# Guidelines for the use of passive flux samplers (PFS) to measure ammonia emissions from mechanically ventilated animal houses

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# Abstract

**J. Mosquera. Guidelines for the use of passive flux samplers (PFS) to measure ammonia emissions from mechanically ventilated animal houses.**

Ammonia emissions from animal houses are an important environmental issue in the Netherlands. The current technique in the Netherlands to measure ammonia emissions in mechanically ventilated animal houses is based on ammonia concentration measurements using the chemiluminescence method (using a $NO_x$ monitor after conversion of $NH_3$ to NO), and ventilation rate measurements using a wheel-fan anemometer. This method is cost and labour intensive, which allows only for a small number of measurements per source type. During campaigns to measure emissions from animal houses, it became clear that management is an important factor in determining the emission level. Differences between animal houses of the same type and kind of animal may differ more than the variation in time and season within one animal house. These management related differences in emission factors point at the need to measure more animal houses during a shorter period. This stresses the need for development of flexible methods to be used in short term measurements, which allows monitoring the ammonia emission from a larger number of animal buildings per year. Passive flux samplers represent such an alternative. This report is meant to be used as a guideline for the use of passive flux samplers to measure ammonia emissions from mechanically ventilated animal houses. First, the validity and field of application of this technique is defined. After describing the theory behind the use of passive flux samplers, the main characteristics of this measurement system are highlighted. Next, the procedures applied to install the passive flux samplers, and to prepare and analyse them in the laboratory, are presented. Finally, the calculation method is described.

*Keywords: Passive flux samplers, animal houses, forced ventilation, ammonia emissions, guidelines*

# Preface

In 1993, a synthesis of the methods used to measure ammonia emissions from animal houses was published. A working group consisting of IMAG, ECN, PV en GD, under the supervision of the Dutch Ministry of Agriculture, Nature management and Fisheries (LNV) reported in 2002 an updated version of this overview. In this update, other components (greenhouse gases, odour, particles), and the new (more open) types of animal houses and animal houses with walking areas, were also treated.

In 2003, a project was started to define new measurement strategies and protocols to measure emissions from agricultural activities, to reduce costs of the measurements, and to allow measuring a larger number of locations. For mechanically ventilated animal houses, use of passive ammonia flux samplers has been suggested as an alternative to the current measurement method (semi-continuous measurement of ammonia concentrations with a $NO_x$ monitor and $NH_3$-converters, and ventilation rate measurements using a fan-wheel anemometer). This report presents the guidelines of the implementation of this new measurement protocol in practice.

The Dutch Ministry of Agriculture, Nature management and Fisheries (LNV) is acknowledged for making this study possible.

Dr. Ir. C.E. van ‘t Klooster

Director Business Unit IMAG

# Contents

# 1 Scope, validity and field of application

Ammonia is an important environmental problem in the Netherlands, leading to acidification, eutrophication and loss of biodiversity. In the Netherlands, approximately 94% of the Dutch ammonia emissions (157 kton in the year 2000) originate from agricultural activities (RIVM and CBS, 2001). Animal houses are an important contributor to these emissions (46% of total ammonia emissions from agriculture in 1997). The aim of the Dutch government is to reduce in 2010 the total ammonia emission to approximately 70% (100 kton) compared with the year 2000 (Sliggers, 2001). Besides, the contribution from Dutch agriculture to the total ammonia emission should be reduced to 86% (86 kton) in 2010.

The current technique to measure $NH_3$ emissions from mechanically ventilated animal houses is based on ammonia concentration measurements (using a $NO_x$-analyser in combination with $NH_3$-convertors), and ventilation rate measurements (using a wheel-fan anemometer) in the ventilation shafts of the animal house (Groenestein, 1993; Groenestein *et al.*, 2001; Scholtens, 1993; Phillips *et al.*, 1998; Groot Koerkamp *et al.*, 1998; Demmers *et al.*, 1999). The ammonia emission can then be calculated as the product of the $NH_3$ concentration and the ventilation rate. By measuring the ammonia emissions from a specific animal housing system ammonia emission factors can be determined. Costs of these measurements on equipment, maintenance and labour are high. Due to these high costs the number of animal houses that can be measured is relatively small. One advantage of using this method is that it is possible to follow and understand the emission processes on a detailed basis. However, differences between animal houses of the same type and kind of animal may differ more, than the variation in time and season within one animal house. These management related differences in emission factors point out the need to measure more animal houses during a shorter period. This stresses the need for development of flexible methods to be used in short term measurements, which allows monitoring the ammonia emission from a larger number of animal buildings per year.

To determine ammonia emission factors, passive flux samplers (PFS) represent an alternative that allows monitoring $NH_3$ emissions from a large number of animal houses at a low price (Michorius and Scholtens, 1995; Monteny *et al.*, 1999; Mosquera *et al.*, 2002). Passive flux samplers collect ammonia at a rate proportional to the wind velocity of the air stream passing it without the need of a pump or other instrument requiring power supply. In this way, wind speed measurements are not necessary. Passive flux samplers are easy to construct, transport and handle, and have little lab requisites. However, as other passive sampling methods, they are based on diffusion to a reaction surface, which leads to a low sampling rate and, therefore, the need for long sampling periods.

The scope of this report is to show how to implement passive flux samplers to measure ammonia emissions from mechanically ventilated animal houses. The procedure reported here is applicable to animal houses with ventilation shafts located high enough to avoid interferences or damage of the sampling material caused by the animals. In section 2, the terms and symbols of interest for this study are reported. Section 3 describes the principle of measurement with passive flux samplers. In section 4, results of the tests performed to characterise and optimise the passive flux samplers, are presented. After section 5, which describes the sampling strategy to be used, section 6 presents the procedure used for the preparation and analysis of the samples. Finally, section 7 shows how to calculate and report the measured data.

