, no nitrogen fertilization; NI, nitrification inhibitor; SI, slot injection.



**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.

problem, the chamber systems require thorough cleaning by, for example, paper towel and flushing with ambient air in-between measurements (Pacholski, 2016).

In our study, the PS background was defined as the cumulated  $\text{NH}_3$  emissions of the NO 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  $\text{NH}_3$  emissions after control subtraction (Table 3, Figure 3), indicating that the determination of the background in the NO plot might sometimes not be representative for the background



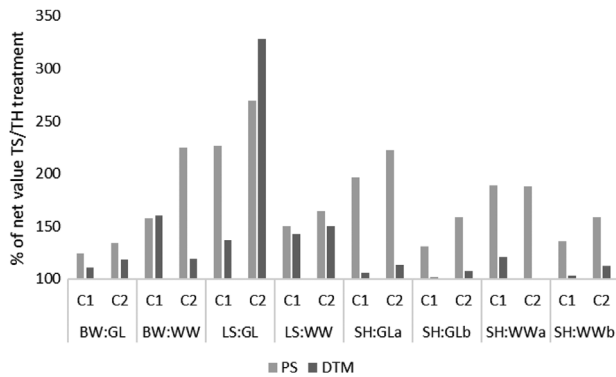
**TABLE 4**  $R^2$  values for the correlation between passive sampler and dynamic tube method data for each site and fertilization campaign.

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*

Note:  $R^2_i$  is the coefficient of determination for the correlation of individual plots;  $R^2_m$  is the coefficient of determination for the correlation of treatment means.

Abbreviations: BW, Baden-Württemberg; GL, grassland; LS, Lower Saxony; SH, Schleswig Holstein; WW, winter wheat.

\*Significant slope ( $p \leq 0.05$ ).



**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. BW, Baden-Württemberg; C, fertilization campaign; GL, grassland; LS, Lower Saxony; SH, Schleswig Holstein; WW, winter wheat.

in the treated plots. That also might at least partially explain the high SD of PS results (Table 3). Besides, varying  $\text{NH}_3$  emissions due to fertilization, the calculated cumulated N emission of each plot was also affected by varying background  $\text{NH}_3$  concentrations. Treatments with high emissions are comparatively less influenced by background noise than treatments with low emissions, which supports our second hypothesis. Regarding the PS, the “gross” emissions in the TH or TS treatment were on average 80% higher than the “net” emissions (range: 24%–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  $\text{NH}_3$  emissions were very low during the whole measurement period.

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 cal-

ulation 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  $\text{NH}_3$  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  $\text{NH}_3$  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  $\text{NH}_3$  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 nonlinear wind speed correction following the 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  $\text{NH}_3$  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 carryover 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 that 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<sub>3</sub> 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 an 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, the 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<sub>3</sub> emissions. In the initial setup 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 setup of this study. As the approach by Pacholski et al. (2006) is based on an empirical formula, small changes of the original setup might finally result in large differences regarding the cumulated NH<sub>3</sub> 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, semiquantitative 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 & Kaupenjohann, 1998). However, in practice, this is probably rarely the case as, for example, NH<sub>3</sub> drift between plots might affect background NH<sub>3</sub> emissions of each individual plot differently.

The TC (Table 5) was calculated for single plots (TC<sub>individual</sub>; Equation 1), treatment means (TC<sub>mean</sub>; Equation 2), or a whole multi-plot

field experiment (TC<sub>total</sub>; 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 treatment with high NH<sub>3</sub> emissions. Under those conditions, the relative influence of background noise is expected to be low.

Calculation of the TC<sub>individual</sub> (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 PS 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<sub>individual</sub> 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<sub>mean</sub> (Equation 2) approach, no negative results occurred for TH, TS, SI, and SI + NI treatment (Table 5). The results according to TC<sub>individual</sub> and TC<sub>mean</sub> approaches 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<sub>3</sub> emissions according to both methods are influenced by background NH<sub>3</sub> emissions and that this background might influence individual plots more than treatment means, calculating TC<sub>mean</sub> seems more reliable than calculating the mean of four TC<sub>individuals</sub>. 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<sub>mean</sub> of the TH or TS treatment with the TC<sub>total</sub> shows that the TC<sub>total</sub> is always higher than the TC<sub>mean</sub> (Table 5). Zero NH<sub>3</sub> emissions according to the PSs do not equal zero NH<sub>3</sub> emissions according to the DTM (Figure 3). When emissions are low, the DTM might overestimate the cumulated NH<sub>3</sub> 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<sub>total</sub> might be less reliable than calculating the TC<sub>mean</sub> based on treatment with high emissions.

## 4 | CONCLUSIONS

Determining NH<sub>3</sub> 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.

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

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

Note: The section  $TC_{\text{individual}}$  (Equation 1) shows mean and standard deviation of the four  $TC_{\text{individuals}}$  belonging to the same campaign and treatment. Bold numbers indicate that at least one of those four respective  $TC_{\text{individuals}}$  were negative.  $TC_{\text{mean}}$  was calculated according to Equation (2).  $TC_{\text{total}}$  was calculated according to Equation (3) for each site.

