Video Article

Calibrated Passive Sampling - Multi-plot Field Measurements of NH₃ Emissions with a Combination of Dynamic Tube Method and Passive Samplers

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Abstract

Agricultural ammonia (NH₃) emissions (90% of total EU emissions) are responsible for about 45% airborne eutrophication, 31% soil acidification and 12% fine dust formation within the EU15. But NH₃ emissions also mean a considerable loss of nutrients. Many studies on NH₃ emission from organic and mineral fertilizer application have been performed in recent decades. Nevertheless, research related to NH₃ emissions after application fertilizers is still limited in particular with respect to relationships to emissions, fertilizer type, site conditions and crop growth. Due to the variable response of crops to treatments, effects can only be validated in experimental designs including field replication for statistical testing. The dominating ammonia loss methods yielding quantitative emissions require large field areas, expensive equipment or current supply, which restricts their application in replicated field trials. This protocol describes a new methodology for the measurement of NH₃ emissions on many plots linking a simple semi-quantitative measuring method used in all plots, with a quantitative method by simultaneous measurements using both methods on selected plots. As a semi-quantitative measurement method passive samplers are used. The second method is a dynamic chamber method (Dynamic Tube Method) to obtain a transfer quotient, which converts the semi-quantitative losses of the passive sampler to quantitative losses (kg nitrogen ha⁻¹). The principle underlying this approach is that passive samplers placed in a homogeneous experimental field have the same NH₃ absorption behavior under identical environmental conditions. Therefore, a transfer co-efficient obtained from single passive samplers can be used to scale the values of all passive samplers used in the same field trial. The method proved valid under a wide range of experimental conditions and is recommended to be used under conditions with bare soil or small canopies (<0.3 m). Results obtained from experiments with taller plants should be treated more carefully.

Video Link

The video component of this article can be found at <http://www.jove.com/video/53273/>

Introduction

Ammonia (NH₃) is the only atmospheric trace gas predominantly (90%) emitted from agricultural sources in the EU. Although agriculture is also a major source (>50% of EU emissions), these contribute only to about ~5% to the total of EU15 anthropogenic greenhouse gas emissions. In contrast, agricultural NH₃ emissions are responsible for about 45% of emission-derived eutrophication, 31% of acidification and 12% fine dust formation within the EU15¹. In addition to detrimental effects to ecosystems and human health, nitrogen (N) loss by NH₃ emission is an economic loss to farmers². Nitrogen fertilizer is essential for the high rate of food production delivered by modern agriculture. Apart of the environmental damage, NH₃ emissions thus, mean a considerable loss of nutrients, as NH₃ is derived from fertilizer ammonium, in addition to nitrate the key mineral nitrogen species directly available to the plant governing crop growth processes and yield. Application of N fertilizers contributes €20-80 billion of profit per year for EU farmers but in turn it was estimated that NH₃ released into the air from agriculture causes ~€50 billion in annual damage in the EU³. Therefore, reduction of NH₃ emissions is essential for both decreasing the environmental effects and increasing the efficiency of the applied N.

In agriculture, NH₃ is mainly emitted from animal houses, manure (slurries, anaerobic digestates (AD), solid manure) storage and management as well as manure field application. The propensity to emit NH₃ differs depending on manure composition, e.g. dry matter content and manure pH. To some extent ammonium and amine based synthetic nitrogen fertilizers as urea and diammonium phosphate also contribute to NH₃ emissions. Although calcareous ammonium nitrate (CAN) is the principal N fertilizer in many European countries, the use of granular urea has increased, and was second to CAN in Central and Western Europe in 2012⁴. Urea is particularly popular in developing countries due to its advantages of a high N content, safety, and easy transportation and is the world's most important synthetic nitrogen fertilizer⁵. However, the increase of pH and surface soil NH₄⁺-concentrations resulting from urea hydrolysis can result in high NH₃ emissions. This can cause low N use efficiency, especially in alkaline soil or soil with low sorption capacity, which limits the use of urea fertilizer in Europe^{6,7}.

Many studies on NH_3 emission from organic and mineral fertilizer application and livestock housing have been performed in recent decades^{6, 8}. Nevertheless, the research related to NH_3 emissions after application of ammonia emitting fertilizers is still limited. This in particular applies to the relationship between ammonia emissions, fertilizer type used, site conditions and crop growth. Under ideal conditions this requires replicated field trials due to the variable response of crops to treatments which can only be validated in an experimental design including field replication for statistical testing.

Ammonia losses should therefore also be determined in replicated multi-plot field trials⁹, but the dominating ammonia loss methods yielding quantitative emissions (i.e. $\text{kg N}/(\text{ha} \cdot \text{h})$) require large field areas (micrometeorological methods), expensive equipment (wind tunnels) or in-field electrical power supply which make their application in replicated field trials difficult or impossible. In addition, specific settings of wind tunnels have been criticized with respect to the accuracy of obtained emission values¹⁰. Therefore, there is a strong need for an ammonia loss method to determine ammonia emissions in replicated field trials. This method could be used to help improve agricultural measures to reduce ammonia emissions based on statistically validated effects of site conditions, fertilizer type, application methods and crop development.