# 2 Terms, definitions and symbols

## 2.1 Terms and definitions.

**Absorption**: the process whereby one substance is physically taken into and included within another substance.

**Absorption capacity**: the ability of a medium to absorb a particular component.

**Absorption medium**: material used to absorb a particular component.

**Accuracy**: closeness of agreement between test result and the accepted reference value. When applied to a set of observed values, describes a combination of random components and a common systematic error or bias component.

**Ammonia**: The molecular formula for ammonia is $NH_3$. Ammonia is one of the most important inorganic nitrogen compounds in atmospheric water droplets. It reacts with strong acids and is one of the few basic, gas phase atmospheric components. Atmospheric ammonia can also enhance the nucleation rate and the production of new particles in the atmosphere.

**Ammonia emission**: The release of ammonia from a particular source.

**Breakthrough**: discharge of a particular component caused by overloading of the absorption medium.

**Capturing efficiency**: the capacity of an absorption medium to capture a specific component.

**Detection limit**: lowest value of the air quality characteristic which, with 95% probability, can be distinguished from a zero sample.

**Discharge:** flow that passes a given point within a given period of time.

**Expected value**: the value approached by the average value with an increasing number of measurement values.

**Flow rate:** the rate at which a volume of air moves through a particular system (ventilation shaft, tubes).

**Forced ventilation**: The process of moving air (changing) into and out of an interior space by mechanically induced (forced) means.

**Measurement:** any physical dimension that is described by units.

**Mechanical ventilation**: see forced ventilation.

**Passive sampling**: the collection of airborne gases of particles at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane, without the active movement of air through an air-sampling pump.

**ppm**: parts of analyte per million parts of sample.

**Precision**: closeness of agreement between independent test results obtained under prescribed conditions. Precision depends only on the distribution of random errors and does not relate to the true value or the accepted reference value. The measure of precision is usually expressed in terms of imprecision and computed as standard deviation of the test results. Higher imprecision is reflected by a larger standard deviation. 'Independent test results' means results obtained in a manner not influenced by any previous result on the same or similar material.

**Random errors**: unpredictable errors which average to zero.

**Sampling strategy**: the general or specific approach used for a set of measurements, both in time and space.

**Specific gravity:** is the ratio of the density (in g/mL) of the compound at standard conditions relative to the density of water at the same conditions. Practically, you can assume that specific gravity equals density, therefore if concentrated sulphuric acid has a specific gravity of 1.832, it has a density of 1.832 g/mL.

**Test result**: the value of a characteristic obtained by completely carrying out once a specific measurement.

**Ventilation fold**: the rate at which indoor air enters and leaves a building. Expressed as the number of times the indoor air is renewed (refreshed) per unit time (air changes per hour).

## 2.2 Symbols, descriptions and units

$A_o$ = surface area of hole in orifice [$m^2$]

$A_p$ = projected area of the object in the direction of motion [$m^2$]

$A_s$ = cross section of the sampler [$m^2$]

$A_{vs}$ = surface area of the ventilation shaft [$m^2$]

$B$ = ratio orifice diameter ($D_O$) to channel diameter ($D_2$)

$C$ = coefficient of discharge []

$C_{NH3}$ = ammonia concentration [ppm]
$C_{NH3}^{in}$ = ammonia concentration in the incoming air [ppm]
$C_{NH3}^{out}$ = ammonia concentration in the outgoing air [ppm]
$D$ = diffusion coefficient [cm$^2$ s$^{-1}$]
$Eff_{coat}$ = efficiency of the coating []
$E_{NH3}$ = ammonia emission [mg.s$^{-1}$]
$F$ = air flow through the tube [cm$^3$ s$^{-1}$]
$F_D$ = drag force [N]
$F_{NH3}$ = ammonia flux [mg.m$^{-2}$.s$^{-1}$]
$k$ = tube depletion rate constant [min$^{-1}$]
$K_D$ = drag coefficient []
$K_O$ = orifice meter constant []
$K_S$ = flux sampler constant []
$L$ = length of the coating in the tube [cm]
$L_0$ = initial length of the coating in the tube (cm)
$P_O$ = pressure drop over the orifice meter [Pa]
$Q_{NH3}$ = ammonia flow rate [ng min$^{-1}$]
$S_{NH3}$ = amount of ammonia captured in the sampling tube [mg]
$t$ = time [min]
$t_1$ = starting time of exposure
$t_2$ = end time of exposure
$T_{cap}$ = tube capacity [ng]
$v_m$ = relative velocity between object and medium [m.s$^{-1}$]
$V_{meas}$ = air velocity measured in the wind tunnel [m.s$^{-1}$]
$V_L^c$ = air velocity in the wind tunnel corrected [m.s$^{-1}$]
$v_0$ = air velocity through orifice [m.s$^{-1}$]
$v_s$ = wind speed [m.s$^{-1}$]
$Y$ = expansion factor []
$\alpha$ = angle between orientation of the sampler and the wind direction
$\rho$ = air density [kg.m$^{-3}$]

# 3 Passive flux samplers: measurement principle

## 3.1 History

Leuning *et al.* (1985) reported the first form of passive flux sampler based on an internal (oxalic) acid coating to capture any ammonia in air flowing at a controlled rate through the sampler. This sampler was equipped with vanes and pivots to keep it pointing always upwind. However, in periods with low wind speeds, the system can have adjustment (orientation) problems and react with some delay to changes in wind direction.

Schjoerring *et al.* (1992) reported a simpler passive flux sampler, originally developed by Ferm (1986). This sampler consists of a combination of 4 glass tubes coated with oxalic acid, in two sets. One set consists of two tubes coupled in series, with a flow restriction (orifice, metallic plate with a hole of 1 mm in the middle) placed at the end of the set, at the right side. The other set of tubes has the restriction at the opposite side. A combination of both sets represents a sampler. As with Leuning's sampler, the principle was to capture ammonia from air flowing through the sampler, quantitatively, in an oxalic acid coating. The sampler, now commonly known as the 'Ferm tube' has been widely used, mainly for measuring fluxes from non-point sources but also for fluxes from manure heaps (Karlsson, 1994; Phillips *et al.*, 1997), slurry stores (Hess and Hügle, 1994; Karlsson, 1996; Sommer *et al.*, 1996; Phillips *et al.*, 1997), and livestock buildings, both force-ventilated (Michorius *et al.*, 1995) and naturally ventilated (Phillips *et al.*, 1998b).