Abbreviations: A, acidification; BW, Baden-Württemberg; CAN, calcium ammonium nitrate; GL, grassland; LS, Lower Saxony; N, nitrogen; n.m., no measurement conducted; NO, no N fertilization; NI, nitrification inhibitor; SH, Schleswig Holstein; SI, slot injection; TH, trailing hose; TS, trailing shoe; WW, winter wheat.

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. Passive sampler 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.

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**DATA AVAILABILITY STATEMENT**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**ORCID**

- Martin ten Huf <https://orcid.org/0000-0002-9538-6449>
- Reiner Ruser <https://orcid.org/0000-0003-0328-1744>
- Caroline Buchen-Tschiskale <https://orcid.org/0000-0003-0540-4883>
- Hans-Werner Olf <https://orcid.org/0000-0001-6046-2803>

## REFERENCES

- Bauer, S. E., Tsigaridis, K., & Miller, R. (2016). Significant atmospheric aerosol pollution caused by world food cultivation. *Geophysical Research Letters*, 43(10), 5394–5400.
- Bobbink, R., Hicks, K., Galloway, J., Spranger, T., Alkemade, R., Ashmore, M., Bustamante, M., Cinnerby, S., Davidson, E., Dentener, F., Emmett, B., Erisman, J.-W., Fenn, M., Gilliam, F., Nordin, A., Pardo, L., & de Vries, W. (2010). Global assessment of nitrogen deposition effects on terrestrial plant diversity: A synthesis. *Ecological Applications*, 20(1), 30–59.
- Emmerling, C., Krein, A., & Junk, J. (2020). Meta-analysis of strategies to reduce NH<sub>3</sub> emissions from slurries in European agriculture and consequences for greenhouse gas emissions. *Agronomy*, 10(11), 1633. <https://doi.org/10.3390/agronomy10111633>
- Erisman, J. W., Sutton, M. A., Galloway, J., Klimont, Z., & Winiwarter, W. (2008). How a century of ammonia synthesis changed the world. *Nature Geoscience*, 1(10), 636–639.
- Fangueiro, D., Hjorth, M., & Gioelli, F. (2015). Acidification of animal slurry—A review. *Journal of Environmental Management*, 149, 46–56.
- Forrestal, P. J., Harty, M., Carolan, R., Lanigan, G. J., Watson, C. J., Laughlin, R. J., McNeill, G., Chambers, B. J., & Richards, K. G. (2016). Ammonia emissions from urea, stabilized urea and calcium ammonium nitrate: Insights into loss abatement in temperate grassland. *Soil Use and Management*, 32, 92–100.
- Freney, J. R., Simpson, J. R., & Denmead, O. T. (1983). Volatilization of ammonia. In J. R. Freney, & J. R. Simpson (Eds.), *Gaseous loss of nitrogen from plant-soil systems* (pp. 1–32). Springer.
- Galloway, J. N., Aber, J. D., Erisman, J. W., Seitzinger, S. P., Howarth, R. W., Cowling, E. B., & Cosby, B. J. (2003). The nitrogen cascade. *Bioscience*, 53(4), 341–356.
- Gericke, D., Pacholski, A., & Kage, H. (2011). Measurement of ammonia emissions in multi-plot field experiments. *Biosystems Engineering*, 108(2), 164–173.
- Hertel, O., Geels, C., Frohn, L. M., Ellermann, T., Skjøth, C. A., Løfstrøm, P., Christensen, J. H., Andersen, H. V., & Peel, R. G. (2013). Assessing atmospheric nitrogen deposition to natural and semi-natural ecosystems—Experience from Danish studies using the DAMOS. *Atmospheric Environment*, 66, 151–160.
- Lelieveld, J., Evans, J. S., Fnais, M., Giannadaki, D., & Pozzer, A. (2015). The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature*, 525(7569), 367–371.
- Möller, K., & Stinner, W. (2009). Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and on gaseous nitrogen losses (ammonia, nitrous oxides). *European Journal of Agronomy*, 30(1), 1–16.
- Ni, K., Köster, J. R., Seidel, A., & Pacholski, A. (2015). Field measurement of ammonia emissions after nitrogen fertilization—A comparison between micrometeorological and chamber methods. *European Journal of Agronomy*, 71, 115–122.
- Ni, K., Pacholski, A., & Kage, H. (2014). Ammonia volatilization after application of urea to winter wheat over 3 years affected by novel urease and nitrification inhibitors. *Agriculture, Ecosystems & Environment*, 197, 184–194.
- Pacholski, A. (2016). Calibrated passive sampling—Multi-plot field measurements of NH<sub>3</sub> emissions with a combination of dynamic tube method and passive samplers. *JoVE (Journal of Visualized Experiments)*, 109, e53273. <https://doi.org/10.3791/53273>
- Pacholski, A., Cai, G. X., Fan, X. H., Ding, H., Chen, D., Nieder, R., & Roelcke, M. (2008). Comparison of different methods for the measurement of ammonia volatilization after urea application in Henan Province, China. *Journal of Plant Nutrition and Soil Science*, 171(3), 361–369.
