

Lessons learnt from the use of passive samplers to measure ammonia emissions in multi-plot experiments

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Abstract: Chemical additives can reduce ammonia emissions from ammonium-containing fertilisers. We aimed to investigate the effect of an additive based on carboxylic acid derivatives on ammonia emissions from slurry. In a randomised multi-plot field trial, three slurry treatments with increasing amounts of the additive based on carboxylic acid derivatives were tested in comparison to untreated slurry and mineral fertiliser. Ammonia emissions were measured with so-called passive samplers, a method already used in numerous studies. However, problems arose during the evaluation of the collected data, so we examined the methodology used in more detail. The results of the measurements were analysed with regard to their spatial distribution and temporal variation. The results show that the more additives were used, the less ammonia was emitted, up to an emission reduction of 48% at the highest additive application rate. However, the spatial distribution of ammonia emissions reveals a drift of ammonia and, thus, an interaction between the plots. Thus, even in unfertilised plots, ammonia emissions of up to 50% of the treatment with the highest emissions were determined. Furthermore, it was also proven that the different times at which the slurry was applied influenced the level of ammonia emissions. Due to the interaction between the plots and the temporal differences in the application of the slurry, measuring ammonia emissions with passive samplers in multi-plot field trials, as presented in this study, is not suitable to quantify differences between the ammonia emissions from different treatments. Based on these results, recommendations for the use of passive samplers to measure ammonia emissions in field trials are proposed.

Keywords: acid traps; ammonia drift; measurement technique; NH₃ emission; slurry additive

The application of fertilisers, particularly those derived from livestock manure, is an important component in crop production and, thus, for global food production. Agricultural activities, particularly the application of ammonium-containing fertilisers (organic manures, (NH₄)₂SO₄), contribute substantially to increasing ammonia concentrations in the atmosphere. In Germany, 95% of ammonia emissions come

from agriculture, two-thirds of which are caused by livestock production (Rösemann et al. 2021).

Livestock manure, which is rich in nitrogen compounds, is proving to be a significant source of ammonia emissions and poses a double challenge. On the one hand, ammonia emissions directly impact human health, with potential effects on the respiratory and cardiovascular systems (Sutton et al. 2011).

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On the other hand, these emissions interact with atmospheric processes, leading to the eutrophication of non-agricultural ecosystems, indirect N_2O emissions, the formation of fine particulate matter and soil acidification, which in turn has further impacts on environmental quality (Mosier 2001, Spirig and Neftel 2006, Fowler et al. 2013, Lelieveld et al. 2015).

In addition, the comparatively low nitrogen (N) fertilisation effect and use efficiency of manure must be improved because, without appropriate mitigation measures to reduce ammonia emissions, a substantial proportion of the plant-available NH_4^+ is emitted as NH_3 and is therefore no longer available to plants (Webb et al. 2013).

There are several ways to reduce ammonia emissions when spreading slurry, e.g., low-emission application systems like trailing shoe systems or injection techniques that place slurry directly into the soil (Misselbrook et al. 2002, ten Huf et al. 2023). The addition of chemical additives to slurry can also alter its properties, reducing ammonia emissions. Substances like urease inhibitors or acidifying agents can help to minimise the conversion of urea to NH_4^+ or of NH_4^+ to NH_3 (Bussink and Oenema 1998).

One of these recently developed additives is based on carboxylic acid derivatives. This additive consists of a mixture of acetic acid (ethanoic acid) and poly-D-galacturonic acid methyl ester (pectin) with 2-hydroxypropane-1,2,3-tricarboxylic acid (citric acid). In addition to these main components, the additive also contains various organic (carbon) acids and a macroalgae extract (providing some galactolipids). The aim is to adsorb the NH_4^+ in the liquid manure to the carboxy groups of the carboxylic acid derivatives. The bound NH_4^+ remains in the slurry and is not emitted as NH_3 . However, as there are no standard methods available for testing and analysing the effectiveness of additives, and many experiments have only been conducted under laboratory conditions and not in agricultural practice, the results are difficult to compare (Giner Santonja et al. 2017).

To evaluate the effects of slurry additives and other emission-reducing measures, it is particularly important to carry out field trials. Various methods have already been developed for measuring ammonia emissions in the field. For example, there are micrometeorological methods for detecting ammonia emissions from larger plots or even entire fields, such as the so-called "integrated-horizontal flux" or the "eddy covariance" methods (Sommer et al. 2004, Sintermann et al. 2012). In addition, some methods

require smaller areas, such as wind tunnel methods, chamber methods, or passive sampler (PS) methods (McGinn and Janzen 1998, Hu et al. 2014, Sommer and Misselbrook 2016). With the latter methods, ammonia emissions can be measured on smaller plots, allowing for the simultaneous measurement of multiple treatments on one field (Misselbrook et al. 2005, Jantalia et al. 2012, Shigaki and Dell 2015, Pacholski 2016).

A frequently used method is the "standard comparison method", according to Vandr  and Kaupenjohann (1998), where ammonia emissions are measured with PS. To compare ammonia emissions from fertilised plots, the background concentration measured on unfertilised control plots is subtracted from the ammonia concentration measured in the treated plots (Vandr  and Kaupenjohann 1998). This method has been adapted in various studies for measuring ammonia emissions in multi-plot field trials (Gericke et al. 2011, Quakernack et al. 2012, Pacholski 2016, Wagner et al. 2021, Nyameasem et al. 2022, ten Huf et al. 2023b). Ten Huf et al. (2023a) evaluated the calibrated PS method in their study, combining the "standard comparison method" according to Vandr  and Kaupenjohann (1998) and the "dynamic tube" method, according to Pacholski et al. (2006). They highlight several challenges when applying this method in multiple plot trials.

To examine the effect of an additive based on carboxylic acid derivatives on ammonia emissions after slurry application and the suitability of measuring differences in ammonia emissions of several treatments using PS, a multi-plot field trial was conducted. The additive was mixed into the slurry at different application rates, and then ammonia emissions were measured after the slurry application using PS. However, problems arose during the analysis of the data collected, so we examined the methodology used, which has already been applied in numerous studies, in more detail. The hypotheses to be assessed were: (1) Measurement of ammonia emissions with PS in a multi-plot field trial is suitable for determining differences between different treatments; (2) ammonia emissions are reduced by the addition of the additive, and (3) the higher the application rate of the additive, the lower the ammonia emissions.