Scholtens (1996) describes a patent for a new passive flux sampler design, based on the passive flux sampler for ammonia proposed by Ferm (1986). In the improved sampler (figure 1) the orifice is placed in the middle of the sampler, connecting two absorption chambers. The second chamber is used as a control for the measurements. If the control tube is also loaded with ammonia, this indicates that either breakthrough of ammonia, or a change in wind direction (the background and source labels in figure 1 are exchanged), has occurred. This symmetrical design minimises the number of analysis but more importantly it greatly improves and simplifies validation procedures.

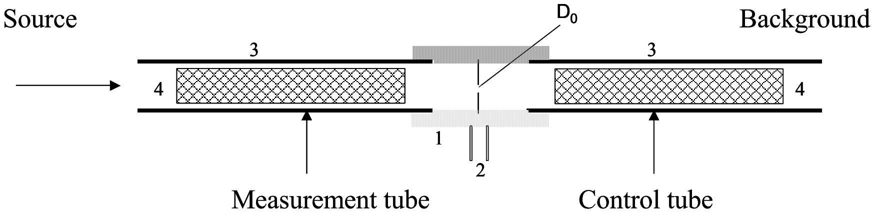

**Figure 1** Schematic drawing of the improved flux sampler. (1) Connecting piece with orifice; (2) Pressure points (optional); (3) Tube; (4) Absorption medium (for measurements in animal houses, filter paper strip loaded with sulphuric acid); $D_o$, orifice diameter

For test purposes (determination of the sampler flux constant) the sampler can be equipped with pressure points (radius pressure taps located at a distance from the orifice plate of approximately ½ $D_o$ (orifice diameter)). In the absorption chambers a specific gas or type of gases can be bound to a gas-absorbing agent. For measurements in animal houses, sulphuric acid loaded glass fibre paper inserts are used as absorption medium, because they have a higher binding capacity than an oxalic acid coating on the wall of a tube of similar size.

## 3.2 Theory

The main characteristic of a passive flux sampler is its ability to sample at a rate proportional to the wind speed outside the sampler. This section summarises the theory supporting this fundamental property of the sampler (Scholtens and Monteny, 1999).

### 3.2.1 Drag force on a cylindrical tube

When there is a relative motion between an object and a surrounding medium (fluid or air), a drag force will be created by the medium (Perry *et al.*, 1985):

$$F_D = K_D \cdot \tfrac{1}{2} \rho \cdot v_m^2 \cdot A_p \qquad (1)$$

For a passive flux sampler (cylindrical tube, figure 2),

$$A_p = A_s \cdot \cos(\alpha) \qquad (2)$$

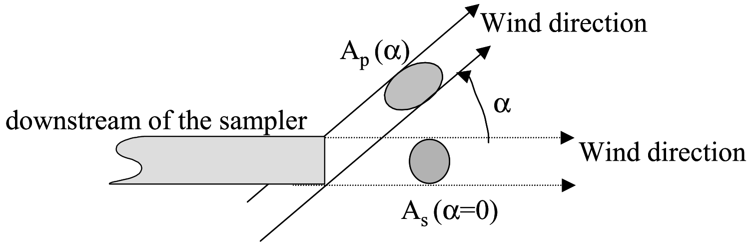

**Figure 2** Schematic drawing of the projected area for different wind directions. $\alpha$: angle between orientation of the sampler and wind direction; $A_s$, $A_p$: projected area for $\alpha=0$ and $\alpha \neq 0$

And combining equations (1) and (2):

$$F_D = K_D \cdot \tfrac{1}{2} \rho \cdot v_m^2 \cdot A_s \cdot \cos(\alpha) \qquad (3)$$

The drag force tries to move the object with the same velocity as the medium. In the case of a passive flux sampler the tube is stationary and $v_m$ equals the wind speed ($v_s$). This results in an under pressure downstream of the sampler, proportional to the drag force, which can be described as:

$$P_D = \frac{F_D}{A_s} = K_D \cdot \tfrac{1}{2}\rho \cdot v_s^2 \cdot \cos(\alpha) \tag{4}$$

The pressure drop over the sampler depends on the wind speed ($v_s$), the density of the air, and has a cosine dependency with the wind direction ($\alpha$).

### 3.2.2 Air velocity through the sampler

The main role of the orifice in a passive flux sampler is to regulate the amount of air flowing through the sampler, but having the orifice in the centre of the sampler, well shielded from turbulence, it can also be used as a flow meter. The relation between discharge through an orifice meter and the pressure drop over the orifice can be described using (Perry *et al.*, 1985):

$$P_O = \frac{(1-B^4)}{Y \cdot C^2} \cdot \tfrac{1}{2}\rho \cdot v_O^2 = K_O \cdot \tfrac{1}{2}\rho \cdot v_O^2 \tag{5}$$

### 3.2.3 Flux sampler constant

Both equation (4) and equation (5) show a square root dependency between air velocity and pressure drop. Assuming $P_D = P_O$:

$$v_O = \sqrt{\frac{K_D}{K_O}} \cdot v_s \cdot \cos(\alpha) = K_S \cdot v_s \cdot \sqrt{\cos(\alpha)} \tag{6}$$

Where $K_S$ is the flux sampler constant. This shows that discharge through the orifice has a square root cosine dependency with the wind direction, instead of a cosine dependency as given by Ferm (1986). With $\cos(\alpha)=1$ the discharge through the orifice is linear proportional with the wind speed.

### 3.2.4 Breakthrough of ammonia

No or negligible breakthrough of ammonia is essential for the correctness of the measurements. As stated before, the flux sampler has two absorption chambers, and if the sampler works properly the first chamber should absorb all the ammonia sampled in the air. The second chamber is used as a control, to check if this really occurs. If the control chamber is also loaded with ammonia, meaning that not all the ammonia is absorbed in the first chamber, an underestimation of the ammonia flux is obtained.