- Pacholski, A., Cai, G., Nieder, R., Richter, J., Fan, X., Zhu, Z., & Roelcke, M. (2006). Calibration of a simple method for determining ammonia volatilization in the field—comparative measurements in Henan Province, China. *Nutrient Cycling in Agroecosystems*, 74, 259–273.
- Paerl, H. W., Gardner, W. S., McCarthy, M. J., Peierls, B. L., & Wilhelm, S. W. (2014). Algal blooms: Noteworthy nitrogen. *Science*, 346(6206), 175.
- Quakernack, R., Pacholski, A., Techow, A., Herrmann, A., Taube, F., & Kage, H. (2012). Ammonia volatilization and yield response of energy crops after fertilization with biogas residues in a coastal marsh of Northern Germany. *Agriculture, Ecosystems & Environment*, 160, 66–74.
- Roelcke, M., Li, S. X., Tian, X. H., Gao, Y. J., & Richter, J. (2002). In situ comparisons of ammonia volatilization from N fertilizers in Chinese loess soils. *Nutrient Cycling in Agroecosystems*, 62, 73–88.
- Seidel, A., Pacholski, A., Nyord, T., Vestergaard, A., Pahlmann, I., Herrmann, A., & Kage, H. (2017). Effects of acidification and injection of pasture applied cattle slurry on ammonia losses, N<sub>2</sub>O emissions and crop N uptake. *Agriculture, Ecosystems & Environment*, 247, 23–32.
- Shindell, D. T., Faluvegi, G., Koch, D. M., Schmidt, G. A., Unger, N., & Bauer, S. E. (2009). Improved attribution of climate forcing to emissions. *Science*, 326(5953), 716–718.
- Sommer, S. G., & Jensen, C. (1994). Ammonia volatilization from urea and ammoniacal fertilizers surface applied to winter wheat and grassland. *Fertilizer Research*, 37, 85–92.
- Sommer, S. G., McGinn, S. M., & Flesch, T. K. (2005). Simple use of the backwards Lagrangian stochastic dispersion technique for measuring ammonia emission from small field-plots. *European Journal of Agronomy*, 23(1), 1–7.
- Sutton, M. A., Howard, C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., & Grizzetti, B. (2011). *The European nitrogen assessment: Sources, effects and policy perspectives*. Cambridge University Press.
- Sutton, M. A., Oenema, O., Erisman, J. W., Leip, A., van Grinsven, H., & Winiwarter, W. (2011). Too much of a good thing. *Nature*, 472(7342), 159–161.
- van Damme, M., Clarisse, L., Whitburn, S., Hadji-Lazaro, J., Hurtmans, D., Clerbaux, C., & Coheur, P. F. (2018). Industrial and agricultural ammonia point sources exposed. *Nature*, 564(7734), 99–103.
- Vandré, R., & Kaupenjohann, M. (1998). In situ measurement of ammonia emissions from organic fertilizers in plot experiments. *Soil Science Society of America Journal*, 62(2), 467–473.
- Velthof, G. L., Oenema, O., Postmus, J., & Prins, W. H. (1990). In situ field measurements of ammonia volatilization from urea and calcium ammonium nitrate applied to grassland. *Meststoffen*, 1(2), 41–45.
- VERA. (2009). *Test protocol for measurement of gaseous emissions from land-applied manure*. VERA.
- Vilms Pedersen, S., di Perta, E. S., Hafner, S. D., Pacholski, A. S., & Sommer, S. G. (2018). Evaluation of a simple, small-plot meteorological technique for measurement of ammonia emission: Feasibility, costs, and recommendations. *Transactions of the ASABE*, 61(1), 103–115.
- Wagner, C., Nyord, T., Vestergaard, A. V., Hafner, S. D., & Pacholski, A. S. (2021). Acidification effects on in situ ammonia emissions and cereal yields depending on slurry type and application method. *Agriculture*, 11(11), 1053. <https://doi.org/10.3390/agriculture11111053>
- Webb, J., Menzi, H., Pain, B. F., Misselbrook, T. H., Dämmgen, U., Hendriks, H., & Döhler, H. (2005). Managing ammonia emissions from livestock production in Europe. *Environmental Pollution*, 135(3), 399–406.
- Webb, J., Pain, B., Bittman, S., & Morgan, J. (2010). The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response—A review. *Agriculture, Ecosystems & Environment*, 137(1–2), 39–46.
- Wilson, J. D., Catchpole, V. R., Denmead, O. T., & Thurtell, G. W. (1983). Verification of a simple micrometeorological method for estimating the rate of gaseous mass transfer from the ground to the atmosphere. *Agricultural Meteorology*, 29(3), 183–189.

Wulf, S., Maeting, M., & Clemens, J. (2002). Application technique and slurry co-fermentation effects on ammonia, nitrous oxide, and methane emissions after spreading: II. Greenhouse gas emissions. *Journal of Environmental Quality*, 31(6), 1795–1801.

### SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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