The basic idea of the new methodology, calibrated passive sampling, is to link a simple semi-quantitative measuring method for the measurement on many plots, with a quantitative method by simultaneous measurements with both methods on a few plots. Passive samplers modified compared to the design in the original publication¹¹ are used as a semi-quantitative measurement method. The Dynamic-Tube Method (DTM)¹², a calibrated dynamic chamber method, is employed to obtain a transfer coefficient, which converts the semi-quantitative losses of the passive sampler to quantitative losses (kg N ha^{-1}). Due to the low air exchange rate in the chamber system uncalibrated emissions obtained from the DTM are about one order of magnitude lower than true emissions. However, this problem was overcome by a calibration equation which corrects the chamber fluxes depending on in-situ wind conditions¹³. These calibration equations can only be applied when chambers have the same internal headspace volume and design as those used in the calibration trials. Chambers can be directly inserted in soil or placed on soil rings. The latter prevent excessive disturbance of the soil and allows an almost airtight introduction of the chambers on dense grass swards or compacted soil. Moreover, the exact amount of fertilizer to be tested can be applied inside the soil rings. However, soil clods on the soil rings can also entail clamping between the chamber and the soil ring.

Figure 1: Simultaneous measurement with passive samplers and chamber method (DTM) in field plot. Passive sampler is located in the center of a square plot 0.15 m above soil/canopy. Measurements with DTM are made at least 2 locations within a plot per measurement date. Areas dedicated for harvest should not be affected by chamber and passive sampler measurement operations.

To derive the transfer coefficients measurements are carried out simultaneously on a small number of plots with both methods (**Figure 1**). It is important that they are applied with the same total measurement duration and that measurements are carried out at the same time (within 1 hr). The principle facilitating the application of a transfer coefficient for many plots is based on the fact that passive samplers placed in a homogeneous experimental field, with appropriate distance to obstacles disturbing the wind field as hedges, buildings etc. (at least 10 times, ideally 20 times of obstacle height)¹⁴, have the same NH_3 absorption behavior under identical environmental conditions. So, for example, 50% lower emission on a plot would directly translate to 50% reduced ammonia uptake by a sampler solution. Therefore, a transfer coefficient used for scaling of acid trap values on a single plot can be used to scale the values of all acid traps used in the same field trial. Due to effects of varying environmental conditions (temperature, wind speed, surface roughness) on ammonia uptake efficiency of passive samplers¹¹ the transfer coefficient has to be derived for each measurement campaign, respectively.

The general features of the two methods applied and the required design of field trials include 4 dynamic chambers placed onto the soil connected with Polytetrafluoroethylene (PTFE) tubing and ventilated by a bellows pump (DTM), passive samplers and large quadratic experimental plots with large buffer spaces for reducing the effect of NH_3 drift between plots on the emission measurement on the actual plot.

The passive samplers are filled with dilute sulfuric acid (0.05 M H_2SO_4) and are placed in the center of the plots. The solution in the passive samplers continuously absorbs ammonia, and is replaced regularly depending on the expected intensity of the emissions. Simultaneously, NH_3 fluxes are measured with the DTM on two treatment plots and a control plot at specific points in time. In contrast to wind tunnels, both methods combined in calibrated passive sampling have only very limited effects on soil moisture, soil temperature and rainfall which can affect ammonia emission losses very strongly^{6, 8}. While passive samplers are mounted 0.15 m above soil and canopy surface, without any effect on those variables, measurements with DTM chambers last only for about 5 min reducing potential chamber effects to a minimum.

Accurate results for NH_4^+ concentrations in the sampling solution can be obtained by measurements with ammonium-sensitive electrodes. Measurements with Continuous-Flow Auto Analyzers can be problematic as pH sensitive color reaction applied in these instruments can be hampered by the acidic pH of the sampling solution and chemicals used require modification. NH_3 concentrations in the air passed through the chamber system of the DTM are instantaneously measured with indicator tubes. The measured NH_3 concentrations are recorded on a data sheet after each measurement.

For DTM, NH_3 fluxes ($\text{mg N}/(\text{m}^2 \cdot \text{h})$) are calculated from measured NH_3 concentrations and air flow rate through the 4 chamber system and the area covered by the chambers (Eq. 1, paragraph 2.5.1). The resulting un-calibrated fluxes (which underestimate the true emissions) are scaled to quantitative losses with a calibration equation (Eq. 2 and 3, see paragraph 2.5.1). Scaled cumulative NH_3 losses ($\text{kg N}/\text{ha}$) of the DTM are calculated by averaging the fluxes between two subsequent measurement dates, multiplying this average flux with the duration of each interval, and adding-up all losses from all measurement intervals of a measurement campaign. Cumulative qualitative NH_3 losses (ppm sum) from passive samplers are calculated by adding up collected NH_4^+ -concentrations (ppm) on a plot within an experimental campaign. This is feasible because under identical volume and measurement temperatures, ppm values directly translate into captured amounts of ammonia. To scale these qualitative losses to quantitative losses the transfer coefficient ($\text{kg N}/(\text{ha} \cdot \text{ppm})$) is derived by relating cumulative final loss of the DTM (kg N ha^{-1}) to the total sum of concentrations in the samplers measured on the same plots. This transfer coefficient is then used to convert semi-quantitative emissions from passive sampling to quantitative fluxes (e.g. $\text{kg N}/\text{ha}$) by multiplying the cumulative concentrations with the transfer coefficient.