MATERIAL AND METHODS

Study site and experimental design. The experiment took place on an agricultural field north of Osnabr ck (52 56'52.908N, 8 16'8.1444E) in

Table 1. Treatment description and time schedule of application of the treatment

Treatment (abbreviation)	Application/start of measurement		Duration of application (min)
	first plot	last plot	
Control (CO)	9:04	9:17	13
Mineral fertiliser (MIN)	9:08	9:22	14
Slurry without additive (S0)	9:44	10:24	40
Slurry + 9 L/m ³ additive (S9)	10:36	11:09	33
Slurry + 18 L/m ³ additive (S18)	11:30	11:56	26
Slurry + 27 L/m ³ additive (S27)	12:05	12:26	21

northwest Germany. This area is characterised by a maritime-subcontinental climate. According to the World Reference Base (IUSS Working Group WRB 2022), the soil type in the field is a Plaggic Anthrosol with a slightly high content of soil organic carbon in the topsoil (13.57 g C/kg, total nitrogen: 1.12 g N/kg) and pH_{CaCl₂} 6.0. The soil texture is sandy loam (7% clay, 19% silt, 74% sand).

The experiment was conducted in mid-April 2019, with temperatures ranging from 5–21 °C and consistently sunny weather. The wind constantly blew from the east at a wind speed of approximately 1–4 m/s.

The field experiment with winter wheat (preceding crop: corn) was set up as a one-factorial randomised block design with four replications. The plots were each 9 m × 9 m in size, and a 9 m wide strip between the individual plots was not fertilised to avoid carryover of ammonia between the plots. Pig slurry (details below) was applied at the 2-node stage of the winter wheat. Treatments included slurry without additives (S0) and three slurry treatments with increasing amounts of an additive based on carboxylic acid derivatives (slurry + 9 L/m³ additive (S9), slurry + 18 L/m³ additive (S18), and slurry + 27 L/m³ additive (S27)), with 18 L/m³ corresponding to the manufacturer's recommendation. In addition, a control without fertilisation (CO) and a treatment with mineral fertilisation (MIN; 105 kg N/ha as urea ammonium nitrate) was established.

Pig slurry (3.5 kg NH₄-N/m³/5.8 kg total N/m³) was used at an application rate of 30 m³/ha (= 105 kg NH₄-N/ha). The slurry was applied on April 16, 2019, from approximately 9:00 a.m. to 12:30 p.m. The mineral fertiliser was applied using a plot sprayer with a 3 m working width. The slurry was spread using a plot slurry tanker with a drag hose (3 m working width with 12 hoses). The additive was mixed into the slurry immediately before each application. The establishment of the experimental plots took place

treatment by treatment. The time of application, and thus the start of the ammonia emission measurement for each treatment, is shown in Table 1.

Measurement of ammonia emissions. Ammonia emission measurements were conducted using PSs in the plots. The PS consist of a square PVC bottle (250 mL) with two openings on each side (22 mm diameter; Figure 1). They are placed on a metal rod approximately 15 cm above the crop in the centre of each plot. The PS was set up immediately after each fertiliser application or in the control plots simultaneously with the application of mineral fertiliser in the plots on April 16. They were filled with 20 mL of 0.05 mol/L sulfuric acid.

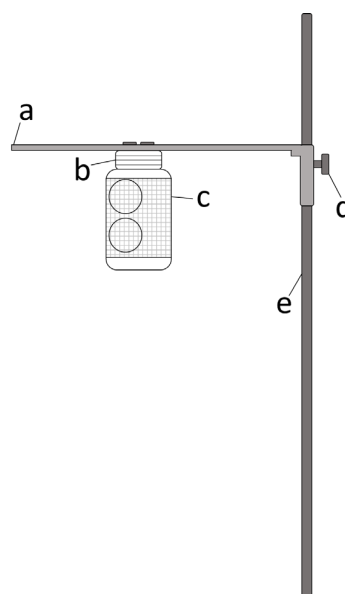


Figure 1. Set-up of the passive sampler. (a) Metal plate; (b) bottle cap (screwed to the metal plate) for mounting the PVC bottle; (c) bottle with two holes (22 mm diameter) on each side covered with mosquito net; (d) screw for adjusting the measuring height, and (e) metal rod for fixing to the ground

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At the end of each measurement period, the solution was transferred to sample containers and stored in a refrigerator until analysis. The ammonia emission measurement continued until 4:30 p.m. on April 18, with the sulfuric acid in the samplers being replaced a total of eight times. This resulted in a total of nine measurement cycles over a period of approximately 55 h.

In the laboratory, the ammonia absorption solutions were made up to 50 mL with distilled water, and the ammonium concentration was determined photometrically using the indophenol method. Taking into account the reference volume of 50 mL, this concentration was then converted into ammonia mass per measurement cycle ($\text{mg NH}_3\text{-N}$). The values were then totalled over all measurement cycles per PS. Assuming that the control plots without fertilisation emitted no NH_3 and that these values represent the background values from the surrounding area, the mean value of the four control plots was subtracted from all other measured values. The average emission per sampler in $\text{mg NH}_3\text{-N}$ was calculated from the mean of the corrected measured values of the four replications. The ammonia flux per measurement cycle in $\text{mg NH}_3\text{-N}/\text{min}$ was calculated by dividing

the measured value of a plot per cycle by the duration of the respective cycle.

Statistical analysis. To verify if the assumptions for statistical analysis are met and to identify outliers or erroneous data points, the measurements' standardised residuals (std. residuals) were calculated. For each plot, the deviation from the arithmetic mean of the corresponding treatment was computed and divided by the standard deviation of all values. The results were statistically evaluated using a one-way analysis of variance (ANOVA) ($P \leq 0.05$), both with and without subtracting the values from the control plots. In the model, the "Treatment" factor was fixed, and the "Block" was set as a random factor. Subsequently, significant differences between the average ammonia emissions per treatment were checked using a post-hoc Tukey's test ($P \leq 0.05$).