When the air is sampled through the flux sampler, the ammonia gas in the air diffuses to the coating surface, where it is absorbed through reaction with the coating acid. Assuming that the flow in the tube is laminar, that all $NH_3$(g) molecules arriving to the coating surface are absorbed, and that the capacity of the absorption medium is infinite, Gormley and Kennedy (1949) proposed the following solution for the transport and diffusion equation for a flow through a cylindrical tube:

$$\frac{C_{NH3}^{out}}{C_{NH3}^{in}} = 0.819 \cdot e^{-3.6568 \cdot \frac{\pi \cdot D \cdot L}{F}} + 0.0976 \cdot e^{-22.3 \cdot \frac{\pi \cdot D \cdot L}{F}} + 0.032 \cdot e^{-57 \cdot \frac{\pi \cdot D \cdot L}{F}} \tag{7}$$

When $C_{NH3}^{out} / C_{NH3}^{in} \geq 0.1$, the second and higher terms of equation (7) are negligible (Bemgård *et al.*, 1995), which is normally the case for passive flux samplers. The efficiency ($\mathrm{Eff}_{coat}$) of the coating is then:

$$Eff_{coat} = 1 - \frac{C_{NH3}^{out}}{C_{NH3}^{in}} \tag{8}$$

Therefore, the absorption efficiency of the coating is a function of the gas flow rate (*F*), the diffusion (*D*) and the length (*L*) of the coating.

However, the assumption of Gormley and Kennedy (1949) that the capacity of the absorption medium is infinite is not correct. Because part of the reagent is used to absorb ammonia, the effective length of the coating, L, is decreasing with time at a rate depending on concentration and airflow through the tube. Braman and Shelley (1982) proposed the following relationship to explain the decrease of the effective length of the coating:

$$\begin{gathered} L = L_0 \cdot e^{-kt} \\ k = \frac{Q_{NH3}}{T_{cap}} \end{gathered} \tag{9}$$

And combining equation (9) with equation (7):

$$\frac{C_{NH3}^{out}}{C_{NH3}^{in}} = 0.819 \cdot e^{-3.6568 \cdot \frac{\pi \cdot D \cdot L_0}{F} \cdot e^{-k \cdot t}} \tag{10}$$

This formula can be used to describe the first phase of the ammonia capturing process, when the effective length is still quite large ($C_{NH3}^{out} / C_{NH3}^{in} \geq 0.1$).

# 4 Sampler characterization and optimalisation

This section presents the main characteristics of the flux sampler: flux sampler constant, cosine dependency, detection limit, accuracy, absorption medium, absorption capacity and tube length. The flux sampler consists of a set of two tubes (glass or synthetic) joined by a connecting piece with an orifice in the middle (figure 1). Both tubes are 10 cm long (see section 4.5) and have a 7mm internal diameter. Two different orifices are considered: when high ammonia concentrations are expected, a small orifice (diameter=0.5 mm) is used to restrict the flow through the sampler. When low concentrations are expected, a bigger orifice (diameter=1mm) is used. Sulphuric acid is used as absorption medium (see section 4.5), since it has a high absorption capacity for ammonia. In general, glass fibre filter papers, introduced in the sampler and coated with sulphuric acid, will be used as absorption medium, since it has a higher absorption capacity than the sampler coated with the acid in the wall.

## 4.1 Flux sampler constant

The relationship between air velocity and pressure drop over the orifice meter was tested in a wind tunnel (figure 3). The sampler was placed horizontally ($cos(\alpha)=1$) in the wind tunnel. Two different orifice sizes were used (0.5 and 1.0 mm). A range of air velocities was applied (0 -15 m.s$^{-1}$) and the pressure drop (corrected after calibration with the calibration pressure meter “DIGIMA >>premo<<”) over the orifice meter in the sampler recorded. The measured air velocities were corrected using the Lambrecht correction:

$$V_L^r = \left(C_5 \cdot V_{meas}^5 + C_4 \cdot V_{meas}^4 + C_3 \cdot V_{meas}^3 + C_2 \cdot V_{meas}^2 + C_1 \cdot V_{meas}^1 + C_0\right) \qquad (11)$$

Where:

| | $V_{meas}$ < 2.1 m.s$^{-1}$ | $V_{meas}$ > 2.1 m.s$^{-1}$ |
|---|---|---|
| $C_0$ | -0.00499786 | 0.649231389500 |
| $C_1$ | 1.2399491 | 0.372856651700 |
| $C_2$ | -1.141792948 | 0.247812975900 |
| $C_3$ | 1.885757356 | -0.03212594340 |
| $C_4$ | -1.166629163 | 0.00173713950 |
| $C_5$ | 0.242920864 | -0.0000330851 |

**Figure 3** Picture of the wind tunnel used in the measurements

A linear regression on the results gives the $K_D$ value 1.29 (1.26) for the sampler design with a 0.5 mm (1 mm) critical orifice. The regression line is forced through zero (figure 4, for the sampler with a 0.5 mm critical orifice).

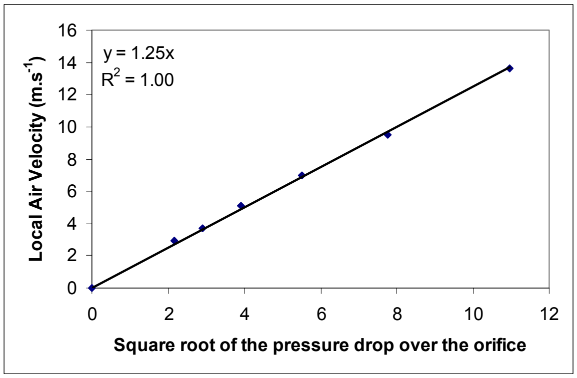

**Figure 4** Relation between the outside local air velocity (m $s^{-1}$) and the square root of the pressure drop over the orifice (0.5 mm) in the sampler (√Pa)

The relationship between air velocity through the orifice meter and the pressure drop over the orifice meter was measured using a soap bubble meter. A range of pressure drops (0-120 Pa) was applied and the airflow registered. In this case the pressure is measured directly. Therefore no corrections are needed. As above, two different critical orifice sizes (0.5 and 1 mm) were tested. The internal diameter of the orifice meter was used to calculate the air velocity. From the results a linear regression is used to calculate the orifice meter constant $K_O$ (2.44 and 2.79 for the sampler with a 0.5mm and 1 mm critical orifice, respectively). Figure 5 shows the relation obtained for the sampler with a 0.5 mm critical orifice.