Loss of water from the collectors through evaporation does not affect the absorption capacity but has to be corrected later for data analysis. Spilling of solution due to during strong winds has not been observed even in the coastal marshes of northern Germany. Decisive for a successful application of this approach is the identical design of all passive samplers applied in the field including identical position and height of placement within a plot. Several designs of passive samplers have been successfully applied in the past. This paper suggests one particular design which has proved reliable and easy to operate in field measurements. The presented approach has been extensively tested by comparison to standard ammonia loss methods (micrometeorological methods) in about 15 field trials confirming the quantitative validity of the procedure^{15,16} and an unbiased representation of the emissions dynamics¹⁷. The coefficient of determination (r^2) of calibrated fluxes compared to the micrometeorological measurements in the calibration study¹³ was 0.84, quite similar to the coefficient obtained by comparing ammonia sensors for measured atmospheric ammonia concentrations in a recent study¹⁸. The relative root-mean-square error of cumulative ammonia losses was 17%, also quite close to values obtained in other studies comparing micrometeorological measurements¹³. In the second validation where the proposed method was compared to micrometeorological measurements of ammonia emissions from organic slurries (5 separate trials), an r^2 of 0.96 (slope of curve ≈ 1) and a relative root-mean-square error of 5% was obtained for final cumulated ammonia emissions¹⁵. The method has proved sensitive in a 3 year field trial using different synthetic N fertilizers¹⁹. The application of this approach is restricted to average wind speeds $\leq 4 \text{ m/sec}$ at 2 m height as the chamber method was only validated under those conditions^{13,15,16}.

A measurement campaign is defined as an experiment testing ammonia emissions after application of fertilizers on several plots lasting for several days, up to weeks. Each measurement campaign on a plot consists of several subsequent sampling intervals (passive sampler) or measurement dates (DTM). Sampling interval is defined as sequential duration of absorbance of emitted ammonia by a sampling solution. Measurement date is defined as sequential point in time at which DTM measurements are done on different plots used for deriving the transfer coefficient.

Protocol

1. Experimental Design and General Operational Instructions

1. Use comparatively large plots ($12 \text{ m} \times 12 \text{ m}$ or $9 \text{ m} \times 9 \text{ m}$) as compared to the sizes usually applied in replicated field trials (e.g. $3 \text{ m} \times 8 \text{ m}$) to avoid effects of uneven fertilizer distribution on ammonia emissions (**Figure 2**). Use square plot shapes to avoid effects of shifting wind directions on ammonia uptake by the samplers. Reduce drift of NH_3 from one plot to the other to an acceptable degree by keeping a buffer area of 1 plot size between plots.

Figure 2: Optimum experimental design for multi-plot ammonia loss measurements with passive samplers. Use relatively large (12 m x 12 m; 9 m x 9 m) square treatment plots separated on each side by untreated guard plots. To avoid canopy effects on NH_3 emissions buffer plots can be fertilized with zero-emission nitrate fertilizers.

2. Add control plots without fertilizer application distributed between the treatment plots.
3. Give number or code to each plot for simple identification of plots and samples.
4. Apply organic or synthetic nitrogen fertilizer to experimental plots ranging between 50 and 150 kg ammoniacal (ammonium + urea) nitrogen (N) per ha as done in earlier studies^{15,16,19}.
Note: Amount of fertilizer may vary depending on experimental goals.
5. Select two treatment plots and one control plot for simultaneous measurement with DTM method and passive sampler. Chose treatment plots with putatively high emissions (based on experience or literature) giving a strong measurement signal.
6. Set up at least two additional plots with evenly distributed fertilizers applied by field trial machinery or accurate trail hose or surface spreading (variation of N applied between replicate plots ~10%), if there is uneven vertical or lateral fertilizer distribution. Note that uneven fertilizer distribution usually occurs after application of slurry by trail hose application, fertilizer and slurry injection, or application of granulated fertilizers with un-calibrated practical spreaders.
 1. Carry out simultaneous measurements with passive samplers and DTM on these additional plots. Use the results from these plots for derivation of the transfer coefficient. Check amount of fertilizer applied by weighing slurry tank or application machinery before and after application.
7. Record the following environmental variables in the field with an *in situ* weather station logging data for 10 min time intervals to calculate the raw and corrected NH_3 loss rates of the DTM by means of equations 1-3 (See Supplemental Code File) and to eliminate errors in the plot measurements:
 1. Record air temperature (1 m height)
 2. Record barometric air pressure (hPa)
 3. Record wind speed at 2 m height with high canopies and also at 0.2 m height (m/sec)
 4. Record wind direction.

Note: For ease of operation staff of three persons is recommended at application of the fertilizer (first measurement date) and installation of the samplers (one person for dynamic chamber method, two for installation of passive samplers and exchange of acid solution). At later measurement dates, two persons are recommended (one passive sampler, one dynamic chamber); however, in case of small plot numbers (<10), it is manageable to cover all the tasks with one person.

2. Preparations Before Going to the Field

1. Prepare for measurement with DTM by following these steps:
 1. Assemble and pack the chamber system (**Figure 3** and **4**) consisting of items given in **Table 1**. Push PTFE tube (length 0.3 m) over the shorter copper pipe of each chamber and connect two PTFE tubes with a y-connector, respectively. Connect each of the two y-connectors with another PTFE tube (0.3 m) and connect both with another y-connector. Put terminal PTFE tube (0.3 m) on the single end of the upper-most connector.
 2. Pack hand pump or automatic pump (**Figure 4**) for ventilating the system. Always pack a hand pump to the field for flushing the system with air with low NH_3 concentration (step 3.4.2). Note: Original pumps by the manufacturer have to be used as the reaction kinetics in the indicator tube is closely linked to the air flux created by the pumps. When an automated pump is used, it does not require additional stopwatch measurements during flux measurements.
 3. If an automatic pump is not used, before or after taking measurements, check the duration of a single stroke of the hand pump. Do this by pumping with an open inserted indicator tube (cut off/broken tube head) and measuring the time until 10 strokes with a stop watch (past values: 4.5 sec/stroke for tubes 0.25/a and 5/a; 7 seconds/stroke for tube 2/a).
 4. Charge the battery for automatic pump dispenser one day before start of experimentation.
Note: Discharged batteries may lead to a significantly slower pumping rate.