RESULTS AND DISCUSSION

Results of ammonia measurements with and without background subtraction. The highest ammonia emissions were measured for the S0 treatment with an average value of $0.37 \text{ mg NH}_3\text{-N}$ (Figure 2). This is followed by the three slurry treatments with

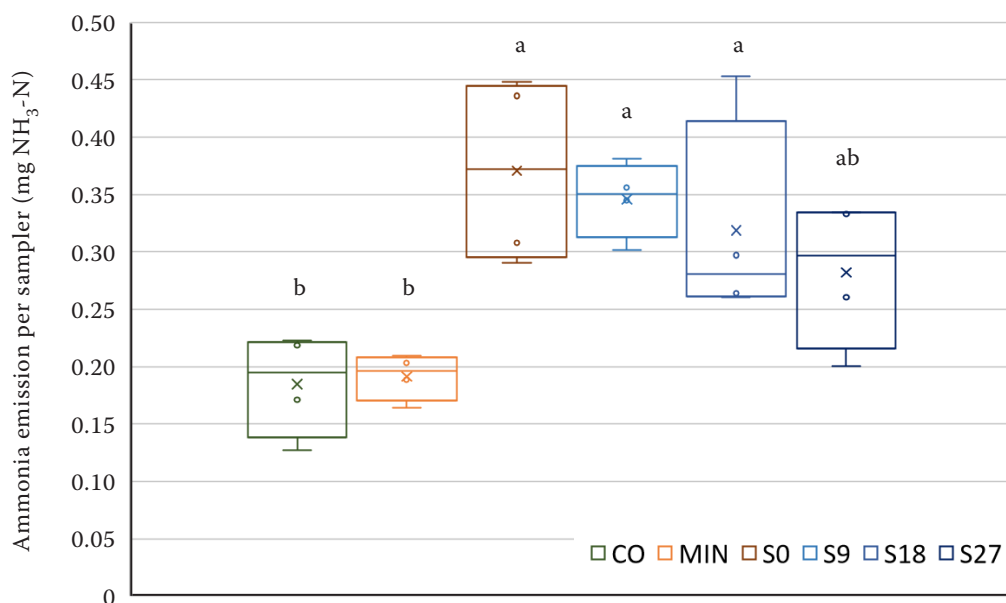


Figure 2. Ammonia emission ($\text{mg NH}_3\text{-N}$ per sampler) is the sum over the sampling period for each treatment. The x shows the arithmetic mean, the lower line outside the box shows the lowest value, and the upper line outside the box shows the highest value per treatment. The lower line of the box represents the lower quartile, the upper line of the box is the upper quartile, and the line in the box is the median of the values. Different letters indicate significant differences (Tukey's test; $P \leq 0.05$) between ammonia emissions of different treatments. CO – control; MIN – mineral fertilisation; S0 – slurry with no additive; S9 – slurry + 9 L/m^3 additive; S18 – slurry + 18 L/m^3 additive; S27 – slurry + 27 L/m^3 additive

additive application, which do not differ significantly from the treatment without additive: 0.35 mg NH₃-N was measured for the lowest additive amount (S9), 0.32 mg NH₃-N for the medium additive amount (S18) and 0.28 mg NH₃-N for the highest additive amount (S27). The control treatment and the mineral-fertilised treatment each had significantly lower ammonia values of 0.19 mg NH₃-N.

To calculate the actual ammonia emissions and the resulting emission reduction due to the use of the slurry additive, the measured value from the control plots was subtracted from the measured values of the treated plots (Table 2). The emissions are lower as the amount of additive increases, and at the highest level, ammonia emissions were reduced by approximately 48%. This outcome aligns with expectations, as similar emission reductions from acidifying slurry additives have been observed in other studies. For instance, Fangueiro et al. (2015) reported in their review that ammonia emissions from field application of pig slurry could be reduced by 40–80% and from cattle slurry by 15–80% through slurry acidification. However, despite the reduction of around 50%, this result could not be statistically verified. Similarly, ten Huf et al. (2023b) were only partially able to statistically confirm the relative emission reductions achieved through the acidification of slurry and digestates. Significant reductions were observed only in cases of very pronounced reductions exceeding 83%. A similar pattern is seen in the results of Wagner et al. (2021), where a 67% emission reduction achieved through the acidification of cattle slurry was statistically significant. For other types of slurry, the emission reduction due to acidification was between 22% and 45% but was not statistically significant.

The inability to statistically validate differences between the treatments, despite a roughly twofold difference, can be mainly attributed to the relatively

large variance in the measured values. High variance in values measured with PS has been demonstrated in other studies as well (Wulf et al. 2002, ten Huf et al. 2023a). However, there are also studies showing low variance in PS measurements (e.g. Gericke et al. 2011, Maffia et al. 2021). Gericke et al. (2011) attribute lower variances to larger plots (12 m × 12 m), resulting in lower heterogeneity in slurry application. In the study by Maffia et al. (2021), the low variance originates from several PS within one plot and not from the measurement of different plots.

The variance is also high relative to the absolute size of the measured values because the values from the unfertilised control plots were subtracted from the values of the individual treatments. This is methodologically correct, as it aims to identify background values in the control plots that do not originate from fertilised plots but may influence the measured values in the experimental plots. This assumes that these background values equally affect all plots. However, in our experiment, subtracting values from the control plots significantly influences the results, as these values represent approximately 50% of the absolute values of the treatment with the highest ammonia emissions (S0). This means that the ammonia emissions of this treatment are halved by subtracting the control. For the other treatments, more than half of the absolute values of ammonia emissions are subtracted (approximately 66% for the S27 treatment). Comparing our results with data from other experiments becomes challenging, as in most cases, it is not clarified how much the subtraction of the control values affected the results of the other treatments. When evaluating experiments using the "calibrated passive sampler method", ten Huf et al. (2023a) revealed that emissions before subtracting the control values were, on average, 80% higher in the highest emitting treatments. The control values averaged 44% of the absolute values of the treat-

Table 2. Ammonia emissions after subtraction of control values (mg NH₃-N per passive sampler)

Treatment	MIN	S0	S9	S18	S27
Mass of ammonia (mg NH ₃ -N)	0.007 ^b	0.186 ^a	0.161 ^a	0.134 ^{ab}	0.097 ^{ab}
Standard error (<i>n</i> = 4)	0.010	0.041	0.017	0.046	0.032
% of S0	3.5	100.0	86.7	72.0	52.4

The standard error of each treatment and the comparison of the emissions in relation to the highest emitting treatment (S0). Different letters indicate significant differences (Tukey's test; *P* ≤ 0.05) between ammonia emissions of different treatments. MIN – mineral fertilisation; S0 – slurry with no additive; S9 – slurry + 9 L/m³ additive; S18 – slurry + 18 L/m³ additive; S27 – slurry + 27 L/m³ additive

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ment with the highest ammonia emissions, roughly consistent with our results.