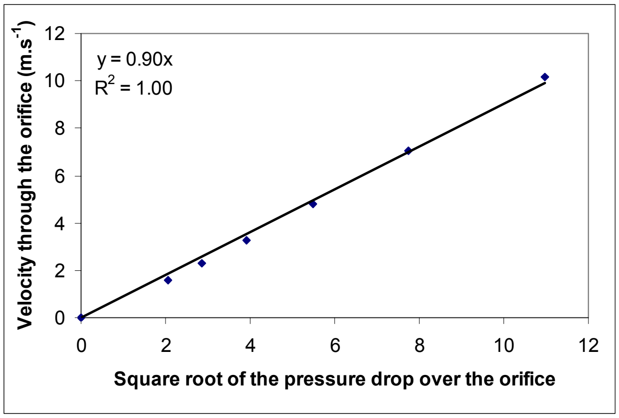

**Figure 5** Relation between the air velocity through the orifice (m $s^{-1}$) and the square root of the pressure drop over the orifice (0.5 mm) in the sampler ($\sqrt{Pa}$)

The flux sampler constant ($K_s$) can then be calculated using equation (6), leading to the values $K_s=0.73$ and $K_s=0.67$ for the sampler with a 0.5 mm and 1 mm critical orifice, respectively. For measurements with passive flux samplers in animal houses (indoor), a critical orifice of 0.5 mm is used.

## 4.2 Cosine dependency

The use of passive flux samplers in or under a ventilation shaft of a mechanically ventilated building to measure gaseous ammonia emissions is straightforward because $\cos(\alpha)=1$.

## 4.3 Detection limit

The detection limit is based on the instrument (spectrophotometer) used for the chemical analysis in the laboratory. Because of the procedure used to determine the amount of ammonia captured in the sampler (section 6), it is necessary that the filter paper has absorbed a minimum of 1.62 µg $NH_4$-N.

## 4.4 Absorption capacity

To make an estimate of the maximum absorption capacity of the sampler, the following information, provided by the coating procedure described in section 6, is necessary:

1. Acid: $H_2SO_4$ (98-100%), molecular weight (MW)=98.087 g.mol$^{-1}$, specific gravity=1.832 g.mL$^{-1}$
    a) First, calculate the mass of 1L of solution

$$\frac{1.832\, g\ concentrated\ solution}{mL\ concentrated\ solution} = \frac{1.832 \cdot 10^3\ g\ concentrated\ solution}{L\ concentrated\ solution}$$

b) The solution is 98% by mass ⇒

$$\frac{1.832 \cdot 10^3\ g\ concentrated\ solution}{L\ concentrated\ solution} \cdot \frac{98\, g\ H_2SO_4}{100\, g\ concentrated\ solution}$$
$$= \frac{1.795 \cdot 10^3\ g\ H_2SO_4}{L\ concentrated\ solution}$$

c) To find the molarity:

$$\frac{1.795 \cdot 10^3\ g\ H_2SO_4}{L\ concentrated\ solution} \cdot \frac{1\, mol\ H_2SO}{98.087\ g\ H_2SO_4} = 18.3\, M$$

2. Solution: 5 ml $H_2SO_4$ (98-100%), 25 ml ethanol 100%, and ether 100% to obtain a 100 ml solution

3. 1 ml of this solution is used to coat the filter paper (absorption medium)

4. The following reaction between $NH_3$ and $H_2SO_4$ occurs:

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4^+)_2 SO_4$$

That means that for every mol of $H_2SO_4$, 34 gr of $NH_3$ (1 mol $NH_3$ = 17 gr $NH_3$) will be absorbed.

Using this information, the ammonia captured in the sampler has an upper limit of:

$$NH_3^{\max}(gr) = 18.3 \cdot \frac{5}{100} \cdot \frac{1}{1000} \cdot 2 \cdot 17 \qquad \Rightarrow \qquad NH_3^{\max}(gr) = 0.031$$

## 4.5 Capturing efficiency

The ammonia capturing efficiency of the sampler depends on several parameters such as tube length, acid strength, airflow and ammonia concentration. Breakthrough curves were determined while varying these parameters (Haest, 1997). Glass fibre filter papers, coated with oxalic acid and inserted into the sampler, showed more absorption capacity than the sampler coated with oxalic acid in the wall. Weak acids (formic acid and acetic acid were used in these tests) showed a low efficiency. A higher absorption capacity was measured when using sulphuric acid instead of phosphoric acid coating the filter paper. To determine the influence of the tube length on the capturing efficiency, 2 tubes with filter papers coated with sulphuric acid were connected in series. Different flow and ammonia concentration values were used to load the papers during a period of 30 minutes. After that, the filter papers were cut in pieces and analysed. From the experiments (Haest, 1997), a length of 10 cm was considered to be the most efficient.

## 4.6 Accuracy

To test the performance of the passive flux samplers to measure the ammonia emission from mechanically ventilated animal houses in practice, measurements were performed in four different compartments of a house for veal calves (see Hol and Groenestein (1997) for a complete description of the measurement location). Each compartment was mechanically ventilated with two fans in the top of the building: one of the fans was continuously working, while the second fan was switched on when the animal house temperature was above 10 °C. When the second ventilator was not operating it was closed with a ventilation flap. To measure the ammonia emission from the animal house, two techniques were used: passive flux samplers placed under the ventilation shaft and a reference method (1. $NO_x$-analyser coupled with $NH_3$ converters for ammonia concentration measurements, and 2. Wheel-fan anemometer for ventilation rate measurements; Scholtens, 1993; Hol and Groenestein, 1997).