5. Prepare a clipboard with worksheets for monitoring of DTM measurements (plot or treatment, date, time, tubes, number of strokes, concentration, and measurement duration if no pump dispensers are used).
6. Prepare one indicator tube box (10 tubes of each concentration range; **Table 2**) to take to the field in order to be prepared for different ammonia flux intensities (**Figure 4**).

Figure 3: Set-up and application of dynamic chamber of Dynamic Tube Method (DTM). Each system consists of 4 chambers connected by PTFE tubing, reduction connection are used to connect all chambers to one pump. Air is drawn through a copper tube perforated at the lower end and sealed at the very bottom, passed over the soil, and sucked at the top of the conical internal volume to another copper tube. The air which has passed through the system is then led via PTFE tubing to the indicator tube for determination of ammonia concentrations.

Figure 4: Indicator tubes with pump dispenser and hand pump. Right side: hand pump (stroke counter, window for pump control with white spot) with used indicator tube; left side: pump dispenser (control display, control buttons) and new indicator tube (0.25-3 ppm). Original filling of indicator tube has a yellow color. Reaction with ammonia results in a change to purple color, color front is dislocated within the scale. Ammonia concentration values are obtained by reading the scale.

no.	Components of Dräger tube system
1	4 stainless steel measuring chambers (Figure 3)
2	7 segments of Teflon tubing (7 mm x 6 mm; 0.3 m length each); replace when strongly kinked
3	3 y-connectors (PP)
4	Optional: soil ring, stainless steel (particularly recommended for measurements on grassland)
5	Hand pump (Figure 4)
6	Indicator tubes (1 box contains 10 tubes) (Figure 4)
7	Optional: pump dispenser (Figure 4)
8	Optional: stopwatch, when hand pump is used for measurements

Table 1: Indicator tubes (concentration ranges) used for ammonia loss measurements.

Tube	Range of concentration (volume ppm; $\mu\text{l/l}$)	Default number of strokes	Comment
Ammonia 0.25/a	0.25 – 3	10	Lowest detectable concentration (ca. 0.05 volume-ppm) can be measured by increasing the stroke number to a maximum of 50 strokes
Ammonia 2/a	2 – 30	5	
Ammonia 5/a	5 – 70 (600 1 stroke)	10	

Table 2: Components needed to set-up a Dynamic Tube Method measurement system.

2. Prepare for passive sampler measurement by following these steps:
 1. Set up passive sampler with items given in **Table 3** as depicted in **Fig. 5** and prepare additional devices for field measurements (**Table 3**).
 2. Calculate number of vials (= number of samplings) for the whole measurement campaign.
 3. Assume about 8 vials per plot after manure application (*i.e.* the solution is exchanged 7 times) and higher numbers for synthetic N fertilizers depending on fertilizer specific dissolution and emissions behavior. Multiply number of samplings with number of plots to calculate the total number samplings (total number = number of plots x number of sampling intervals). Include 10 extra vials in case any spills occur.
 4. Calculate total volume of solution required by multiplying total number of samplings with 0.02 L of 0.05 M H_2SO_4 solution.
 5. Prepare total volume of 0.05 M H_2SO_4 solution by adding 9.8 g of concentrated sulfuric acid (98%) per liter of distilled water. **IMPORTANT:** Add water first then concentrated sulfuric acid, and wear safety glasses.
 6. Weigh each empty vial with lid before filling with acid solution or use a number of vials (*e.g.* 10) and calculate average weight of vials and note results.
 7. Fill all small vials with 0.02 L of 0.05 M H_2SO_4 , *e.g.* with bottle-top dispenser.
 8. Label vials, both bottle and lid with waterproof ink with trial number, plot number, and order of the sampler solutions within the measurement sequence, for *e.g.*, B1 P1 T2 (barley trial 1, plot 1, 2nd solution: solution following the first fill at onset of experiment) or B1 P23 T1 (barley trial 1, plot 23, 1st solution).
 9. Sort small vials for each measurement event of a measurement campaign in a plastic bag labeled with experiment number, year, *etc.* For larger plot numbers a tray with sorted vials is preferable. After sampling transfer vials from tray to labeled plastic bags.

Figure 5: Set-up of passive sampler (acid trap). The main part of the sampler consists of an acid proof bottle with 1-2 windows at each side (size depends on size of the bottle). A drill hole at an upper edge is used to drain the bottle. Therefore windows are slightly shifted from this corner of this edge of the bottle to allow easy handling while draining. The bottle is filled through the mouth at the top with sampling solution and fixed with the mouth to the lid which is screwed to the stainless steel roof. Roofs can be attached by a flexible screw fixing to the steel rod to allow adjustment to different canopy heights by using only one length of the steel rod.

no.	Components of passive sampling system
1	Steel rod with attachment point for plastic roof (length 0.5 m)
2	stainless steel roof
3	Cubic passive sampler made from an acid resistant PE bottle with 1-2 mosquito net covered windows on each side. At one upper edge a hole is drilled for draining used sampling solution. Shift windows slightly from the center to allow dispensing of solution through the hole with low risk of spilling through the windows. Fix lid of the bottle with 2 screws to the steel roof. Screw bottle on the lid.
4	Small vials for transport and refilling of sampler solution (20 ml 0.05 M H_2SO_4 solution) — several hundred for large trials
5	Large containers/bottles with sampler solution (0.05 M H_2SO_4 solution) for all vials
6	Bottle-top dispenser to fill the small containers with collector solution (20 ml)
7	Freezer for sampling solution storage

Table 3: Components needed to set-up a passive sampler and for carrying out passive sampling measurements.