This subtraction of the values from the control plots considerably increases the relative differences between the treatments compared to the differences in absolute measured values without control subtraction. For instance, the reduction in the treatment with the highest additive amount is approximately 48% compared to untreated slurry, but without control subtraction, it would have been only 24%. On the other hand, the absolute values of standard deviations remain unaffected by the control subtraction. However, in relation to the measured values, the standard deviations increase because the measured values become smaller due to control subtraction. This makes the measured values less reliable for statistical analysis, and it becomes more difficult to validate differences statistically.

Evaluation of the spatial distribution of measured values. Relatively high values in the control plots likely originate from neighbouring plots and

are transported into the control plots with the wind from the fertilised plots (Figure 3). If the control plots are influenced by neighbouring plots, then it can be concluded that all plots are affected by the plots located upwind. This is clearly visible in the spatial visualisation of the ammonia emission values. The plots with the lowest values per treatment are at the bottom and left sides of the experimental field. The plots located at the other side of the experimental field in the wind direction (top right), with several plots in the downwind direction, exhibit the highest values per treatment. This shows the ammonia drift with the wind. Other studies have also reported the existence of drift between plots, influencing values in ammonia emission measurements with PS. Wulf et al. (2002) found in their experiments that the highest values were most often found near their standard plots (plots with a high emitting ammonia source), suggesting that the distances of 8 m and 12 m between the plots were not large enough to prevent drift effects. Gericke et al. (2011) conducted

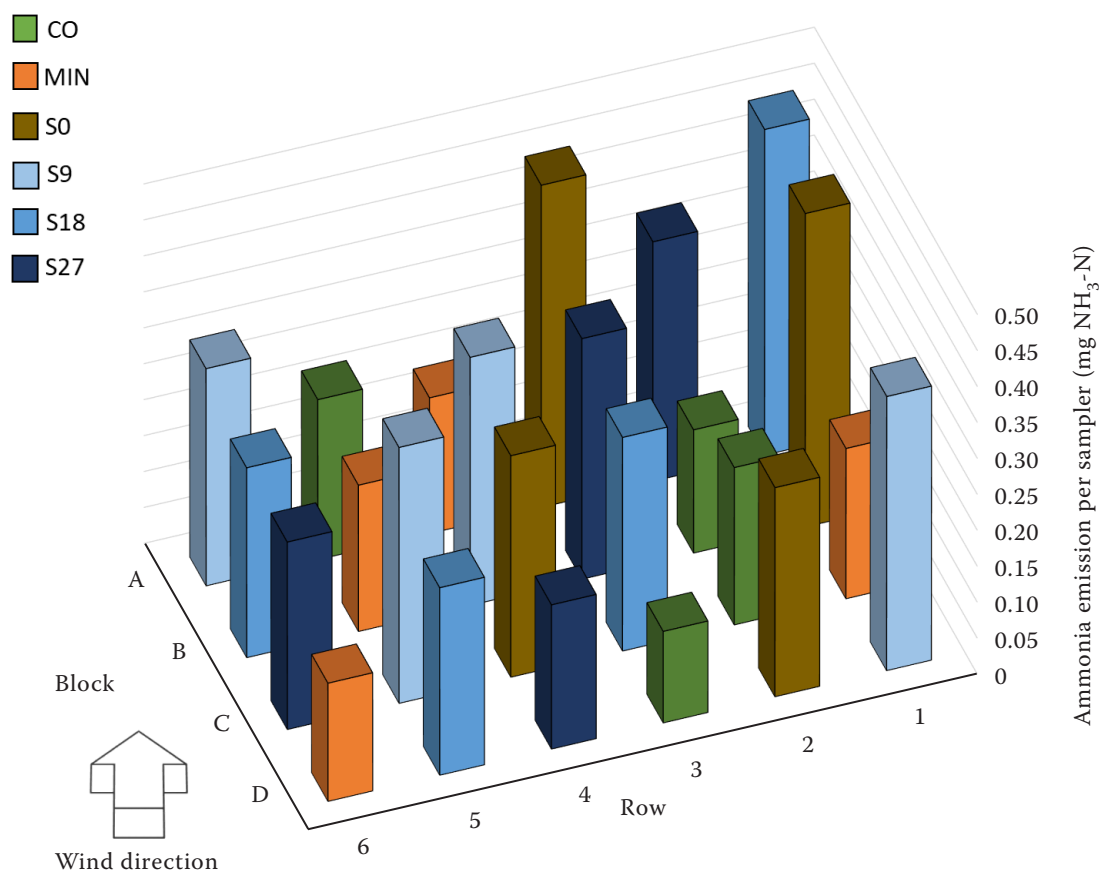


Figure 3. Spatial visualisation of ammonia emissions per plot over the whole measurement period. CO – control; MIN – mineral fertilisation; S0 – slurry with no additive; S9 – slurry + 9 L/m³ additive; S18 – slurry + 18 L/m³ additive; S27 – slurry + 27 L/m³ additive

a grid experiment to assess drift between plots. They showed that, under constant wind conditions, 25% of the ammonia concentrations of a fertilised plot could still be detected at a distance of 36 m. In the upwind direction, for plots at a distance of 12 m, approximately 10% of the ammonia concentrations of the fertilised plots were measured. Levin et al. (2023) were able to detect increased ammonia concentrations in wind direction up to 130 m away from fertilised plots. In the PS placed 10 m away from fertilised plots (approximately the distance between two plots in our experiment), the ammonia concentration was sometimes even higher than that measured directly in the fertilised plot.

This means that the basic assumption that the treatments do not influence each other is often not fulfilled in such plot experiments to assess ammonia emissions. Therefore, the question arises as to what extent it is reasonable to subtract the background values from the other measured values.