A statistical test (t-test) was performed to see the accuracy of passive flux sampler measurements when compared with the reference method. This statistical test shows whether or not the difference between the measurements obtained with both methods (reference and passive flux samplers) is significant. The results of this analysis are summarised in table 1. We can see that the differences between both methods were not significant (at the 95% significance level) for the three group-housing systems. In the individual-housing system, the correlation between both methods was good but the differences were significant. When comparing the results in both ventilation systems, or from the animal house as a whole, the differences between both methods were not significant.

**Table 1** Statistical t-test (95% significance level) of the difference between the passive samplers and the reference system for each housing system and ventilation type

| | Housing system | | | | Ventilation type | | Total Animal House |
|---|---|---|---|---|---|---|---|
| | Group | | | Individual Boxes | With lid | Without lid | |
| | Flushing | Synthetic | Reference | | | | |
| Number of measurements | 6 | 7 | 5 | 10 | 29 | 28 | 28 |
| Average of \|NOx\|-\|PFS\| (g.h$^{-1}$) | 1.98 | 0.78 | 0.71 | -1.54 | 0.15 | 0.36 | 0.20 |
| Standard deviation | 3.15 | 2.24 | 3.32 | 1.26 | 1.82 | 2.17 | 2.66 |
| \|t\| | 1.54 | 0.92 | 0.48 | **3.87** | 0.44 | 0.88 | 0.39 |
| t (95%) | 2.57 | 2.45 | 2.78 | 2.26 | 2.05 | 2.05 | 2.05 |

Passive flux samplers represent, when looking at these results, an accurate method to measure ammonia emissions from this type of mechanically ventilated animal houses. However, as shown in figure 6, the data shows still a high variation (dispersion). This variation, however, is attributed not only to the passive flux sampler measurements, but also to the reference method. The data presented in figure 6 as squares, showing the overload (breakthrough) of the flux sampler with ammonia, were not used in the linear regression. For a single measurement, the results obtained with both methods show large differences (40-50% for the two points where ammonia emission measured with the passive flux samplers was the lowest, for the rest differences up to 30%). However, when all measurements are combined, the "average" difference between both methods is lower than 3%.

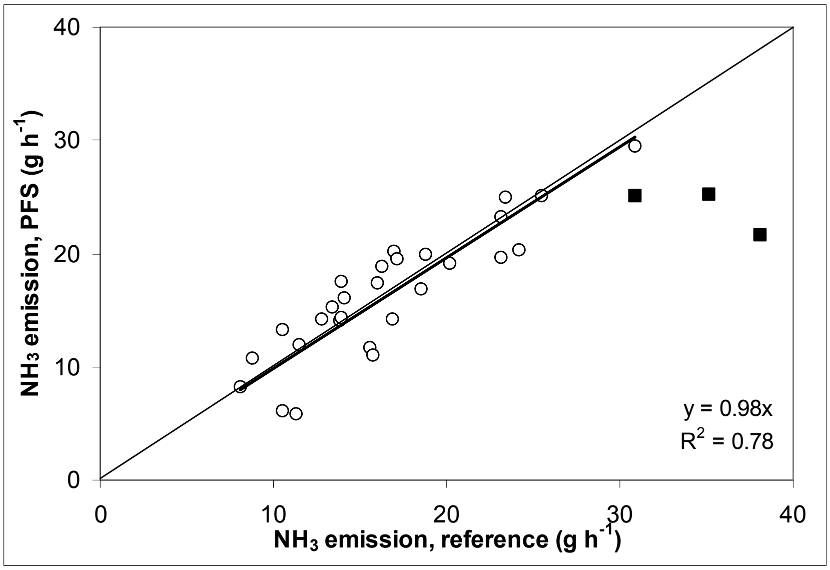

**Figure 6** Comparison between a reference method (1. $NO_x$-analyser coupled with $NH_3$ converters for ammonia concentration measurements, and 2. Wheel-fan anemometer for ventilation rate measurements), and passive flux samplers (PFS) for measuring ammonia emissions (g.$h^{-1}$) from mechanically ventilated buildings. The squares represent observed overload (breakthrough) of the passive flux samplers, and were not used in the linear regression calculations

# 5 Installation procedure

## 5.1 Requirements

Before starting with the installation of the equipment, the strategy to be used should be clearly defined. During the first visit to the measurement location, it should be controlled if the animal house satisfies the following requisites:

1. The main characteristic of the passive flux sampler is that it samples at a rate proportional to the wind velocity of the air stream passing through it. For animal houses, this means that inlets and outlets should be clearly defined. This is generally a problem for naturally ventilated animal houses, but not for mechanically ventilated animal houses, where the air usually leaves the house through the ventilation shafts used to regulate the ventilation rate in the animal house.

2. The ventilation shafts must lead directly the air outside the building. For animal houses where the air goes previously to a central passage above the ceiling, and afterwards outside the building, further revision is necessary.

3. Samplers should be located in every outlet (ventilation shaft) to have a good estimate of the emission from the animal house.

4. The ventilation shafts should not be too low. This to avoid the animals to be in direct contact with the equipment.

5. The flux samplers and the ventilator in the ventilation shaft should be separated for a minimum distance of approximately the diameter of the ventilation shaft.

6. Although not necessary, it is convenient that the ventilation shafts are not too high, or located directly above the animal compartments. This makes it easier to handle and change the samplers.

It should be registered whether or not the ventilation shaft is continuously open, or if it is provided with a ventilation lid that closes under specific conditions. It should also be clearly defined who the contact person is, both within IMAG and on the farm.