3. After Going to the Field and Making Measurements

- Take the following additional equipment to the field for ease of operation: paper towels and bag for disposal of used paper towels, clipboard for making notes, tray for (sorted) vials, acid proof gloves for handling of the acid solution.
- Carry out measurement by DTM and exchange passive sampler solutions simultaneously or without large time differences, especially at the beginning of a measurement campaign or at expected high NH_3 losses.
- Make control measurement with the DTM (step 3.4) on unfertilized control plots at the beginning and the end of each measurement date. Follow this sequence: control, treatments, control.
 - Measure over 3-6 days to obtain reliable ammonia loss measurements for the time span of a whole day by accounting for changing emissions due to varying temperatures and wind speeds. Make measurements at these times: early morning (shortly after sunrise), late morning, early afternoon, late afternoon, and shortly before sunset.
 - If soil rings are used, press rings at two easily accessible available locations within the plots into the soil. Use four rings for each location and take care that distances between rings at each location can be reached by one of the four connected chambers of the chamber system (**Figure 3**). Insert soil rings into the soil by a wooden board placed on the rings to evenly distribute the pressure.
 - Cover the rings with small plastic sheets during fertilization of the plots if synthetic fertilizer (e.g. calcareous ammonium nitrate, urea) is applied. Immediately following the machine application, apply the required aliquot of fertilizer with high accuracy by hand within the area of the soil rings.
 - In case of manure fertilization, first apply manure (e.g. by trail hoses), then insert rings. Take care that the fertilizer is very evenly distributed.

Note: As good empirical value for valid measurements after trail hose fertilization the following distribution of chambers was shown to provide accurate results^{13,14}: two chambers on fertilized track, two chambers on the unfertilized area in between. If there is a very large amount of slurry with low viscosity applied by trail hoses also place four chambers onto the fertilized soil.

4. Procedure for measurement with DTM

1. Set the stroke number to 50 if an automatic pump is used for ease of operation.
Note: This way stroke numbers in between 5 and 50 strokes can be easily applied, stroke numbers smaller than 50 strokes can be achieved by stopping the pumping process.
2. Rinse the DTM system with NH₃-free air by lifting the chambers to a height of about 1 m above ground and pumping air through the PTFE tubing and chambers (20-30 strokes) with the hand pump directly connected to the terminal PTFE tube of the chamber system.
3. Press DTM chambers directly into the ground to a depth of about 15 mm (depth is marked by a rim at the chamber bottom) or into soil rings (collars). Make sure soil clods do not get lodged in between the soil ring and the chamber.
4. Perform the first 20 preparatory pump strokes with a used low concentration indicator-tube (0.25-3 ppm, **Table 1**) to create quasi-steady-state conditions.
Note: Ammonia concentrations are indicated by a color change of the pH sensitive granules inside the tube from dark yellow to bluish purple. The front of this color change within the tube shows the NH₃ concentration as long as it is located within a scale printed on the tube.
5. Chose concentration range (out of three possible tubes with distinct concentration ranges; **Table 1**) of the new indicator tube to be applied in the next measurement based on the information obtained from the color change of the used tube employed in step 3.4.4.
Note: In most cases tube '0.25/a' is used. Immediately after surface application of slurry and under high temperatures tubes '2a' and '5a' should be used in many cases. This is indicated when the indicator granules of a slightly colored used '0.25/a' tube has completely turned blue after more than 10 preparatory strokes.
6. Open a new indicator tube at both ends by breaking the heads off using the tube breaker installed on the pump case.
7. Insert the indicator tube between terminal PTFE tubing and pump by pressing the tube ends into the PTFE tubing and the pump mouth. Insert tube end with lowest value on the scale printed on the tube into the PTFE tube, and the end with the highest value into the pump mouth. Start pumping up to the default stroke number by pressing the OK button of the automated pump or compressing the hand pump. Keep the pause between pre-pumping with the used tube (3.4.4) and beginning of the actual measurement as short as possible.
Note: Detailed description of pump operation is provided by the manufacturer.
8. If a hand pump is used for measurements, start the stopwatch simultaneously with the first stroke of the hand pump.
9. Terminate the measurement when the standard stroke number (10 strokes, 5 strokes with tubes 2/a) is reached and hand pump is fully relaxed (value of default stroke number shows up on display of automatic pump or on mechanical stroke counter of the hand pump). With relaxation of hand pump terminate stopwatch measurement (hand pump). Terminate automated pumping by pressing the 'stop' button when the stroke number = standard stroke number - 1 is displayed.
10. Increase stroke number to a maximum of 50 strokes if the first line indication of the lowest value of the scale printed on the tube (see **Figure 4**) is not reached after the standard stroke number. Use indicator tube readings only when at least the first line on the scale of an indicator tube is reached.
11. Do not exceed the line indicating highest value on the scale. Before this value is reached reduce number of strokes below the standard stroke number, stop pumping and record the number of strokes employed.
12. Read the farthest color change on the tube from all sides (line of coloring is often slightly slanted or uneven) and record concentration value.
13. Note the following values on the record sheet: plot, date, time of measurement, number of strokes (for hand pump: duration of measurement (sec)), reading in ppm (see Supplemental Code File - example field record sheet).
14. Clean rim of the chambers from sticking soil, manure or fertilizer components with a clean paper towel.
15. Lift DTM system from the ground and flush (see 3.4.2).
16. Make several measurements, at least two, at different locations within a plot to increase the reliability of the measurements.
17. Repeat operations 3.4.3-3.4.16 on other plots and in subsequent measurements.

5. Procedure for measurement with passive samplers.

1. Place passive samplers fastened to the steel rods in the center of the experimental plot at 0.15 m height (window of the collector) above soil or canopy surface immediately after application of fertilizer to a plot. Hurry with the slurry/fertilizer application tractor/system to install the sampler without delay. In case of dry soil, insert the steel rod into the soil with a hammer.
2. Walk with subdivided tray/bag with sorted filled acid vials for the first sampling interval (e.g. B1/P1/T1) to the passive sampler. Put on gloves before handling the vials with acid solution. Take out the vial for the respective plot and sampling interval. Unscrew the bottle of the passive sampler. Pour the 0.05 M H₂SO₄ solution from the vial into the mouth of the bottle. Screw the lid of the vial on the empty vial and return vial to the tray/bag.
3. Write plot number on the metal roof of the sampler for identification of plots.
4. Take subdivided tray with vials for two subsequent sampling intervals according to the actual and subsequent sampling intervals (or two bags for different sampling intervals) at all other exchange dates.
5. Return to the plot to exchange 0.05 M H₂SO₄ solution after the sampling interval has elapsed.
6. Remove the 0.05 M H₂SO₄ solution in the passive sampler by carefully unscrewing the passive sampler and cautiously routing the solution between the 'windows' through the discharge hole into empty original vial (e.g. B1/P1/T1). Re-fill sampler through the bottle mouth with new 0.05 M H₂SO₄ solution from subsequent unused vial (B1/P1/T2). Screw on lids with correct labeling on both vials. Fix passive sampler to the rod by screwing it on the lid connected to the steel rod.
7. Note plot number, filling-time (= emptying time → end time of previous sampling) on record sheet.
8. Exchange the sampling solutions after 3-6 hr on the first day immediately after application of organic N fertilizers. Reduce the exchange rate to 12 hr (i.e. one sampling for both night time and day time emissions) on the second day and for all samplings of synthetic N fertilizers.
Note: sampling can be extended to 24 hr, however, in summer and under high temperatures evaporation of water may be high hampering ammonia uptake.

9. Measure ammonium concentrations in the passive sampler solutions (as described below) directly after concluding the experimental campaign or freeze samples at -18 °C for maximum 1 week and measure later.

4. Calculation of NH₃ Fluxes

1. Calculation of ammonia fluxes for DTM.
 1. Create a spreadsheet to automatically perform the following calculation steps.
 2. First, calculate uncorrected fluxes obtained from the measurement with DTMs (mg N/(m²*hr)) using Eq. 1 (See Supplemental Code File) from concentration readings (ppm NH₃), measurement duration, air volume passed through system and area covered by the chamber.
 3. Convert the dimension of the uncorrected fluxes into the dimension kg N ha⁻¹ hr⁻¹ by dividing by 100.
 4. Scale these values to quantitative emissions by application of calibration formulas (Eq. 2 and 3)¹² (See Supplemental Code File) which correct the effect of *in situ* wind speed on the difference between uncorrected fluxes of the DTM and the true emissions. Apply two different equations to account for the particular conditions in two canopy classes: Eq. 1 for low canopies <0.3 m/uncovered ground and Eq. 2 for canopies >0.3 m.
 5. Do not apply the calibration equations (Eq. 2-3) when chambers do not have the same internal volume and set-up as used in the original calibration trials¹².
 6. Perform calculations only with ppm readings obtained from default stroke numbers, i.e. 5 or 10 strokes, corresponding to 0.5 L or 1 L air passed through the system. If the number of strokes deviates, correct the ppm reading and the measured time duration applied in Eq. 1 according to the number of strokes:
ppm = ppm * default number of strokes [5, 10] / actual stroke number during measurement = reading time (sec) * default number of strokes [5, 10] / actual stroke number during measurement
 7. Derive average emissions for each plot by calculating the mean flux of repeated measurements within a plot for each measurement date.
 8. Calculate mean ammonia fluxes for time intervals between two measurement dates.
 9. Calculate ammonia loss (kg N/ha) for the interval between two DTM measurements by multiplying mean flux (kg N/(ha*hr), 4.1.8) by duration of this interval (hr).
 10. Calculate cumulative total loss for a particular plot by adding up all ammonia loss values (see 4.1.9) obtained during the measurement campaign.
2. Calculation of the fluxes from the passive samplers:
 1. Discard values if solution is lost by spilling, in this case the whole plot may be removed from the data. Check whether data gap can be filled by, for example, average values from replicate plots during the same sampling interval.
 2. Determine the solution volume: subtract vial weight (see step 2.4) from weight of vial with sample solution and assume a density of 1.0 g/ml.
 3. Measure NH₄⁺ concentrations in sample solutions by using an ammonia sensitive electrode according to manufacturer's instructions.
 4. If sample volume deviates from standard volume, correct concentration: corrected ppm [mg NH₄⁺-N/L] = measured ppm * volume measurement [x ml] / default volume [20 ml]
 5. Subtract average concentration obtained from control plots from treatment plot reading for each sampling interval. Set values to 0 in case of negative values.
 6. Sum up the volume and control corrected ppm values of all measurement intervals obtained from a plot within a measurement campaign to obtain the cumulative concentration.
 7. Remove strongly positively deviating NH₃ emission values from the data set if causation of bias can be identified. Identify outliers by taking into account the wind direction during sampling as strongly deviating plots from the other replicates are probably affected by ammonia drifting from upwind high emissions plots.
3. Calculate quantitative losses from plots equipped with passive samplers by application of transfer coefficient.
 1. Obtain transfer coefficient (kg N/(ha*ppm)) by dividing final cumulative quantitative DTM loss (4.1.10) by cumulative ammonia uptake of the samplers (4.2.6) (Eq. 4). For example: DTM_{final}: 10 kg N ha⁻¹; Sampler_{cumulative}: 20 ppm [mg N/L] → transfer coefficient = 0.5 kg N/(ha ppm): 1 ppm absorbed NH₃ corresponds 0.5 kg/ha emitted NH₃-N
 2. Multiply ppm-values of all passive samplings by transfer coefficient to obtain quantitative emissions from all trials plots.
 3. Derive loss rate for a measurement interval by multiplying the ppm reading for the sampling interval by the transfer coefficient and thereafter divide by duration of sampling interval. For example (sampler uptake 12 ppm after 6 hr): 0.5 kg N ha⁻¹ ppm⁻¹ * 12 ppm / 6 hr = 1 kg N ha⁻¹ hr⁻¹.

Representative Results

In year 2014, a field trial was set up in the center of Denmark for testing the effects of several methods to reduce ammonia emissions after application of cattle slurry: incorporation with a rotary tiller, incorporation of acidified slurry and closed slot injection (injection of slurry in soil with subsequent coverage with soil). As a comparison with a high emission application technique and in particular for proper application of the chamber method trail hose application of slurry was also included. Altogether 24 plots were included in this study. Cattle slurry was applied at a rate of 80 kg NH₄⁺-N/ha.

Figure 6: Time courses of cumulative ammonia emissions from replicated field trial using different slurry application methods. Dairy cattle slurry was applied by trail hose (surface) application, surface application and subsequent incorporation, incorporation of slurry acidified with sulfuric acid, closed slot injection (injection slot covered with soil). Transfer coefficients were obtained from trail hose application treatment, error bars depict standard deviations, letters indicate significance levels (Tukey HSD) at $p < 0.05$ (one way ANOVA).

The method proved sensitive, and very high and very low emissions could be distinguished without strong interference of ammonia drifting from high emission plots to low emission plots. As a result, the method yielded highly significant differences between ammonia emissions of slurries applied by the different techniques (**Figure 6**). As theoretically expected, emissions from trail hoses were highest while incorporation reduced emissions by less than 60%. Highest loss reductions were obtained by application with closed slot injection or acidification with subsequent incorporation (about 90%). This way the method gave highly relevant information under a practical perspective, as acidification with subsequent incorporation is much more labor efficient and cheaper than closed slot injection.

In another trial carried out in Germany in 2012, the effect of urease inhibitors on ammonia emissions from urea applied to winter wheat was tested. Urea is the most problematic synthetic N fertilizer with respect to ammonia emissions but is globally most important. Emissions may be reduced when urea hydrolysis is slowed down by application of urease inhibitors. In addition, nitrification inhibitors are added to reduce the built-up of nitrate in soil which may stimulate the emission of the greenhouse gas nitrous oxide (N_2O). However, longer duration with sustained high NH_4^+ concentration may stimulate additional NH_3 emissions. In this trial both, different urea fertilizers and connected application strategies (3 versus 2 applications for fertilizers with nitrification inhibitor) were tested. The results show that ammonia emissions were strongly reduced by use of urease inhibitors (**Figure 7**) independent of the use of nitrification inhibitors. Urea only combined with nitrification inhibitors showed the highest emissions connected to soil and weather effects stimulating ammonia emissions at specific application dates. This strong effect of weather conditions at different application dates can be seen from varying time courses of ammonia emissions obtained by this method (**Figure 8**). The first two application dates showed comparatively low ammonia emissions due to low temperatures and regular but small precipitation events at the first application, while stronger rainfall decreased emissions after the first few days at the second application. At the third and fourth application higher temperatures prevailed with highest temperatures and emissions at the third application. At both dates emissions were stopped by stronger rainfall events. The strong effect of weather conditions on the intensity of emission at particular application dates explains the difference of average emissions between plain urea (3 applications) and urea with nitrification inhibitor (2 applications) (**Figure 7**) as plain urea was also applied at the fourth application date with lower relative emissions.

Figure 7: Cumulative ammonia emissions after application of different urea fertilizers for different application dates (upper graph) and cumulated for all applications (graph at the bottom). Granular fertilizers were applied at the surface to winter wheat at different growth stages, inhibitors are used to decrease ammonia emissions (UI) or to slow down transformation of nitrate to ammonium (NI) (U = urea, UI = urease inhibitor, NI = nitrification inhibitor, CAN = calcareous ammonium nitrate); U, CAN, U+UI were applied on three dates, U+NI, U+UI+NI on two dates, APP = application date, error bars depict standard error, letters indicate significance levels (Tukey HSD) at $p < 0.05$ (one way ANOVA).

Figure 8: Time courses and weather conditions of ammonia emissions from four urea fertilizers and CAN applied at different dates and doses to winter wheat. Air temperature and precipitation (upper graph) and time courses of NH_3 emissions (graph at the bottom), this Figure exemplifies that with the proposed method quite different time courses of ammonia emissions can be distinguished depending on fertilizer type (U = urea, UI = urease inhibitor, NI = nitrification inhibitor, CAN = calcareous ammonium nitrate) and weather conditions, U, CAN, U+UI were applied on three dates, U+NI, U+NI+UI on two dates, error bars depict standard deviation, letters indicate significance levels (Tukey HSD) at $p < 0.05$ (one way ANOVA).

The measurement approach allows also for testing the effect of ammonia emissions on grain yield and grain N uptake (**Figure 9**). An analysis of covariance was applied to test the effect of ammonia emissions, application strategy (2 vs. 3 applications per vegetation period) and year on grain N uptake. There existed only significant effects of ammonia loss (slope, identical between years) and year (intercept) on grain N uptake. The intercepts of the two curves show the year effect on N uptake (weather, soil conditions *etc.*) whereas the slope of the curve represents the effect of ammonia emissions on this variable. Other potential nitrogen losses affecting crop N-uptake, in particular N losses with leaching water, were monitored by intensive soil sampling and analysis (data not shown). No nitrate leaching was observed during the vegetation period. Therefore, most strikingly, the value for the slope ($= 1$) shows that ammonia losses directly translated in reduced N uptake in this trial. This also confirms the order of magnitude of ammonia losses determined by this method.

Figure 9: Relationship between ammonia emissions and grain nitrogen uptake of winter wheat fertilized with different urea fertilizers. Ammonia emissions are losses of directly plant available nitrogen which should have effects on plant growth. This graph shows that emitted ammonia measured with the calibrated passive sampling method can be related to nitrogen uptake, data analyzed by two-way ANOVA.

Discussion

It was shown that the proposed method can be used to compare ammonia emissions from different fertilizer treatments in replicated field trials and to use the obtained statistically significant information from these measurements to improve management of N fertilizers. The quantity of emissions obtained by this approach has been validated in earlier studies by comparison with micrometeorological measurements^{13,15,16}. In this paper, the quantitative validity of this approach was indirectly demonstrated by a close linear relationship between measured ammonia emissions and crop N uptake. Therefore, the method can be considered applicable for the determination of agronomically relevant nitrogen losses by ammonia emissions. The application of this approach for quantification of ammonia losses is restricted to average wind speeds ≤ 4 m/sec at 2 m height as the calibration of the chamber method was only validated under those conditions.

However, there are conditions which make the application of this approach difficult. At very low and zero wind speeds double accounting of ammonia by re-deposition at the emission site was observed²⁰ and cannot be accounted for by passive sampling. Such situations may occur at night time and under specific geographic conditions (shelter by mountains, high obstacles). In this case it is very difficult to quantify emissions as the transport behavior of emitted ammonia is uncertain¹⁴. However, this problem affects almost all ammonia emission methods and, from an emission perspective, zero emission should be assumed under such conditions or such measurement intervals should be discarded. Drifted ammonia from neighboring fields into the multi-plot experimental field poses no problem to the presented methodology as they can be accounted for by control measurements (no fertilization treatments). However, if this influence exceeds the ammonia concentrations from the treatment plots, determination of ammonia losses may be impossible. Therefore, fertilization of fields neighboring the experimental site should be controlled and no ammonia should be emitted from those fields. Under conditions when fertilizer is unevenly distributed or (unevenly) incorporated in soil, it is difficult or impossible to properly apply the chamber system as measured fluxes may not be representative for the field due to unknown fertilizer distribution. In this case another treatment has to be included with well-known fertilizer distribution which can be properly be accounted for by the placing of the chambers on soil. This can be seen from above given example where trail hose application was added as soil coverage by slurry with trail hoses was visibly known. If such measures are not possible the presented methodology cannot be applied. However, the passive sampling, which is not affected by this restriction, would at least give semi-quantitative differences between treatments though no precise quantitative emissions. The problem of not appropriately accounting for uneven fertilizer distribution is an issue with all chamber or wind tunnel systems. However, wind tunnels may have larger soil coverage, thereby averaging micro-scale unevenness in fertilizer distribution. Therefore, the chamber method used in this approach may be replaced by another method which gives quantitative emissions from plot measurements (e.g. wind tunnels). But only specific designs of wind tunnels give precise quantitative values^{10,21} and often give wrong information if they cannot be removed before rain events and replaced thereafter.

Apart of the specific problem of fertilizer distribution, there is still an ongoing debate on the validity of different ammonia loss measurement systems for precisely quantifying ammonia losses, and chamber systems are generally questioned²⁰. However, it was shown in earlier studies^{15,16} that the presented method gives the actual quantitative ammonia losses relevant for most agronomic research questions with sufficient accuracy. This is also supported by the results on grain N uptake presented in this paper. If high precision and high temporal resolution

of ammonia emissions is required for a specific research question, other methods should be applied, e.g., open path FTIR or TDL systems combined with micrometeorological modelling^{18,20}. But such systems are not applicable in replicated field trials.

High canopies >0.3 m still pose a challenge for the applied chamber system and all dynamic chamber systems including wind tunnels. Past testing showed a good agreement between the method presented in this paper and micrometeorological results. However, future testing is necessary to confirm these results.

In the long run, it would be most desirable to use the passive sampler results without a quantitative method based on a separate calibration equation. Past efforts to derive such an equation base on wind speed, temperature *etc.* were not successful. This is probably due to changing of passive sampler design — method was still under development — and canopy effects. In the future a defined design of the samplers will be proposed and after a large number of experiments the derivation of a calibration equation should be possible to be applied for this specific type of passive samplers. As an alternative to the self-made passive samplers in this study employing liquid dilute sulphuric acid, ready-made acid traps²², e.g. ALPHA samplers²³, are available where acid is bound in a matrix with no risk of spilling and more ease of handling. However, these samplers may require longer exposure times than those applied in this method²² and have not yet been tested in a similar approach.

A new method, calibrated passive sampling, to quantitatively measure ammonia emissions in replicated field trials was presented. The method proved valid under a wide range of experimental conditions and is recommended to be used under conditions with bare soil or small canopies. Results obtained from experiments with larger plant canopies should be treated more carefully. If a user is still in doubt with respect to the quantitative validity of the method, it can be tested by combining this approach with a simultaneous measurement with micrometeorological and chamber technique under identical soil and canopy conditions and subsequent comparison of emissions obtained. The passive samplers proved a very robust tool to qualitatively measure ammonia emissions in multi-plot field trials and can be used with different scaling methods to obtain a transfer coefficient. Requirement for such a scaling method is its applicability on the same plot as those employed for the passive samplers. After defining a final design of the samplers or in applying ready-made passive samplers, a separate calibration equation for such samplers could be developed and a simultaneous measurement with a quantitative method may be dispensable.

Disclosures

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