Instead of subtracting the background values on average of all replications, the background values could be subtracted block by block to minimise the problem of interaction. This approach was used in the experiments by Nyameasem et al. (2022) and ten Huf et al. (2023a). However, the analysis of variance does not show a significant block effect. This is partly because the wind direction was not perpendicular to the orientation of the blocks and because it very much depends on which treatment is upwind of the treatment under consideration.

For instance, the control plot in block B has a relatively low value for its position in the field trial. This could be because the control plots in blocks C and D are adjacent to this plot in the opposite direction to the wind. The control plot in block C, on the other hand, has a relatively high value because there are two plots with the application of slurry without additives next to it, for which high ammonia values were determined. Therefore, a plot's measurement value is influenced by neighbouring plots (especially those that are upwind). This example clearly shows that the control values, at least in this experiment, cannot be subtracted block by block from the values of the other treatment.

These effects become more apparent when examining the standardised residuals of the measured values (Figure 4). Values greater than zero indicate a positive deviation, and negative values indicate a negative deviation from the arithmetic mean of the respective treatment. The higher the value, the

greater the deviation from the corresponding mean. Evidently, the plots in row 6 and block B, except for Plot D1 (i.e., the plots located upwind at the front end of the experimental area), deviate negatively from the mean, indicating relatively low values. On the other hand, plots in row 1 and block A, except for Plot A6 (i.e., the plots located upwind at the rear end of the experimental area), exhibit relatively high values. Plot A1, with the highest number of neighbouring plots upwind, also has the highest positive residual. This is influenced not only by the location of the plot itself but also by the fact that two plots of the same treatment are positioned in row 6 and block D, suggesting that these plots are potentially less influenced by neighbouring plots. This shows that the extent of the measured ammonia emissions in a plot depends not only on the treatment in that plot but also on its location and neighbouring plots, especially those upwind.

To understand to what extent the ammonia concentration measured in individual plots is due to drift, it is important to know where the ammonia is coming from. For the plots in the control treatment, it is reasonable to assume that no ammonia is emitted directly from the plot and that the measured ammonia concentration originates only to a minor part from the background contamination but is basically caused by the drift from neighbouring plots in the field trial. Subtracting this value from the values of the other treatments seems logical and correct at first. However, the measured value of a specific plot is also influenced by the treatment of the plots in the vicinity (especially those located upwind). The arrangement of these neighbouring plots is random in a randomised experimental design. This effect might be negligible with many replications, as each treatment would have every other treatment as a neighbour upwind. However, this is not the case with the usual number of replications in typical field experiments ranging from $n = 3$ to 6.

The extent of the interaction between two plots depends not only on the location of the plot but also on other factors. Wind speed, in particular, influences the drift between plots, as higher wind speeds transport emitted ammonia over a longer distance (Denmead 1983, Ryden and McNeill 1984), thereby more significantly affecting plots downwind. The emission strength of individual treatments also affects the drift between plots. The higher the ammonia emission, the more ammonia can be transported to neighbouring plots with the wind. This especially af-

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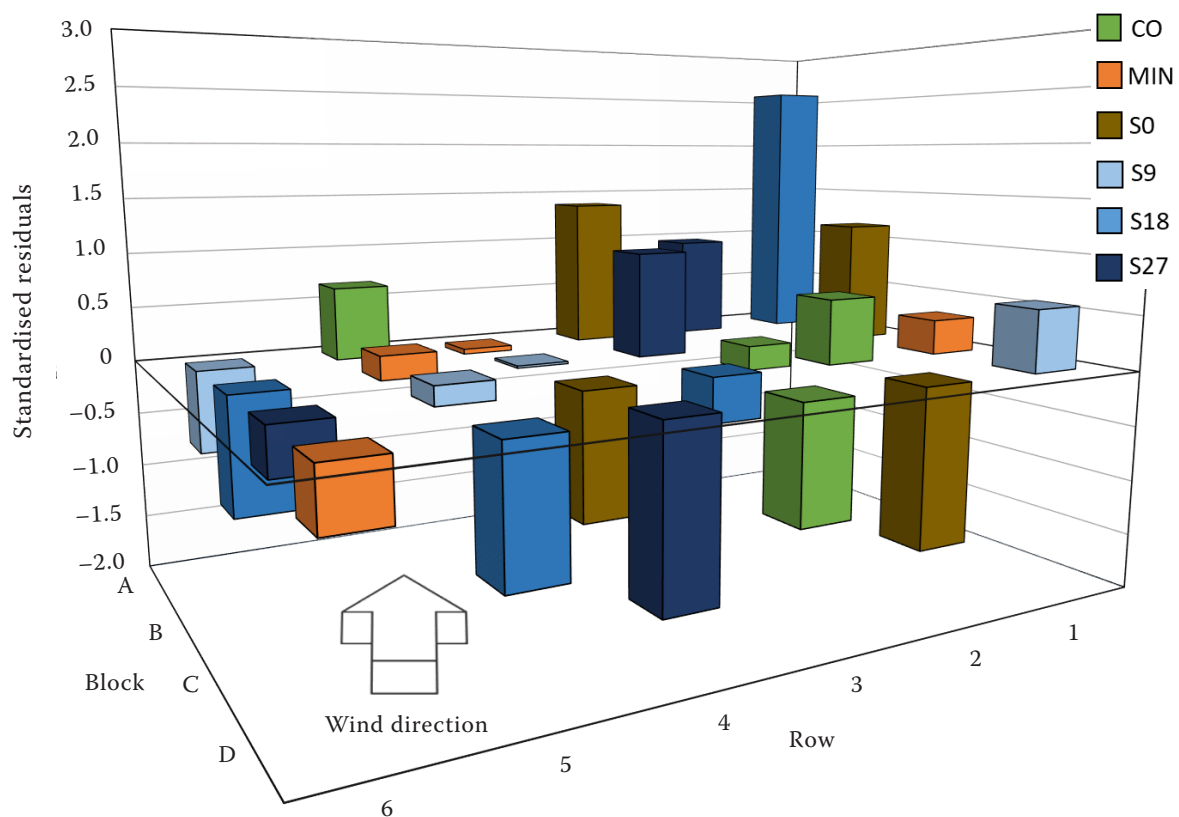


Figure 4. Spatial visualisation of the standardised residual of each plot. CO – control; MIN – mineral fertilisation; S0 – slurry with no additive; S9 – slurry + 9 L/m³ additive; S18 – slurry + 18 L/m³ additive; S27 – slurry + 27 L/m³ additive

fects plots that emit little or no ammonia, as the drift particularly affects their ammonia concentrations. Subtracting control values in such cases may even lead to negative values for low-emitting treatments. Drift between plots is a relevant issue, especially for treatments with substantially different emission levels, as drift from highly emitting treatments can mask the values of a less emitting treatment. This is confirmed by other studies (Gericke et al. 2011, ten Huf et al. 2023a).

Wind direction is also a decisive factor. In our field experiment, wind direction varied little during the 55 h ammonia emission measurement period, making the drift effects between plots well noticeable and understandable. If the wind direction changes during a measurement campaign, spatial representation of the data may not clearly indicate whether there was a specific interaction between plots due to ammonia drift with the wind.

Analysing individual subperiods of the measurement series could provide better information if the wind direction remains relatively constant during that phase. In the study conducted by Levin et al.

(2023), the wind direction changed between the first and second day after fertiliser application, so it was possible to evaluate the drift for two wind directions. However, the dependence of the interactions between individual plots in combination with the wind direction also means that it will often not be possible to quantify this effect by modelling mathematically.

Effect of the timing of fertiliser application.

Another factor affecting the level of ammonia emissions per treatment is the actual time the mineral fertiliser or the slurry was applied to each plot. This is particularly relevant for treatments fertilised with slurry. Since four plots need to be fertilised per treatment, with three passes (3 m working width, 9 m plot width) required, and one tank load of slurry is sufficient for about two plots, requiring a refill in between, the establishment of one treatment takes approximately 45 min on average (Table 1). With only one plot slurry tanker available, the slurry treatments were established consecutively. This means that almost 3 h had passed between the application in the first plot of the first slurry treatment (S0) and the last plot of the fourth slurry treatment (S27) in our

field trial. However, this sequential establishment of experimental plots is typical for field experiments (e.g. Ni et al. 2012, Wagner et al. 2021). Consequently, the treatments were applied under different weather conditions. In Figure 5, the measured ammonia fluxes and air temperature over the course of the experiment are presented. The temperature at the time of establishing treatment S0 was below 7 °C; when establishing treatment S27, it was approximately 12 °C. It can be assumed that during this period, the temperature at the soil surface also increased. Higher air and soil temperatures lead to increased ammonia emissions (Beauchamp and Kidd 1982, He et al. 1999, Sommer and Hutchings 2001). According to model evaluations by Pedersen et al. (2021), an increase in temperature during the application from 5 °C to 15 °C is predicted to result in a 5- to 10-fold increase in ammonia emissions.

In contrast, early applications leave more time until emissions are substantially lower again in the evening. In their studies, Gericke et al. (2011) demonstrated a significant time-of-day effect on the level of ammonia emissions: the later the application, the lower the ammonia emissions. The results are supported by various model calculations (e.g. Smith et al. 2009, Ni et al. 2012). Similarly, the calculations by Sommer and Olesen (2000) indicate that slurry application

early in the morning or the evening can considerably reduce ammonia emissions compared to application at midday. The results of Rana and Mastrorilli (1998) also show that a substantial proportion of ammonia is emitted around midday. The question arises of how the background values can be correctly subtracted in view of the different exposure periods. The semi-continuous measurement with PS generates an average emission flux over the respective exposure period of the acid in the PS. Thus, it is not possible to calculate the temporal course of emissions during this period. There is only the option to subtract the complete value of the control plots. As shown in Figure 5, these measurement periods are almost identical from the second run (i.e. from 13:37) onwards, allowing the subtraction of the value from the control treatment. However, in the first run, measurement periods for the individual plots differed substantially, so subtracting the control value would not be correct. In the first run, however, ammonia flux is clearly highest, so it is decisive for the emission calculations. The fact that ammonia emissions are highest in the first hours after fertiliser application has been confirmed by many other experiments (e.g. Sommer and Hutchings 2001, Wulf et al. 2002, Quakernack et al. 2012). On the other hand, one can calculate a time-weighted background value and subtract it from the

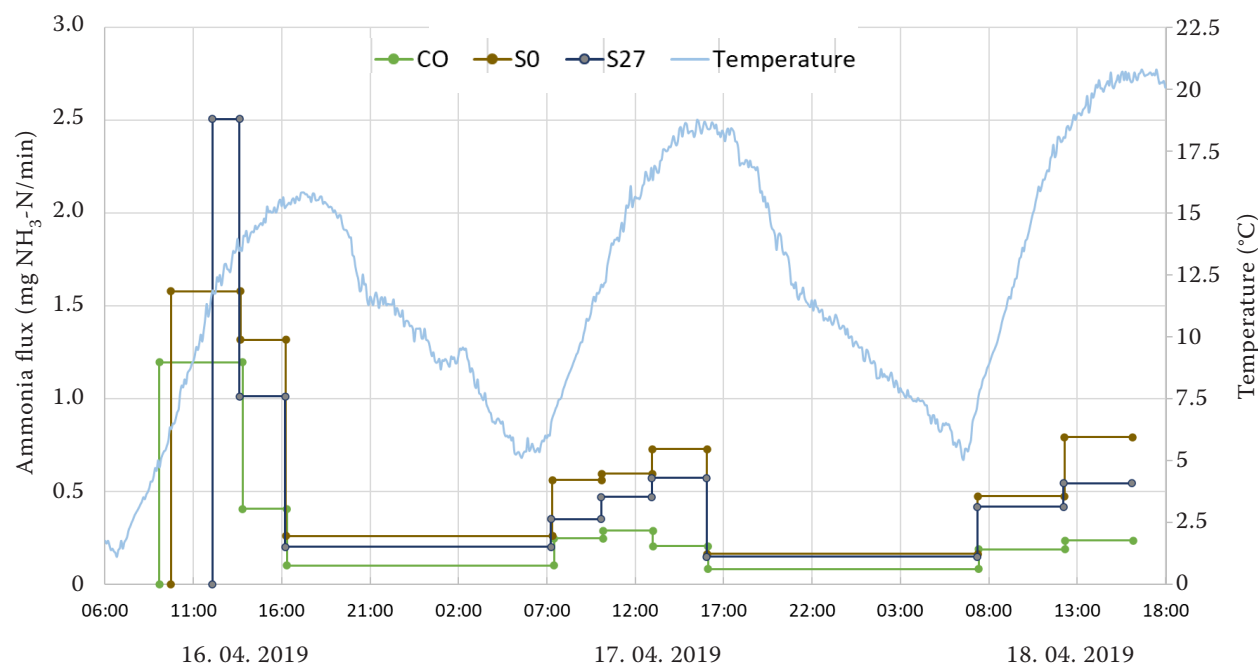


Figure 5. Changes in air temperature and ammonia fluxes for one exemplary selected plot for each of the three treatments CO, S0 and S27 over the measurement period of 55 h. CO – control; S0 – slurry with no additive; S27 – slurry + 27 L/m³ additive

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actual measured value. However, this assumes that the background value remains constant during the considered period. This is implausible, as during the first run, more and more slurry is applied, increasing the baseline noise in the experimental area through drift between plots. Additionally, during the first run, temperatures rise, causing ammonia emissions from fertilised plots to increase.

Under these circumstances, there is no correct method to subtract background values over the course of the experiment. To enable this, the PS solutions in the controls would have to be exchanged after establishing each plot or at least each treatment. This way, one could correctly subtract control values for each treatment, as the control values from the corresponding measurement periods would be available.

Measuring ammonia emissions with PS in multi-plot field trials, as presented in this study, is therefore not suitable for quantifying differences between ammonia emissions from different treatments. So, the first hypothesis, that the measurement of ammonia emissions with PS in a multi-plot field trial is suitable for determining differences between different treatments, must therefore be rejected.

Consequently, no quantitative differences between the ammonia emissions of the individual treatments and, therefore, no reduction potentials using slurry additives could be calculated. The ranking of the slurry additive treatments corresponded to our expectations, and the second hypothesis was that a higher dosage of the additive leads to lower ammonia emissions. However, as the first hypothesis had to be rejected, the second and third hypotheses regarding the effects of slurry additives can neither be confirmed nor rejected. Therefore, the emission reductions of up to approximately 48% by using the slurry additive should be interpreted with caution.

Recommendations for the measurement with PS. In the following, we present recommendations for the use of PS to measure ammonia emissions in multi-plot field trials based on the lessons we have learned:

- For studies focusing on the general effectiveness of measures to reduce ammonia emission and their quantification, conducting laboratory experiments under controlled conditions might be more appropriate.
- If field experiments are preferred, the individual treatments should be established under conditions as similar as possible (time of fertiliser application, temperature, etc.).

- To enable the correct subtraction of background values over the course of the experiment, the PS solutions in the control plots should be exchanged after establishing each plot or at least each treatment. This way, the correct control values can be subtracted for each treatment, as the control values from the corresponding measurement periods are available.
- To improve the quality of the results of ammonia emission measurements in multi-plot field trials, testing as few treatments as possible is recommended.
- The distances between plots should be larger than those in our field experiment (9 m) to reduce the interaction between individual plots due to ammonia drift.
- Additionally, smaller plots are recommended to minimise ammonia drift. However, as the effects of different treatments on yield are of interest in almost all field studies, a representative area of each plot that can be harvested is required. This is only possible to a limited extent with smaller plots, as smaller plots with larger spacing between the plots might increase the heterogeneity (e.g. soil properties, fertiliser application measures), which would be detrimental to a reliable agricultural evaluation.
- Therefore, it would be advisable to split the trials to determine the ammonia emissions on the one hand and to investigate agricultural aspects, such as fertiliser effects on yields, in a separate trial.

REFERENCES

- Beauchamp E., Kidd E. (1982): Ammonia volatilization from liquid dairy cattle manure in the field. *Canadian Journal of Soil Science*, 62: 11–19.
- Bussink D.W., Oenema O. (1998): Ammonia volatilization from dairy farming systems in temperate areas: a review. *Nutrient Cycling in Agroecosystems*, 51: 19–33.
- Denmead O.T. (1983): Micrometeorological methods for measuring gaseous losses of nitrogen in the field. In: Freney J.R., Simpson J.R. (eds.): *Gaseous Loss of Nitrogen from Plant-Soil Systems. Developments in Plant and Soil Sciences 9*. Dordrecht, Springer Science Business Media B.V., 133–157. ISBN: 978-90-247-2820-6
- Fangueiro D., Hjorth M., Gioelli F. (2015): Acidification of animal slurry – a review. *Journal of Environmental Management*, 149: 46–56.
- Fowler D., Coyle M., Skiba U., Sutton M.A., Cape J.N., Reis S., Sheppard L.J., Jenkins A., Grizzetti B., Galloway J.N., Vitousek P., Leach A., Bouwman A.E., Butterbach-Bahl K., Dentener F., Stevenson D., Amann M., Voss M. (2013): The global nitrogen