## 5.2 Installation

A system is designed which allows varying the position of the samplers relative to the axis of the ventilator (figure 7). To have a representative sample, the flux sampler should be located where it can measure at the average wind speed of the wind speed profile in the ventilation shaft for a particular ventilation rate. Relative to the ventilator axis, this leads to a distance between 1/2 and 2/3 of the ventilation shaft radius for a laminar flow. To have a better estimate of the ammonia emission, a set of two samplers is placed under the ventilation shaft as shown in figure 7. Both samplers are at the same distance relative to the ventilator axis. The designed system allows to increase the number of samplers and to change their position. To optimise the performance of this measurement system, the effect of changing the number and position of the samplers on the measured emission, under practical conditions, should be studied.

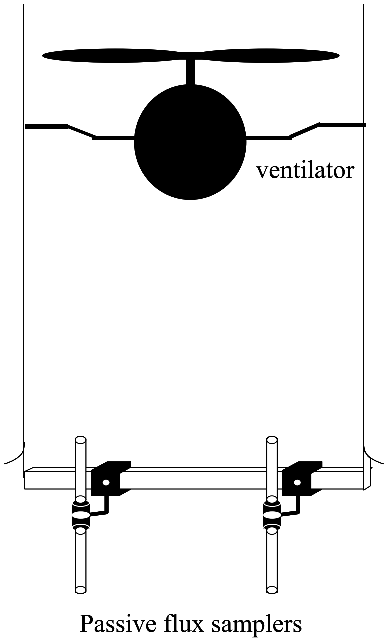

**Figure 7** Schematic representation of the use of passive flux samplers under a ventilation shaft

## 5.3 Regular activities at the measurement site

The following activities are performed regularly, generally on a weekly basis, and registered in a logbook:

- Date and time where the measurement period started and ended.
- Controlling whether or not there is dust in the samplers or close to the samplers.
- Changing the samplers and filling the corresponding form (see appendix A).
- Recording the data available of the ventilation activity (ventilation on/off).
- Although not necessary, it is convenient to record the ventilation rate for every ventilator.

## 5.4 Procedure to change the samplers under practical conditions

In this section, the procedure to follow to change the samplers under practical conditions is described. While this procedure will be performed in some cases by IMAG personal, this is not a requisite, and can also be performed by the farmer itself.

### 5.4.1 New samplers

In some cases, instead of having separately the sampling tubes and the central part, the farmer will receive a box with the whole sampler already labelled. This reduces the time needed to change the samplers, as well as the error associated with an extra manipulation of the sampler.

0) To avoid contamination of the sample, use gloves during the whole process.
A) Remove the top from one end of a sampling tube, which does not have a marked line. Introduce the open end of the tube in the central part of the sampler and repeat this process with a second sampling tube (figure 8).
B) Place the complete sampler at the right location under the ventilation shaft.
C) Remove the tops from both ends of the sampler.

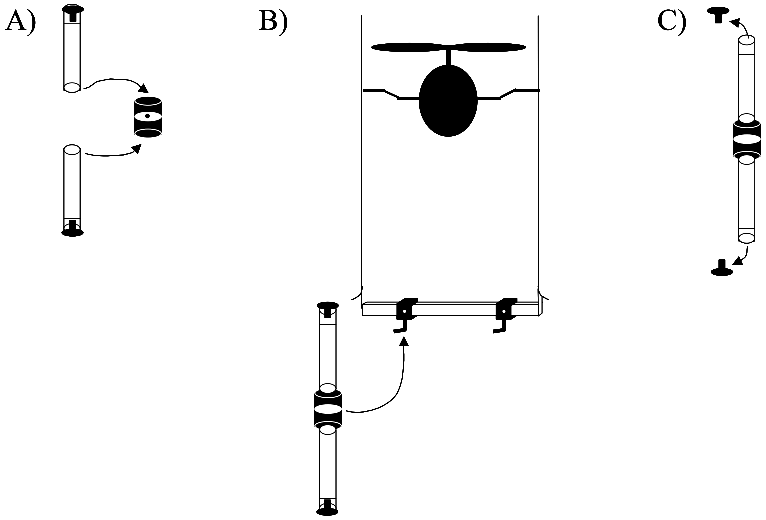

**Figure 8** Procedure to install samplers for new measurements

### 5.4.2 Remove samplers

If possible, it is desirable to proceed with steps A-B (figure 9) before taking the samplers out, i.e. while the samplers are still hanging under the ventilation shaft. This will reduce contamination problems and errors in the identification of the samplers. If this is not possible (difficult access to the ventilation shafts, risk of animals in the neighbourhood, etc), we will first proceed with step C (figure 9).

In some cases, the farmer will be asked to do the whole procedure and to send to IMAG the complete sampler for analysis. Previously, the farmer will receive the complete sampler already labelled. In this case, steps B and D in figure 9 can be skipped.

The following procedure should be performed for every sampler:

0) To avoid contamination of the sample, use gloves during the whole process.

A) Put tops at both ends of the sampler. To avoid contamination of the sample, use only clean tops.

B) Mark both tubes with an etiquette that contains enough information to identify the sampler. It is important to know:
   - The measurement period.
   - A reference to identify the ventilation shaft where it has been located (for example with a colour codification).

C) Take the complete sampler out of the ventilation shaft.

D) Remove the central part of the sampler and put tops at the end of both sampling tubes.

E) Store the closed sampling tubes in a box, which should be kept in a dark and dry place. When step D is skipped, the whole sampler will be stored in the box and sent to IMAG for analysis.