- cycle in the twenty-first century. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 368: 1–13.
- Gericke D., Pacholski A., Kage H. (2011): Measurement of ammonia emissions in multi-plot field experiments. *Biosystems Engineering*, 108: 164–173.
- Giner Santonja G., Georgitzikis K., Maria Scalet B., Montobbio P., Roudier S., Delgado Sancho L. (2017): Best Available Techniques (BAT) Reference Document for the Intensive Rearing of Poultry or Pigs. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). Luxembourg, Publications Office of the European Union.
- He Z.L., Alva A.K., Calvert D.V., Banks D.J. (1999): Ammonia volatilization from different fertilizer sources and effects of temperature and soil pH. *Soil Science*, 164: 750–758.
- Hu E., Babcock E.L., Bialkowski S.E., Jones S.B., Tuller M. (2014): Methods and techniques for measuring gas emissions from agricultural and animal feeding operations. *Critical Reviews in Analytical Chemistry*, 44: 200–219.
- IUSS Working Group WRB (2022): World Reference Base for Soil Resources. International soil classification system for naming soils and creating legends for soil maps. 4th Edition. Vienna, International Union of Soil Sciences.
- Jantalia C.P., Halvorson A.D., Follett R.F., Alves B.J.R., Polidoro J.C., Urquiaga S. (2012): Nitrogen source effects on ammonia volatilization as measured with semi-static chambers. *Agronomy Journal*, 104: 1595–1603.
- Lelieveld J., Evans J.S., Fnaiss M., Giannadaki D., Pozzer A. (2015): The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature*, 525: 367–371.
- Levin K.S., Winkhart F., Hülsbergen K.J., Reents H.J., Auerswald K. (2023): Artefacts in field trial research – lateral ammonia fluxes confound fertiliser plot experiments. *Agriculture*, 13: 1617.
- Maffia J., Pelissetti S., Balsari P., Dinuccio E., Sacco D. (2021): Testing the efficiency of a passive sampler for ammonia monitoring and comparison with alpha-samplers. In: Proceedings of the 2021 IEEE International Workshop on Metrology for Agriculture and Forestry, MetroAgriFor 2021 – Proceedings, Trento-Bolzano, 3 – 5 November, 2021: 157–161.
- McGinn S.M., Janzen H.H. (1998): Ammonia sources in agriculture and their measurement. *Canadian Journal of Soil Science*, 78: 139–148.
- Misselbrook T.H., Nicholson F.A., Chamber B.J., Johnson R.A. (2005): Measuring ammonia emissions from land applied manure: an intercomparison of commonly used samplers and techniques. *Environmental Pollution*, 135: 389–397.
- Misselbrook T.H., Smith K.A., Johnson R.A., Pain B.F. (2002): Slurry application techniques to reduce ammonia emissions: results of some UK field-scale experiments. *Biosystems Engineering*, 81: 313–321.
- Mosier A.R. (2001): Exchange of gaseous nitrogen compounds between agricultural systems and the atmosphere. *Plant and Soil*, 228: 17–27.
- Ni K., Pacholski A., Gericke D., Kage H. (2012): Analysis of ammonia losses after field application of biogas slurries by an empirical model. *Journal of Plant Nutrition and Soil Science*, 175: 253–264.
- Nyameasem J.K., Zutz M., Kluß C., ten Huf M., Essich C., Buchen-Tschiskale C., Ruser R., Flessa H., Olf H.-W., Taube F., Reinsch T. (2022): Impact of cattle slurry application methods on ammonia losses and grassland nitrogen use efficiency. *Environmental Pollution*, 315: 120302.
- Pacholski A. (2016): Calibrated passive sampling – multi-plot field measurements of NH₃ emissions with a combination of dynamic tube method and passive samplers. *Journal of Visualized Experiments*, 109: 53273.
- 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.
- Pedersen J., Andersson K., Feilberg A., Delin S., Hafner S., Nyord T. (2021): Effect of exposed surface area on ammonia emissions from untreated, separated, and digested cattle manure. *Biosystems Engineering*, 202: 66–78.
- 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 and Environment*, 160: 66–74.
- Rana G., Mastroianni M. (1998): Ammonia emissions from fields treated with green manure in a Mediterranean climate. *Agricultural and Forest Meteorology*, 90: 265–274.
- Rösemann C., Haenel H.-D., Vos C., Dämmgen U., Döring U., Wulf S., Eurich-Menden B., Freibauer A., Döhler H., Schreiner C., Osterburg B., Fuß R. (2021): Calculations of gaseous and particulate emissions from German agriculture 1990–2019. Report on methods and data (RMD) Submission 2021 R. Braunschweig, Johann Heinrich von Thünen-Institut.
- Ryden J.C., McNeill J.E. (1984): Application of the micrometeorological mass balance method to the determination of ammonia loss from a grazed sward. *Journal of the Science of Food and Agriculture*, 35: 1297–1310.
- Shigaki F., Dell C.J. (2015): Comparison of low-cost methods for measuring ammonia volatilization. *Agronomy Journal*, 107: 1392–1400.
- Sintermann J., Neftel A., Ammann C., Häni C., Hensen A., Loubet B., Flechard C.R. (2012): Are ammonia emissions from field-applied slurry substantially over-estimated in European emission inventories? *Biogeosciences*, 9: 1611–1632.
- Smith E., Gordon R., Bourqu C., Campbell A., Générmont S., Rochette P., Mkhabela M. (2009): Simulated management effects on ammonia emissions from field applied manure. *Journal of Environmental Management*, 90: 2531–2536.
- Sommer S.G., Hutchings N.J. (2001): Ammonia emission from field applied manure and its reduction – invited paper. *European Journal of Agronomy*, 15: 1–15.

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- Sommer S.G., Misselbrook T.H. (2016): A review of ammonia emission measured using wind tunnels compared with micrometeorological techniques. *Soil Use and Management*, 32: 101–108.
- Sommer S.G., Olesen J.E. (2000): Modelling ammonia volatilization from animal slurry applied with trail hoses to cereals. *Atmospheric Environment*, 34: 2361–2372.
- Sommer S.G., Schjoerring J.K., Denmead O.T. (2004): Ammonia emission from mineral fertilizers and fertilized crops. *Advances in Agronomy*, 82: 557–622.
- Spirig C., Neftel A. (2006): Ammonia emissions from agriculture and particulate matter. *AGRARForschung*, 13: 392–397.
- 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, Cambridge University Press. ISBN: 9780511976988
- Ten Huf M., Reinsch T., Kluß C., Essich C., Ruser R., Buchen-Tschiskale C., Pacholski A., Flessa H., Olfs H.-W. (2023a): Evaluation of calibrated passive sampling for quantifying ammonia emissions in multi-plot field trials with slurry application. *Journal of Plant Nutrition and Soil Science*, 186: 451–463.
- Ten Huf M., Reinsch T., Zutz M., Essich C., Ruser R., Buchen-Tschiskale C., Flessa H., Olfs H.-W. (2023b): Effects of liquid manure application techniques on ammonia emission and winter wheat yield. *Agronomy*, 13: 472.
- Vandré R., Kaupenjohann M. (1998): *In situ* measurement of ammonia emissions from organic fertilizers in plot experiments. *Soil Science Society of America Journal*, 62: 467–473.
- 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: 1053.
- Webb J., Sørensen P., Velthof G., Amon B., Pinto M., Rodhe L., Salomon E., Hutchings N., Burczyk P., Reid J. (2013): An assessment of the variation of manure nitrogen efficiency throughout Europe and an appraisal of means to increase manure-N efficiency. *Advances in Agronomy*, 119: 371–442.
- Wulf S., Maeting M., Clemens J. (2002): Application technique and slurry co-fermentation effects on ammonia, nitrous oxide, and methane emissions after spreading. *Journal of Environmental Quality*, 31: 1789–1794.

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