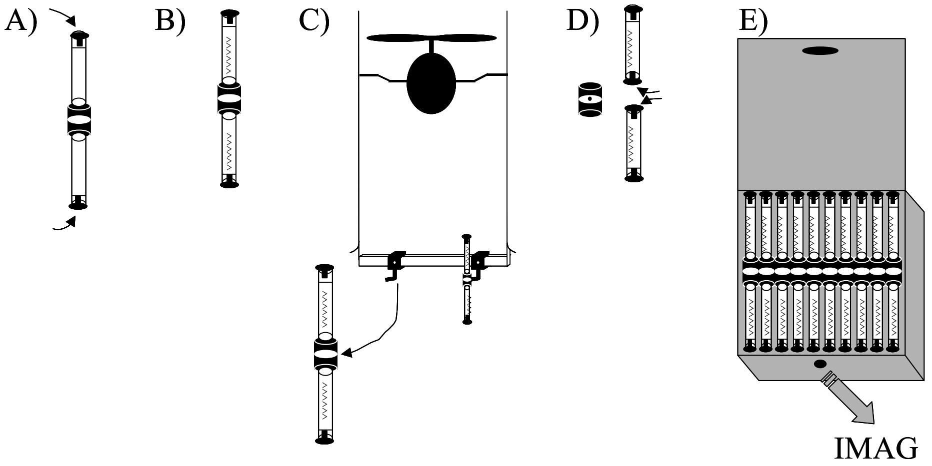

**Figure 9** Procedure to remove the samplers after measurements

# 6 Preparation and analysis of the samples in the laboratory

This section describes the preparation and the analysis of passive ammonia flux sampler Teflon tubes (length: 100 mm; external diameter: 10 mm; internal diameter: 7 mm) with sulphuric acid soaked glass filter papers.

### 6.1.1 Material

List of materials needed for lining the tubes:

- Pipette 1 ml (eppendorf)
- 1 rack for every 48 flux tubes
- Filter paper GF 52 (21x70 mm) S&S code 10428234
- Glass beaker
- Plastic pot
- Gloves
- Tweezers (long and tapered)
- Sulphuric Acid (Concentrated 98%, 18M)
- Ethanol (100%)
- Ether (100%)
- Vacuum dryer
- Fume cupboard
- Teflon tubes
- Stoppers

### 6.1.2 Procedures

1. Inserting the filter paper (untreated) in the tubes
    - Use the tweezers to fold (roll up) the glass filter paper length ways
    - Use the tweezers to insert the rolled glass fibre sheet in the tube stopping at the blue line
    - Use the tweezers to gently align the rolled sheet in the tube if necessary

- Place stoppers on the tubes
- Store the tubes in a sealed box dressed with some oxalic acid coated filter paper (to scavenge ammonia)

2. Preparation of the sulphuric acid solution (solution A)
   - Add 5 ml sulphuric acid (98%, 18M) to 25 ml ethanol (100%). There will be some warming of the solution. Let the solution cool down, and add ether (100%) to a final volume of 100 ml.
3. Treating the filter paper with sulphuric acid solution
   - Use a fume cupboard and gloves.
   - Put a number of tubes fitted with glass filter paper in a rack.
   - Place a double sheet of filter paper under the rack.
   - Using the 1 ml pipette, dispense carefully 1 ml of the solution through the glass filter paper, holding the tube over a glass beaker.
   - Place the tube back in the rack. When the rack is complete, place the rack in a vacuum dryer at approximately 70°C. Evaporating the ethanol takes about 60 minutes.
   - When the tube is dry, place both stoppers on the tubes.
   - The samplers can be preserved for a period between 1 day and 2 weeks. When the tubes are stored in a dark and cold room, this period can be increased.
4. Sampler preparation (after exposure) and analysis
   - Use gloves during the whole procedure.
   - Place tubes vertically in a rack.
   - Remove top cap, add 3000 μl mili-Q water into the tube and close the tube again. This should be done as fast as possible, to avoid contamination with ammonia. Invert the tube 2 to 3 times gently to dissolve the coating completely.
   - Transfer the solution gently to a sample vessel without mixing or even inverting the tube. Careful handling is essential to minimize transfer of glass fibres in the sample solution, which will interfere with the analysis.
   - Take a known volume (i.e. 0.2ml) from each sample vessel and dilute it five-fold for analysis (i.e. add four volumes of water and mix thoroughly).
   - The amount of ammonia in the sampler is determined by spectrophotometry. Analysis is performed following the Dutch standard NEN 6472.

5. Tube cleaning
    - The glass fibre liners are flushed out using tap water and are discarded.
    - The tubes and caps are then placed in a rack and cleaned in a dishwasher machine.
    - The tubes are thoroughly rinsed with demineralised water during the last step of the washing procedure.

### 6.1.3 Remarks

- The five- fold dilution with water is to minimise pH-interference on the colour reactions involved. Solution A treated tubes can still have a lot of free sulphuric acid in them even when the ammonia load is low. Without dilution, this can interfere with the analysis (NEN-6472).
- Avoid contamination with ammonia at all stages. Do enough blanks.

# 7 Data calculation and reporting

The amount of ammonia captured by the sampler can be described as:

$$S_{NH3} = K_S \cdot A_O \int_{t1}^{t2} v(t) \cdot C_{NH3}(t)dt \tag{12}$$

The horizontal ammonia flux is then calculated from the amount of ammonia captured as:

$$F_{NH3} = \frac{S_{NH3}}{K_s \cdot A_o \cdot (t_2 - t_1)} \tag{13}$$

And the emission through the ventilation shaft can be derived from:

$$E_{NH3} = F_{NH3} \cdot A_{VS} \tag{14}$$

The total emission from the animal house is then calculated as:

$$E_T = \sum_{i=1}^{n} E_{NH3}^{i}$$

Where n represents the number of ventilation shafts in the animal house. To calculate the ammonia emission factor per animal:

$$E_a = \frac{E_T}{N}$$

With N the number of animals confined in the house during the measurement period.

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# Appendix A: general information and activities form

| CONTACT PERSON (FARM) | CONTACT PERSON (IMAG) |
|---|---|
| Name:<br>Address:<br>Telephone: | Name:<br>Address:<br>Telephone: |

| VENTILATOR | | | START SAMPLING | | END SAMPLING | |
|---|---|---|---|---|---|---|
| Code | Hours ON | Hours OFF | Date | Time | Date | Time |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |
| | | | | | | |

| Department code | Animal type | Age | Weight (kg) | Number of animals | Max. number of animals | House system |
|---|---|---|---|---|---|---|
| | | | | | | |
| | | | | | | |
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Comments: