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# Literature review on the performance of diffusive samplers for the measurement of ammonia in ambient air and emissions to air



**Centre for  
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# **Literature review on the performance of diffusive samplers for the measurement of ammonia in ambient air and emissions to air**

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## **Executive Summary**

The information in this document has formed the basis from which a new standard on measurements employing ammonia diffusive samplers by CEN TC264 WG11 'Ambient air - Diffusive samplers' is being developed and provides an open reference document for the ammonia passive sampling techniques.

This document briefly summarises the importance of ammonia as a key atmospheric pollutant, together with information on relevant EU and other international legislation and protocols that are in place to regulate its concentration.

An extensive review of the technology that is currently employed to monitor this molecule is presented. Denuders, which are considered the unofficial international reference method are described and other technologies outlined.

The report summarises information on ammonia diffusive samplers from different manufacturers that are currently available in the market and presented an extensive literature summary of quality assurance and calibration which has been carried out both by manufacturers and sampler users.

Results are provided from a recent European study ("Metrology for ammonia in ambient air (MetNH3)"), which targeted improvements in traceability and accuracy of ambient ammonia diffusive samplers. New traceable measurements of the ammonia diffusive sampling rates for passive samplers in common use are presented, and an evaluation of the expanded measurement uncertainty for the calculations of ambient ammonia concentrations.

**August 2018**

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# 1. Introduction

## 1.1 Background

Atmospheric ammonia ( $\text{NH}_3$ ) is a pollutant of major environmental concern with adverse effects on forests, species composition of semi-natural ecosystems and soils [1-4]. Emission and deposition of  $\text{NH}_3$  can contribute significantly to total nitrogen deposition to the environment, contributing to eutrophication (nutrient enrichment) and acidification (oxidation of  $\text{NH}_3$  to nitrate resulting in release of  $\text{H}^+$  ions) of land and freshwaters, leading to a reduction in both soil and water quality, loss of biodiversity and ecosystem change [5-10].

In addition to these effects,  $\text{NH}_3$  is the major precursor for neutralization of atmospheric acids, affecting the long-range transport distance of both  $\text{SO}_2$  and  $\text{NO}_x$  and leading to the formation of secondary particles (primarily ammonium sulphate and ammonium nitrate) [11-13]. These particles have multiple impacts including effects on atmospheric visibility, radiative scattering (and the greenhouse effect) and on human health.

The recognition of  $\text{NH}_3$  as an important air pollutant led to its inclusion in international agreements to reduce air pollutant emissions, first under the 1999 UNECE Gothenburg Protocol and then the National Emissions Ceilings Directive (NECD) (2001/81/EC) of the EU. The target of both these agreements is that  $\text{NH}_3$  emissions should not exceed emission ceilings set for EU member states, with a particular focus on reducing the extent of critical loads exceedance for acidification and eutrophication effects.

Revision of the Gothenburg Protocol (2012) and the NEC Directive (2016) include new, more stringent emission ceilings for 2020 that seek more environmental protection and improvement in air quality than has so far been committed, including the introduction of an emissions ceiling for particulate matter (PM). Under the 2012 UNECE Gothenburg protocol, EU member states must jointly cut their emissions of  $\text{NH}_3$  by 6 % and particles by 22 % between 2005 and 2020. As a precursor of PM, controlling ammonia is important to reducing particle emissions of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ . A recent study employing three chemical transport models found that the models underestimated the formation of ammonium particles and concluded that the role of  $\text{NH}_3$  on PM is larger than originally thought. Thus the implementation of 2020 targets detailed above may not be enough to deliver compliance with proposed particle limit values, and further local measures may be required to be compliant [14].

Other legislations to abate ammonia emissions include the Industrial Emissions Directive (IED) (2010/75/EU) which requires pig and poultry farms (above stated size thresholds) to reduce emissions using Best Available Techniques. In Germany, the recommended exposure limit for the protection of ecosystems is  $10 \mu\text{g}/\text{m}^3$  (TA Luft, Annex 1, [15]). For the protection of vegetation and ecosystems, new revised "Critical Levels" (CL) of  $\text{NH}_3$  concentrations were adopted in 2007, of  $1 \mu\text{g}/\text{m}^3$  and  $3 \mu\text{g}/\text{m}^3$  annual mean for the protection of bryophytes/lichens and vegetation, respectively, which replaced the previous CL annual mean value of  $8 \mu\text{g}/\text{m}^3$ . A monthly critical level of  $23 \mu\text{g}/\text{m}^3$  was retained as a provisional value in order to deal with the possibility of high peak emissions during periods of manure application (e.g. in spring) [16].

**Table 1.1 – Summary of critical NH<sub>3</sub> values for ecosystems**

<b>Concentration (µg/m<sup>3</sup>)</b>	<b>Specification</b>	<b>Types of locality</b>
1	UNECE Critical Level for lichens and bryophytes, where they form a key part of the ecosystem integrity [16]	e.g. Raised bogs and mires and fens, temperate heath and scrub Natura 2000 sites under the: Habitats Directive ( <a href="#">Council Directive 92/43/EEC</a> ).
3	UNECE Critical Level for other vegetation [16]	e.g. Natural and semi-natural grassland formations, forests Natura 2000 sites under the: Habitats Directive ( <a href="#">Council Directive 92/43/EEC</a> )
10	German First General Administrative Regulation Pertaining the Federal Immission Control Act Maximum near installations where ecological monitoring undertaken.	Receptors near installations
23	Monthly critical level (only used for manure spreading)	Receptors in close proximity to emission sources

Improving knowledge on levels of ammonia in the ambient air and near sources is therefore important for the assessment of:

- Environmental effects on ecosystems (Contribution to eutrophication and acidification processes);
- Contributions to the formation of PM<sub>10</sub> and PM<sub>2.5</sub>;
- Evidence-base to assess effectiveness of current and future abatement measures to reduce ammonia emissions.

The simplest to the latest state-of-the-art techniques for measurement of atmospheric ammonia are presented in Table 1.2.



**Table 1.2 - Measurement methods suitable for determination of atmospheric ammonia gas and/or ammonium particle concentrations (*n.b. non-exhaustive selection*)**

<b>Monitoring Methods</b>	<b>Time resolution</b>	<b>References</b>
<b>Integrative methods: Passive</b>		
– Passive diffusion samplers, e.g. ALPHA, Gradko, Passam, Ferm, Ogawa, Radiello, Willems	daily to monthly	See chapters below
<b>Integrative methods: Active</b>		
– Filter packs (NH <sub>x</sub> = sum of NH <sub>4</sub> <sup>+</sup> and NH <sub>3</sub> )	daily to monthly	[17]
– Impingers (NH <sub>x</sub> = sum of NH <sub>4</sub> <sup>+</sup> and NH <sub>3</sub> )	daily to monthly	[18]
– Simple denuder systems with offline chemical analysis, e.g. Ferm samplers, CEH DELTA system	daily to monthly	[19]
– Annular denuder systems (ADS) with offline chemical analysis: – Italian ADS, EMEP ADS, commercial ADS (Chemspec, URG), Honeycomb denuders	hourly to daily	[20]
– COTAG flux measurement system (conditional sampling with denuders at different heights).	weekly to monthly	[21]
<b>Continuous: wet chemistry methods</b>		
– Annular Denuder Systems with online analysis: AMANDA / AMOR	continuous	[22]
– Membrane stripping with online analysis: AiRRmonia	continuous	
– Steam Jet Aerosol Collector Systems for gas and aerosol (GRAEGOR/ MARGA)	0,5 hour	[23] [24]
<b>Continuous: optical methods</b>		
– FTIR; DOAS (Differential Optical Absorption Spectrometry)	from < 1s to >1 h	[25] [26]
– TDL & QCL AS (Tunable Diode Laser Absorption Spectrometry and Quantum Cascade Laser)	from < 1s to >1 h	[27]
– Photoacoustic spectrometry, e.g. NITROLUX™ – Chemiluminescence with catalytic conversion	from < 1s to >1 h	[28]

Integrative atmospheric sampling methods such as passive diffusion samplers and active samplers provide measurement of concentrations of  $\text{NH}_3$  averaged over the chosen sampling time. The diffusive samplers used include those that are available commercially (e.g. Radiello) and those that have been developed in-house by organisations to meet specific research requirements (e.g. Willems). A full validation of diffusive sampling methods for ammonia in accordance with the European Standard (EN 13528-2, [29]) would be costly and would also require specialist facilities only available at well-equipped larger metrological institutes.

Validation of the quantitative measurement of ammonia through comparison with “reference” methods is problematic for ammonia as there is currently no accepted and defined reference method. Automatic continuous analyzers, using spectroscopic or other techniques, as used for other inorganic gases still suffer from a lack of robust published calibration demonstrated at ambient concentrations and conditions.

Though at first glance ammonia measurement should be relatively simple, there are a number of physicochemical issues that mean that measurements need to be done carefully. The major issues are mostly (but not limited to):

– ***Gas-particle interactions***

Determination of ammonia in air can be complicated by interference from particle-borne ammonium ions. When ammonia is released into the atmosphere, the reactive ammonia gas can react with acidic compounds such as  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  and  $\text{HCl}$  to form ammonium salts in particulate form. The reaction with  $\text{H}_2\text{SO}_4$  to form ammonium sulphate is irreversible. However, equilibrium exists between gaseous ammonia and aerosol components  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  which are appreciably volatile at ambient temperature. Measurement techniques must therefore be able to accurately determine gaseous ammonia and particulate ammonium without disturbing the partition existing in the atmosphere at the time of sampling.

– ***Water-ammonia-surface interactions***

Ammonia forms chemically stable bonds with water either as clusters in the atmosphere or on surfaces (e.g. plants, buildings, instrument inlets). As with ammonium nitrate PM, the stability of ammonium solutions is a function of other trace constituents and the ambient atmospheric temperature and relative humidity fluctuations.

– ***Temperature and humidity effects***

The rate of  $\text{NH}_3$  emission increases with an increase in temperature, according to Henry’s law which expresses the equilibrium between  $\text{NH}_3$  in the aqueous and gas phases. The equilibrium concentration of ammonia with a surface approximately doubles for every  $5^\circ\text{C}$  increase in temperature, hence temperature stability is an important factor for on-line instruments measuring ammonia.

Denuders minimise many of the issues of ammonia measurements listed above; separating the gas from the aerosol by diffusion sampling in a laminar flow, by chemically trapping the ambient ammonia on an acid impregnated denuder, so temperature and surface effects are minimized. After sampling, the “trapped ammonia” is extracted from the denuder and analysed off-line or flushed and analysed online with wet chemical methods for continuous ammonium analysis. These types of denuder methods are currently considered by experts to be robust, simple and accessible “reference” samplers for ammonia. However, over the past decade, other fast response techniques are showing promise for direct online measurement of ammonia, including quantum cascade laser (QCL) infrared spectrometers, cavity ring down (CRD) infrared spectrometers, mass spectrometry, differential optical absorption spectrometry (DOAS) and photoacoustic techniques [30-33].

## **1.2 Purpose of the review**

This report provides information on the design and operation of denuders that are suitable for use as reference samplers for ammonia and also on the range of diffusive samplers currently available. The availability of validated traceable reference methods for ammonia is important for calibration of passive samplers and to assess accuracy and uncertainty of these methods.

Passive samplers are widely used for monitoring ammonia, e.g. in national monitoring networks in the UK [34] the Netherlands [35, 36], Switzerland [37] and for environmental impact assessments (e.g. Vogt et al. [38]; Yao et al. [39]). Users wishing to apply diffusive sampling in ammonia measurements often have to rely on critical information such as uptake rates provided by commercial laboratories. Some suppliers of samplers may require that analysis of their diffusive samplers be performed only by their laboratory. Independent validation of measurement is needed to ensure accuracy of the measurement results and it is important that each laboratory applying these methods can demonstrate performance against validated and traceable reference methods for ammonia results.

A European Standard has been written providing guidelines to selection, use and maintenance of diffusive samplers for the determination of concentrations of gases and vapours (EN 13528-2). There is however to date, no formal guidance documents on ammonia measurements with passive samplers. In order to facilitate the drafting of a standard, CEN/TC264 WG11 'Ambient air - Diffusive samplers' has taken the initiative to perform pre-normative research.

This review collates existing information on ammonia diffusive sampling in ambient air. The emphasis in this review is on passive diffusive samplers that are available without commercial restrictions and for which well-defined performance characteristics are published and accessible.

## 2. Performance requirements for NH<sub>3</sub> diffusive samplers

### 2.1 Application for ambient and hot spot monitoring

In this review, two purposes of deployment of ammonia diffusive samplers are distinguished:

- Measurements near sources with the aim of estimating emissions and emission factors;
- Measurements in ambient air, relatively remote from sources aimed at establishing regional or background concentrations of ammonia.

Levels of ammonia near point sources as high as 10 mg/m<sup>3</sup> have been reported in the literature [40]. However, these levels tend to drop rapidly with increasing distance from the source [41]. Mean background ambient air concentrations range from <0,1 µg/m<sup>3</sup> to >10 µg/m<sup>3</sup> in Europe (ref: NAMN in UK, MAN / Ammonia network in NL), although values reported can be < 0,02 µg/m<sup>3</sup> in an individual month [42]. In urban areas, e.g. in China [43] up to about 100 µg/m<sup>3</sup> have been reported. Work place exposure limits are set for works, e.g. poultry housing, but there is currently no set human exposure level for ambient air.

It is proposed to split the range of use into two partly overlapping ranges for sampling periods of 24 h up to 4 weeks or monthly:

- From 50 µg/m<sup>3</sup> to 10 mg/m<sup>3</sup> (immediate vicinity of point source)
- From < 1 µg/m<sup>3</sup> to 100 µg/m<sup>3</sup> (ambient air)

### 2.2 Temperature dependence

In measurements where end users record the temperature, then an appropriate temperature dependent sampling rate may be applied. This could apply either the annual mean temperature for the monitoring site (or country, if applicable) or the site mean temperature for the duration of each sampling period, as applied in EN 16339:2013 [44]

The temperature dependency of diffusion coefficients in binary gas mixtures varies between  $T^{1.5}$  and  $T^2$  [45]. This range of temperature dependence is also reported in the European Standard for diffusive samplers, EN 13528-3 [46] For some relevant atmospheric pollutants, such as NO<sub>2</sub> and NH<sub>3</sub>, Massman [47] reports a temperature dependency of  $T^{1.81}$  near standard conditions. This dependence has been described in the European Standard EN 16339:2013 [48] to correct for the temperature effect on NO<sub>2</sub> passive samplers and may be applied to ammonia as well. The dependence of the diffusion constant of ammonia may be calculated from:

$$D_T = D_{298K} \cdot (T/298)^{1.81} \quad (1)$$

where

T is expressed in K.

Measured concentrations may be reported in units of  $\mu\text{g}/\text{m}^3$  at a reference temperature of 293 K (20 °C). For such conditions a temperature correction shall be applied to the concentration of  $\text{NH}_3$ , as follows:

$$[\text{NH}_3]_{293\text{K}} = [\text{NH}_3]_{\text{T}} \cdot (\text{T}/293) \quad (2)$$

where

$[\text{NH}_3]_{\text{T}}$  is the concentration at the measured temperature T;  
 $[\text{NH}_3]_{293\text{K}}$  is the required concentration corrected to 293 K.

### 2.3 Performance characteristics

The most common characteristic to quantify the performance of a sampler is its expanded uncertainty (95 % confidence limits). A major challenge when estimating the expanded uncertainty of a passive sampler is in the availability of reliable data on the traceability of the reference ammonia measurement techniques that the passive sampler is compared against. Many of the measurement techniques for ammonia summarised in Table 1.2 are subject to artefacts and measurement uncertainties (Pogany et al. [32]. “Reference” systems for measuring ammonia have uncertainties associated with them and, in practical use, can be less reliable than diffusive samplers themselves if the issues of ammonium aerosol and temperature and relative humidity are not taken into account, see Martin et al. [49] for an example of this.

Target levels of 1,3, 10 and 23  $\mu\text{g}/\text{m}^3$  were selected based on Table 1.1.

This review is intended to provide the background to underpin the establishment of performance requirements for ammonia diffusive samplers. These requirements may subsequently be used to “screen” published results of samplers in order to obtain information about their suitability for the measurement of ammonia. The following performance characteristics and requirements are proposed (Table 2.1).

**Table 2.1 - Performance characteristics and proposed requirements for ammonia diffusive samplers**

**General**

<b>Performance characteristic</b>	<b>Requirement</b>
Relative humidity range	20 % to 80 %
Temperature range	-10 °C to 40 °C
Maximum storage period before deployment (under specified conditions)	6 months
Maximum storage period after deployment (under specified conditions)	6 months
Blank levels	≤ 10 % of target dose sampled

**Emission monitoring**

<b>Performance characteristic</b>	<b>Requirement</b>
Deployment period (capacity)	≥ 8 hours
Limit of detection	≤ 5 µg/m <sup>3</sup>
Precision (replicate samplers)	≤ 10 %
Bias from reference (well-defined)	≤ 25 %
Expanded uncertainty at 1,0 mg/m <sup>3</sup>	≤ 30 %

**Ambient measurements**

<b>Performance characteristic</b>	<b>Requirement</b>
Deployment period (capacity)	≥ 7 days
Limit of detection	≤ 0,1 µg/m <sup>3</sup>
Precision (replicate samplers)	≤ 10 %
Bias from reference (well-defined)	≤ 25 %
Expanded uncertainty at 1, 3 and 23 µg/m <sup>3</sup>	<i>Under WG review for standard</i>

### **3. Reference methods for ammonia**

#### **3.1 Introduction**

Reference methods for ammonia are needed to allow calibration of ammonia passive samplers and to ascertain the quality (i.e. accuracy) of the passive method. Denuder methods are simple to deploy and are suitable as reference methods and are described in this Chapter. Other promising methods, such as recent developments in optical methods are also discussed and are included at the end of this Chapter.

#### **3.2 General description of denuders**

A denuder is a sampling technique that permits the selective removal of atmospheric reactive gases on a chemically impregnated tube [50], the denuder and subsequent collection of particles on a downstream aerosol filter, [51]. When a laminar air stream passes through a tube coated on the inside with an acid, ammonia is captured by the acid walls, while ammonium aerosol pass through unaffected and may be collected on a post-denuder filter. In this approach, the separation of particles from gaseous species is achieved due to the much more rapid diffusion of gaseous species to the tube wall compared with that of particles. The residence time of air in the denuder is of the order of tenths of seconds. Therefore the partition equilibrium between ammonia in the gas phase and ammonium in the particulate phase should not be perturbed and potential artefacts caused by phase interactions associated with filter packs and bubblers are avoided [52].

In the most basic form of a denuder system, a simple tube is used for the selective collection of gaseous species on its walls (Figure 3.1). The simplest denuder method is the original design of Ferm [19]. The Ferm denuders are 0,5 m long (3 mm id) operated at 3 l/min air sampling rate that is suitable for sampling periods of between 1 - 24 h. The DELTA (DEnuder for Long-Term Atmospheric) sampling system developed by CEH uses shorter borosilicate glass tubes (10 cm long, 6,5 mm id) and a lower flow rate (0,2 – 0,4 l/min), designed for longer-term sampling (weekly to monthly).

Simple tubular denuders attain good sorption efficiency only at low air flow rates. Annular denuder systems (ADS) [53] and honeycomb denuders [54, 55] typically operate at much higher flow rate of 10-15 l/min and are designed for short-term sampling of between 1-24 h. The design of the annular denuders consists of coaxial tubes, forcing the sample stream to flow through the annular space between the outer and inner tubes. The configuration increases the surface area for retention of gaseous  $\text{NH}_3$ , thereby allowing higher operating flow rate and a shorter length of collection tube. Honeycomb denuders are compact, measuring 47 mm in diameter, and only 38 mm long. They contain a large internal surface area of 508 cm<sup>2</sup>, made possible by 212 hexagonal flow channels that are 2 mm wide. [54] This results in a much higher loading capability than conventional annular denuders.






### 3.3 Off-line denuders

In a manual denuder system, the denuder is removed and extracted back in a laboratory for chemical analysis (e.g. Ferm, DELTA).

### 3.4 On-line denuders

In an on-line system, the ammonia trapped on a denuder is pumped into a detector for continuous analysis (e.g. AMOR, AMANDA).

**Table 3.1 - Types of Denuders**

	DELTA Denuder	FERM Denuder	Annular Denuders		Honeycomb Denuder
			2 concentric rings	3 concentric rings	
Design					
Dimension L (m) x Diameter (m)	0,1 x 0,01	0,5 x 0,01	0,18 x 0,04	0,15 x 0,04	0,038 x 0,047
Sampling rate (L min <sup>-1</sup> )	0,2 – 0,4	4	10 - 15	10 – 15	10
Sampling Duration	1 week – 3 months	1 - 24 hrs	1 - 24 hrs	1 - 24 hrs	1 - 24 hrs
Costs (approx. / £)	2 - 4	10	180	400	1000
Offline/online analysis?	Offline	Offline	Offline (ADS) Online (e.g. AMOR)	Offline	Offline
Advantages	Small, robust, low cost, easy to post	Low cost	shorter tube to operate at high flow	shorter tube to operate at high flow	Very compact
Design	0,1 x 0,01	0,5 x 0,01	0,18 x 0,04	0,15 x 0,04	0,038 x 0,047



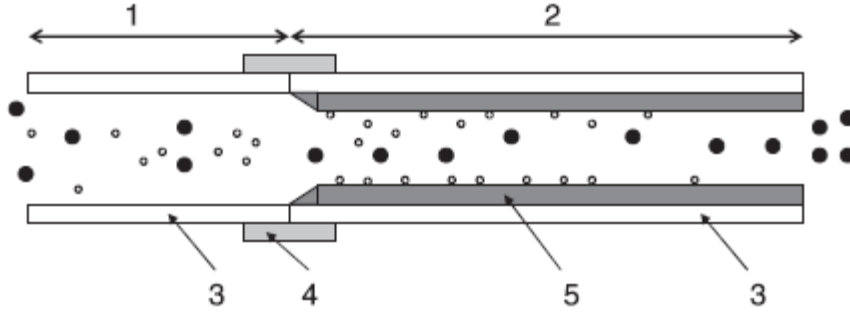


Figure 3.1 - Schematic of a denuder operation. 1: inlet section, 2: coated section, 3: glass tube, 4: coupling, 5: reactive coating, gas molecules, • particles

### 3.5 Basics of working with denuders

In order to quantitatively measure the concentration of ammonia in air, it is critical to measure accurately the volume of air sampled during the measurement period. Denuders are operated under a constant flow rate which may be achieved using either an air pump in conjunction with a mass flow meter, a calibrated gas meter, or a mass flow controller. In some cases, a critical orifice is used to set the particle size cut-off. Time resolutions in the range of 1 hour to monthly are normal, but the criteria are set by the measurement requirements of the experiment or monitoring. In the case of long-term sampling, mass concentrations should be expressed in  $\mu\text{g}/\text{m}^3$  taking into account the relevant environmental conditions (e.g. pressure, temperature).

### 3.6 Denuder theory

The length of a denuder required to obtain near complete capture of ammonia gas is a function of the diffusion coefficient of ammonia and the air sampling rate.

For cylindrical tubes, with laminar flow and where the tube wall is a perfect sink for the gas of interest, Gormley [56] showed that the collection efficiency of a simple denuder for a reactive gas may be calculated using Equation 3:

$$\eta = 1 - \frac{\beta_1}{\beta_0} = 1 - 0.819 \cdot e^{-14.6272\delta} + 0.0976 \cdot e^{-89.22\delta} + 0.01896 \cdot e^{-212\delta} \quad (3)$$

where

- $\eta$  is the collection efficiency of the denuder;
- $\beta_1$  is the mass concentration of ammonia at the denuder outlet, in  $\mu\text{g}/\text{m}^3$ ;
- $\beta_0$  is the mass concentration of ammonia at the denuder inlet, in  $\mu\text{g}/\text{m}^3$ .

$\delta_z$  is described by:

$$\delta_z = \frac{\pi \cdot D \cdot L}{4\phi} \quad (4)$$

where

- D is the molecular diffusion coefficient of ammonia, in cm<sup>2</sup>/s (0,209 cm<sup>2</sup>/s @ 10 °C (Hargreaves and Atkins) [57];
- L is effective length of the denuder, in cm;
- ϕ is the air flow rate through the denuder, in cm<sup>3</sup>/s.

Ferm [17] showed that for collection efficiencies greater than 95 %, contributions from terms 2 and 3 in Equation 3 are insignificant (< 0,3 %) and only the first term is significant. Equation 3 may then be simplified to Equation 5:

$$\eta = 1 - \frac{\beta_1}{\beta_0} = 1 - 0.819 \cdot e^{-14.6272 \left( \frac{\pi DL}{4\phi} \right)} \quad (5)$$

Equations 3 to 5 do not apply for annular denuders. For annular denuders, Pozzanzini et al. [53] showed that the collection efficiency for a reactive gas may be calculated using Equation 6:

$$\eta = 1 - \frac{\beta_1}{\beta_0} = 1 - 0,819 \cdot e^{-22,53\delta_r} \quad (6)$$

where

- η is the collection efficiency of the denuder;
- β<sub>1</sub> is the mass concentration of ammonia at the denuder outlet, in µg/m<sup>3</sup>;
- β<sub>0</sub> is the mass concentration of ammonia at the denuder inlet, in µg/m<sup>3</sup>.

δ<sub>r</sub> is described by

$$\delta_r = \frac{\pi \cdot D \cdot L (d_2 + d_1)}{4\phi (d_2 - d_1)} \quad (7)$$

where

- d<sub>2</sub> is the internal diameter of the outer annular denuder tube, in cm;
- d<sub>1</sub> is the internal diameter of the inner annular denuder tube, in cm.

The diameter and air flow should be chosen such that the Reynolds number (Equation 8 for cylindrical denuders; Equation 9 for annular denuders) lies within the laminar region, *i.e.*, do not exceed a value of 2000.

$$\text{Re} = \frac{4\phi}{\pi \cdot \gamma \cdot d} \quad (8)$$

$$\text{Re} = \frac{4\phi}{\pi \cdot \gamma \cdot (d_2 + d_1)} \quad (9)$$

where

$\gamma$  = kinetic viscosity of air (0,152 cm<sup>2</sup>/s @ 20 °C at 1 atm)

Laminar flow is achieved a short distance from the inlet. The minimum length of tube at inlet not coated with sorbent,  $L_{min}$  to fully develop laminar flow is given by Equation 10.

$$L_{min} = 0,05.Re.d \quad (10)$$

For annular denuders where the annular gap is small relative to the radius of curvature, then the minimum length of tube at inlet not coated with sorbent,  $L_{min}$  to fully develop laminar flow is given by Equation 11

$$L_{min} = 0,04.Re.x \quad (11)$$

where

$$x = (d_1 + d_2)/2$$

If filters or combinations of filters are used, the change in pressure loss caused by loading the filters should be taken into consideration in the flow calculations.

**Table 3.2 - Example results of calculation**

Type of denuder	NH <sub>3</sub> Diffusion coefficient (D) @10 °C (cm <sup>2</sup> /s)	Flow rate (m <sup>3</sup> /s)	Length of uncoated tube (0,65 mm id) required to develop laminar flow (cm)	Length of coated denuder required to achieve ≥95 % collection efficiency (cm)
DELTA	0,209	Adjustable Usually 0,12-0,24	2,3	8
AMOR	0,209	0,00028	7	30

Continuous wet annular denuder methods with on-line analysis are available for atmospheric monitoring of NH<sub>3</sub> (e.g. AMOR [58]; AMANDA [59]). The AMOR system operates with an hourly time resolution and was used in the Netherlands up till 2014 in the Dutch ammonia network to provide the concentration field for atmospheric NH<sub>3</sub> at 8 stations [60]. The AMANDA gradient system [61] has been used to provide long-term average fluxes of NH<sub>3</sub> over grassland, moorland and coniferous forest [61, 62].

The MARGA (Monitor for Aerosols & Gases in Ambient Air; <http://www.metrohm-applikon.com>) is a similar instrument based on the AMANDA system, but with a steam-jet

aerosol trapping device for aerosols that provides hourly concentrations of reactive gases ( $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{HONO}$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ) and aerosol ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) [63].

### 3.7 Denuders as ammonia network reference methods

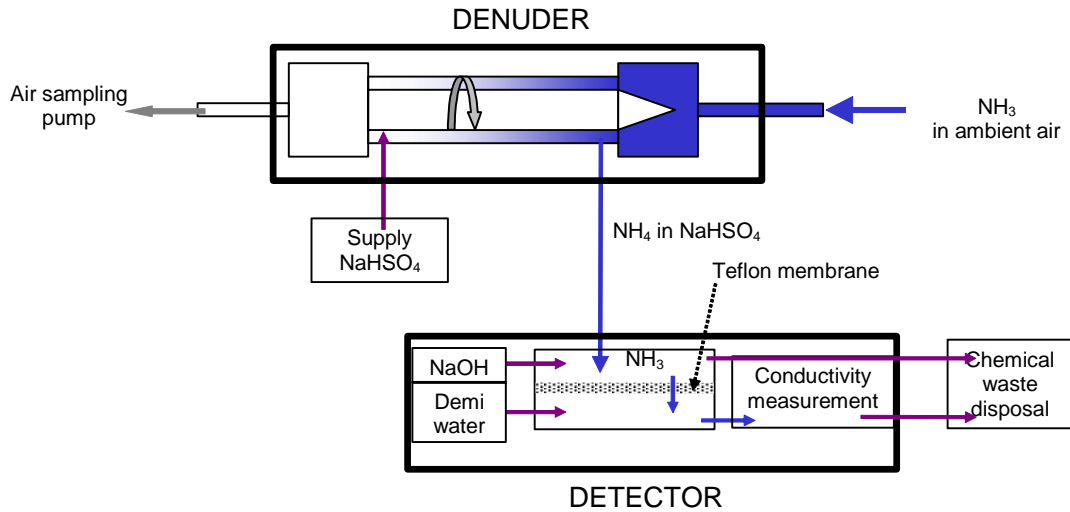
Denuders have been used over the past three decades in both research experiments and as part of local, regional and national long term monitoring. A complete review of all applications is outside the scope of this document, but a few examples of each type of application are highlighted below.

In the UK, the Netherlands and several other countries, monitoring of ammonia is done either on a long-term basis or for a shorter period of the order of a year. Some networks use entirely denuder-based measurements or a combination of denuders and passive samplers e.g. Netherlands: Dutch ammonia network with passive samplers and AMOR (hourly) until 2015 when the AMOR wet chemistry method was replaced by an optical method, DOAS [64]. In the UK, a mixture of denuder and passive sampler methodologies, e.g. UK: National Ammonia Monitoring Network with DELTA [65] Regional monitoring in China has been undertaken with denuders and diffusion samplers [66]. In the USA, testing of standard denuder measurements against on-line measurements with the Monitor for AeRosols and GAses in ambient air (MARGA, semi-continuous) have been reported [67] Denuder systems have been used for both short term and long-term research. UK: EMEP supersites Auchencorth and Harwell with MARGA (continuous). Other denuder measurements have been summarised in Tang et al. [17].

#### 3.7.1 Dutch National Ammonia Network: AMOR

Ammonia concentrations in the Netherlands are monitored since 1993 on a short time scale (hourly) at six stations of the Dutch National Air Quality Monitoring Network (LML), operated by RIVM [60]. Three of the six locations are located in areas with high ammonia emission densities, two in areas with moderate emissions and one near the coast with low local emissions. The measurement height is 3,5 m. Specifically, the concentrations of ammonia in air were measured with the AMOR-technique (continuous flow denuder system, Wyers et al. [59] until 2015 when they have been replaced by DOAS equipment.

The detection limit of an AMOR system is  $0,12 \mu\text{g}/\text{m}^3$  and the uncertainty in the annual concentration is about 7 %. The AMOR system consists of a rotating annular denuder, an air sampling pump, and a conductance detector unit. The Ammonia loaded ambient air is sampled through the denuder containing a 0,1 M  $\text{NaHSO}_4$  absorption liquid. By rotating the denuder, an absorption solution film on the denuder wall is created, in which the  $\text{NH}_3$  is absorbed as  $\text{NH}_4^+$ . The solutions are continuously transported from the denuder to the detector part of the AMOR system. Subsequently, in the detector part  $\text{NaOH}$  is added, so that the  $\text{NH}_4^+$  is liberated as  $\text{NH}_3$  from the solution. Next, the  $\text{NH}_3$  diffuses through a semi-permeable Teflon membrane to dissolve as  $\text{NH}_4^+$  in deionised water. This solution passes a conductivity cell equipped with a thermistor to measure conductivity and temperature. The  $\text{NH}_3$  concentration in the sample air is calculated from the temperature corrected increase in conductivity and the gas- and liquid flow rates. A schematic representation of the measurement principle of AMOR is given in Figure 3.2



**Figure 3.2 - Schematic representation of the measurement principle of AMOR**

### 3.7.2 UK National Ammonia Monitoring Network (NAMN): ALPHA and DELTA

The NAMN was established in 1996 to provide a measured  $\text{NH}_3$  concentration field for the UK and at the same time to provide data for the assessment of models. The strategy for the network was to sample at a large number of sites to assess spatial variability, using low-frequency sampling (monthly) to allow temporal patterns and long-term trends to be assessed economically [68].

Measurement of  $\text{NH}_3$  is made using active DELTA sampling system complemented by passive samplers (3,5 cm Gradko membrane diffusion tubes from Sep 96 – April 2000, replaced by the higher sensitivity ALPHA samplers from May 2000 onwards).

A small flow rate (between 0,2 – 0,4 l/min), compared with the classical implementation for daily sampling by Ferm [19] is used. This means shorter 10 cm glass tubes are used compared with 50 cm long Ferm tubes. Stable sampling rates are achieved using low flow air pumps, with air volumes being measured by a high sensitivity dry gas meter.

A simple enclosure is used, which may be mounted on a pole (1,5 m above ground) for monitoring outdoors. Monitoring may also be made *via* a sampling line in a protected cabin. In this case, the same enclosure is used, but mounted on a desk or wall rather than mounted outside on a pole. When sampling *via* an inlet tube, the inlet tube should be made of polyethylene (0,5 mm id) and preferably < 2 m long.

### 3.8 Differential Optical Absorption Spectroscopy as network reference method

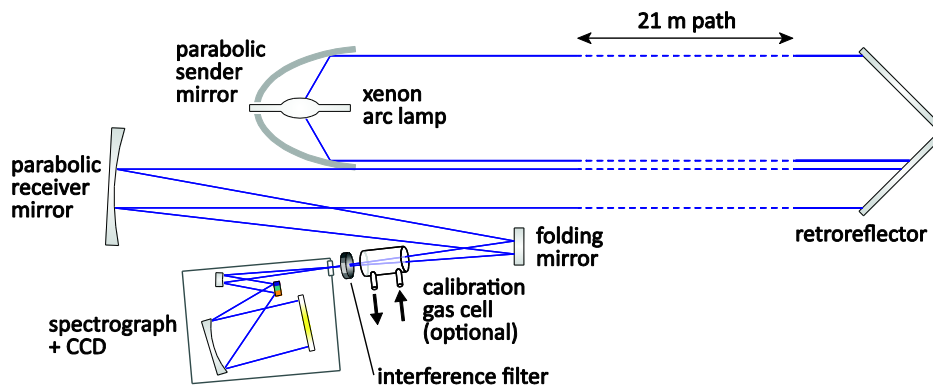
A number of spectroscopic techniques have been developed to measure trace gases including ammonia. These rapid on-line methods such as cavity ring-down spectroscopy (CRDS) [69] have the potential to overcome the limitation of the techniques described above. Ammonia sensors based on CRDS and on multiple-pass cells with quantum-cascade lasers (QCL) [70-72] and differential optical absorption spectroscopy (DOAS) [73-79] have been reported in the literature. Before these sensors can be deployed routinely in the field, their potential drawbacks such as spectral cross-interference and effects of collisional broadening on the ammonia lines of interest must be addressed in long-term deployments through robust quality assurance procedures [49].

In the Netherlands, a miniaturized DOAs system, the “miniDOAS” system [35, 73, 74, 78] replaced the AMOR as the ammonia monitoring system in the Dutch monitoring network LML on January 1st, 2016. The transition, including a 15 months test period of parallel operations is described in Berkhout et al [35]. Currently, miniDOAS systems provide continuous monitoring with 1 minute resolution at 6 LML stations in the Netherlands and 2 in Belgium. The miniDOAS is extensively described in Volten et al. [78] and Berkhout et al. [35].

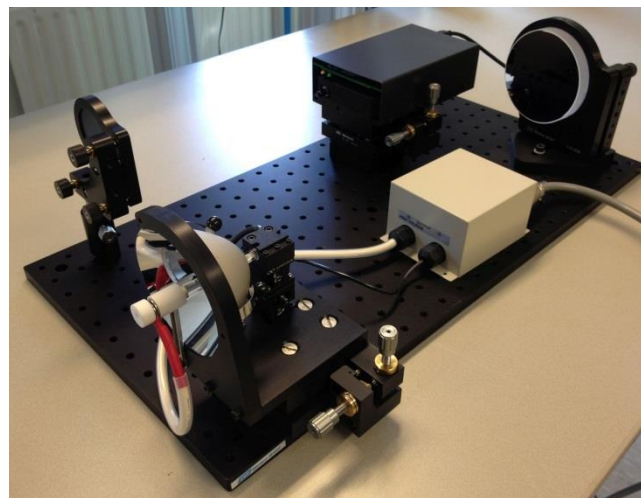
The instrument uses a xenon lamp as ultraviolet light source and a retroreflector to measure optical absorption spectra along an open path, typically 42 m long. It uses the DOAS technique [80] to retrieve concentrations of several atmospheric trace gases along this path, including ammonia. See Figure 3.3 for a schematic representation of the optical set-up of the instrument, Figure 3.4 for a photo. It was developed from a much larger system, also described in Volten et al.[78]. By using smaller and less expensive parts, the physical dimensions, the power consumption and the price tag of the miniDOAS were much lower than the original system, hence the name. The specifications of the measurements are given in Table 3.3 below.

**Table 3.3 - Specifications for the miniDOAS, for 1-minute values**

<b>Specification</b>	<b>Value</b>
Detection limit ( $\mu\text{g}/\text{m}^3$ )	0,25
Precision ( $\mu\text{g}/\text{m}^3$ )	0,25
Time resolution (min)	1



**Figure 3.3 Schematic representation of the miniDOAS, with an optional calibration gas cell in the optical path**



**Figure 3.4 - Photo of the miniDOAS. The instrument is 380 mm wide, 600 mm long and 180 mm high. Not shown: the lamp power supply (282 × 144 × 90 mm) and the instrument computer**

## 4. Passive samplers

### 4.1 Gradko samplers

#### 4.1.1 Sampler design

There are two types of Gradko samplers:

- 3,5 cm short membrane diffusion tube;
- DIFRAM-400 badge-type sampler.

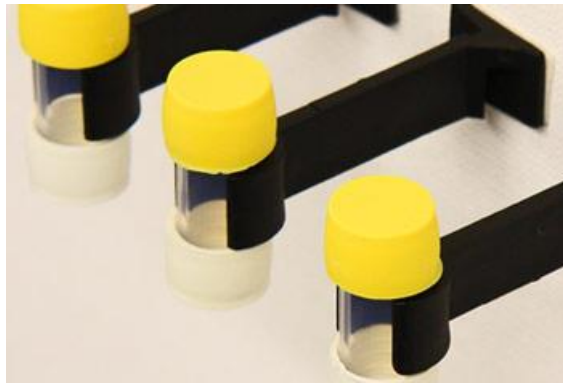


Figure 4.1 - Short 3,5 cm Membrane Diffusion Tube samplers.



Figure 4.2 - Difram

The Palmes tube-type samplers are hollow cylindrical tubes oriented vertically. A cap at the top end holds in place either a filter paper or stainless steel grid, which is coated with an absorbent that collects the gas of interest. For  $\text{NH}_3$  sampling, a number of acids have been used, including citric, phosphoric, phosphorous, sulphuric and tartaric acid [81]. The lower end of the tube capped with a membrane in the case of the 3,5 cm membrane diffusion tube [82].



The 3,5 cm diffusion tube has a gas permeable membrane placed at the inlet to establish a turbulent free layer of air inside the sampler [83]. The membrane does however impose an additional resistance against gas diffusion, which needs to be taken into account when deriving a sampler's effective sampling rate. The DIFRAM-400 sampler is a badge-type sampler for enhanced sensitivity over the tube-type samplers.

#### 4.1.2 Extraction and analysis

Acid impregnated grids in diffusion tubes are usually extracted into deionized water and analysed using an IC method, and this method of analysis is available from commercial laboratories. Other laboratories use different techniques, for example. Sutton et al. [18] used flow injection analysis method with detection of conductivity (AMFIA; [59])

#### 4.1.3 Application range and conditions

The application range and conditions recommended for use by manufacturers or by CEH researchers are summarised below in Table 4.1.

**Table 4.1 - Performance data of 3,5 cm ammonia membrane diffusion tube**

Parameter	Value(s)	references
Sampling rate	3,27 ml/min 2,53 ml/min 2,70 ml/min	[59] [82] [68] [51, 83]
Working range	1 – 35 $\mu\text{g}/\text{m}^3$	[82] [68]
Sampling period	Weekly – 8 weeks	
Detection limit	0,3 $\mu\text{g}/\text{m}^3$ for 4 week exposure < 1,5 $\mu\text{g}/\text{m}^3$ for 4 week exposure	[82] [84]
External influences: - wind speed - temperature - relative humidity	influence of wind speed < 10 % up to 4,5 m/sec using protection shelters T: no influence between 10 – 30 °C RH: no influence between 20 – 80 %	
Storage	Before use: 8 weeks from preparation	
Interferences	Potential volatile aerosol particles containing $\text{NH}_4$ on the permeable membrane. Avoided by removing membrane after sampling and sealing the inlet with a clean cap	[51]
Expanded uncertainty	12 % at 1 $\mu\text{g}/\text{m}^3$ level, laboratory conditions	

#### 4.1.4 Uptake rate and environmental effects

The theoretical sampling rate of the 3,5 cm membrane diffusion tube with a membrane, based on its geometry and using a diffusion coefficient of  $0,209 \text{ cm}^2/\text{s}$  is calculated to be 3,38 ml/min at a temperature of  $10 \text{ }^\circ\text{C}$ .

For the 3,5 cm diffusion tubes fitted with a gas permeable membrane at the air inlet, the manufacturer recommends to use a practical sampling rate of  $162,2 \text{ cm}^3/\text{h}$ . Prior to 2012, the sampling rate recommended by the same manufacturer was  $152 \text{ cm}^3/\text{h}$ , which is based on information provided by Thijssse et al. [82] [82] who compared the performance of the membrane Gradko samplers with automated rotating denuders (AMOR) in the field. However, from Thijssse et al. [75], it is unclear for which temperature this sampling rate holds. The sampling rate was determined during a year of parallel sampling. Estimating the average yearly temperature in the Netherlands to be  $11 \text{ }^\circ\text{C}$ , one may assume that the sampling rate holds for this temperature. Using Equation 1 (see Section 2.2), the effective sampling rate at  $25 \text{ }^\circ\text{C}$  may then be calculated as  $166 \text{ cm}^3/\text{h}$ . Comparison with the theoretical sampling rate given above results in a sampling efficiency caused by the introduction of the membrane of 0,74. This corresponds well with the sampling efficiency reported by the authors as the result of the introduction of the membrane ( $\approx 0,73 - 0,77$ ) [75]. Consequently, it may be assumed that the sampling rate of  $152 \text{ cm}^3/\text{h}$  holds for a temperature of about  $11 \text{ }^\circ\text{C}$ .

In windy conditions, air moving over the open end of a diffusion tube generates turbulence inside that can lead to a reduction in the diffusion length, referred to as 'wind-shortening' (e.g. Brown 2000 [85], Hargreaves & Atkins 1987 [57], Atkins & Lee 1992 [86]). This results in an increase in the effective sampling rate so that the air concentration is overestimated if the theoretical rate is used. The increase is variable, depending on wind speed and location of the samplers (Ferm 1991 [50], Campbell et al. 1994 [87]), because the angle of wind is also important (Hargreaves 1989 [88]).

The wind-shortening effect can be minimised when using open diffusion tubes, by the careful selection of sampling sites where vertical movement of air is avoided (Brown 2000 [85]), and in exposed windy locations, the use of some form of wind shield can also reduce wind turbulence (Hargreaves 1989 [88]). In general, if the general guideline for the location and exposure of the open diffusion tube is followed, wind speed is considered to have minimal or negligible influence on its sampling rate because of the large length to area ratio of the tube. (Brown 2000 [85], Atkins & Lee [86, 89]). The 3,5 cm diffusion tube has a gas permeable membrane placed at the inlet to establish a turbulent free layer of air inside the sampler (Tang et al., 2001 [83]) The membrane does however impose an additional resistance against gas diffusion, which needs to be taken into account when deriving a sampler's effective sampling rate. The DIFRAM-400 sampler is a badge-type sampler for enhanced sensitivity over the tube-type samplers. The manufacturer's original diffusive sampling rate is  $47,0 \text{ ml}/\text{min}$ , while a more recent study (See Section 5) indicates a value of  $52,8 \text{ ml}/\text{min}$ .

## 4.1.5 Validation of sampler performance

### 4.1.5.1 Laboratory experiments

There has been a wind tunnel study undertaken by Wyers et al. [90] at Schagerbrug at windspeeds of 1, 3 and 6 m/s. 3,5 cm membrane diffusion tubes were exposed over 12 partly overlapping periods of four weeks from Jan to July 1995. All measurements were carried out in triplicate. The chemical analysis were performed within a fortnight of collection. For this experiment, the reference method was the AMANDA (Ammonia Measurement by ANular Denuder with online Analysis) developed by ECN [59].

The 3,5 cm membrane diffusion tubes with a gas permeable membrane placed at the inlet were not subject to wind shortening artefacts. For these, compared to the calculated uptake rate, the effective uptake rate of the diffusion tube with membrane at the inlet is 23 – 27 % lower. The use of a shelter made no difference to the results.

**Table 4.2 - Results of linear regression analysis (intercept 0, P < 0,05) for diffusion tubes vs reference AMANDA method**

Tube type	Shelter?	Slope	R <sup>2</sup>
3,5 cm tubes, gas permeable membrane at inlet	Yes	0,725 ± 0,040	0,853
3,5 cm tubes, gas permeable membrane at inlet	No	0,774 ± 0,034	0,929

### 4.1.5.2 Field experiments

In an intercomparison study between the Netherlands and the UK ([90], [87], [83]), relatively high concentrations of ammonia (2-20 ug/m<sup>3</sup>) were measured in the Netherlands. The field locations were Vredepeel, Wekerom (Dutch Air Quality Monitoring Network, operated by RIVM) and Schagerbrug (ECN) sites in the Netherlands and Auchencorth field in Scotland. The types of diffusion samplers tested were:

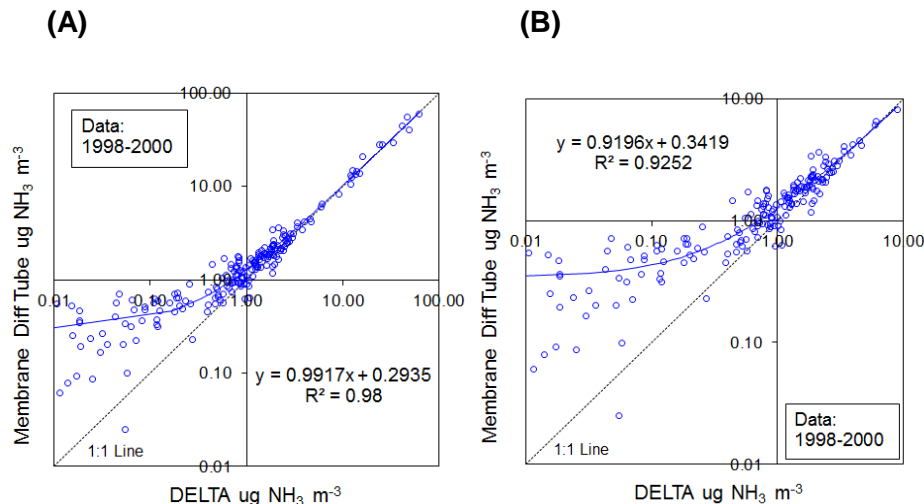
- 3,5 cm membrane diffusion tube, mounted in a shelter, as above;
- 3,5 cm membrane diffusion tube, exposed without shelter.

The reference DELTA system was tested in this study at prototype stage: two 10 cm acid coated glass denuders in series (single system). In addition, a bubbler (single system) was also tested. The locations, estimated annual average ammonia concentration and the recommended method for using as a reference are summarised below in Table 4.3- (from [83]).

**Table 4.3- Sites for the ammonia measurement intercomparison, showing concentrations anticipated from previous studies and the method used to provide the reference ammonia concentration during the intercomparison**

Site name	Location	Estimated annual mean concentration ( $\mu\text{g}/\text{m}^3$ )	Method used to provide reference concentration
Inverpolly	Scotland	0,05	FRAME model plus previous campaigns using AMANDA in region
Auchencorth	Scotland	0,8	AMANDA monitoring
Bush	Scotland	1,4	AMANDA monitoring
Petten	Netherlands	2,5	Daily Ferm denuder monitoring
Zegfeld	Netherlands	9	AMOR monitoring
Vredepeel	Netherlands	17	AMOR monitoring

The UK has operated a national network, named the National Ammonia Monitoring Network (NAMN) [18, 19]. At the inception of the network, the 3,5 cm membrane diffusion tube samplers were tested at several UK NAMN and European sites against the CEH DELTA system [87].



**Figure 4.3 - Comparison of individual monthly  $\text{NH}_3$  concentrations from triplicate 3,5 cm membrane diffusion tubes (calculated from theoretical uptake rate @10°C) operated alongside an active denuder system, as part of the methods validation at 9 sites in the UK. (A) 9 ambient sites + 1 high  $\text{NH}_3$  farm site, (B) 9 ambient sites only.**

Results from an intercomparison between the membrane 3,5 cm diffusion tubes (exposed in triplicate) and the CEH DELTA system in the UK for the period 1998 to 2000 are shown in Figure 4.3. Measurements were carried out in parallel at nine sites in the UK network. Scatter in the data below  $1 \mu\text{g}/\text{m}^3$  is due to the low sensitivity of the diffusion tubes, which make them rather uncertain for measurements at these concentrations, where they also overestimated  $\text{NH}_3$  concentrations.

#### **4.1.6 Measurement uncertainty**

From 2008 to 2012, 287 data pairs from Dutch monitoring sites have been collected at six locations for sampler triplicates (averaged) and “reference” (AMOR) measurements, each for an exposure period of one month. The data pairs have been compared by orthogonal regression according to the procedure laid down by the EC Working Group [91]. From this, the uncertainty of the results of the diffusive sampler has been calculated, employing an user derived calibration (see 4.1.7). In this calculation the input uncertainty of the reference measurement results is 5,1 % ( $k=1$ ).

The results of the regression and uncertainty evaluation for the full dataset are given in Figure 4.4. The relative uncertainty of the results of the Gradko sampler for the full dataset is 14 %. The mean value of the sampler is  $9,7 \mu\text{g}/\text{m}^3$ , equal to the mean “reference” value (AMOR). In order to investigate whether these findings are affected by the measured concentration ranges, the dataset has been split into two sets: one for 3 stations with relatively high results and one for 3 stations with relatively low results. The results of this evaluation for the stations with high results are presented in Figure 4.5, those for the stations with low concentrations in Figure 4.6, with 2 outliers removed.

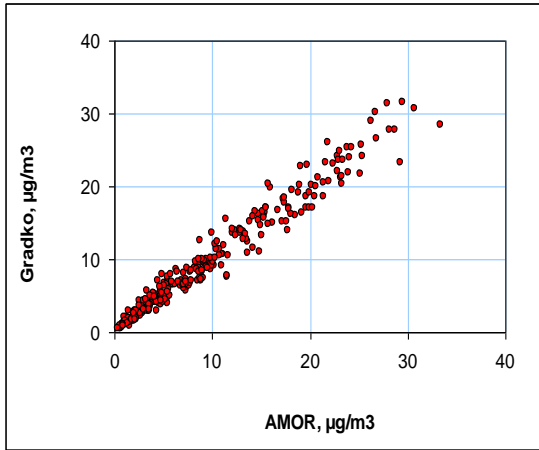


Figure 4.4 - Results of comparison of Gradko and AMOR: full dataset

<i>REGRESSION OUTPUT</i>	
slope b	0,991
uncertainty of b	0,0108
intercept a	0,16
uncertainty of a	0,133
number of data pairs	287
r <sup>2</sup>	0,97
<i>EQUIVALENCE TEST RESULTS</i>	
random term	1,3 µg/m <sup>3</sup>
bias at reference value	0,0 µg/m <sup>3</sup>
combined uncertainty	1,3 µg/m <sup>3</sup>
<b>relative uncertainty</b>	<b>13,9 %</b>
ref uncertainty	0,5 µg/m <sup>3</sup>
mean reference value	9,7 µg/m <sup>3</sup>

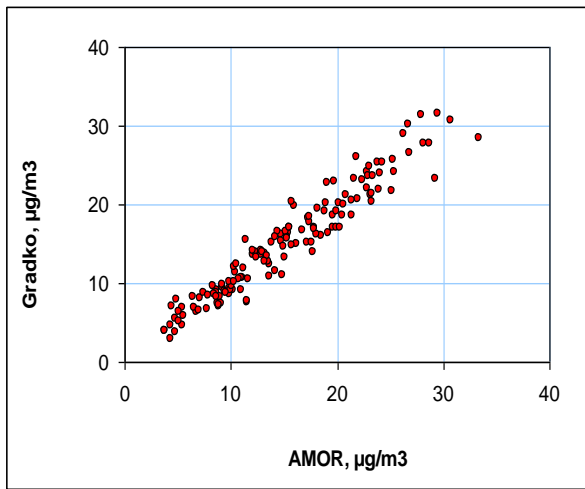
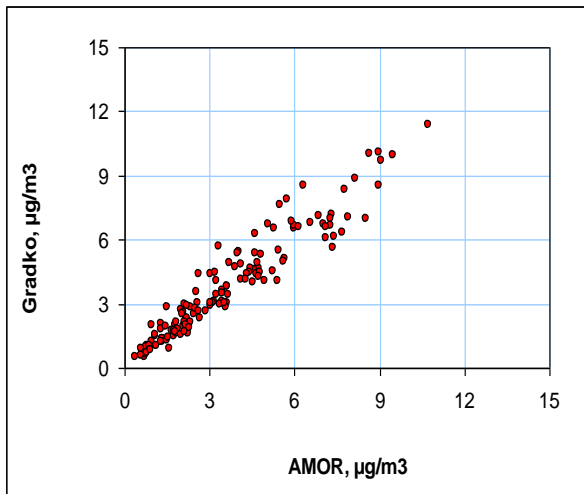


Figure 4.5 - Results of comparison of Gradko and AMOR: high concentrations

<i>REGRESSION OUTPUT</i>	
slope b	0,980
uncertainty of b	0,0208
intercept a	0,18
uncertainty of a	0,353
number of data pairs	146
r <sup>2</sup>	0,93
<i>EQUIVALENCE TEST RESULTS</i>	
random term	1,7 µg/m <sup>3</sup>
bias at reference value	-0,1 µg/m <sup>3</sup>
combined uncertainty	1,7 µg/m <sup>3</sup>
<b>relative uncertainty</b>	<b>10,9 %</b>
ref uncertainty	0,8 µg/m <sup>3</sup>
mean reference value	15,3 µg/m <sup>3</sup>



<b>REGRESSION OUTPUT</b>	
slope b	1,027
uncertainty of b	0,0260
intercept a	0,01
uncertainty of a	0,115
number of data pairs	139
r <sup>2</sup>	0,91
<b>EQUIVALENCE TEST RESULTS</b>	
random term	0,7 µg/m <sup>3</sup>
bias at reference value	0,1 µg/m <sup>3</sup>
combined uncertainty	0,7 µg/m <sup>3</sup>
<b>relative uncertainty</b>	<b>19,2 %</b>
ref uncertainty	0,2 µg/m <sup>3</sup>
mean reference value	3,7 µg/m <sup>3</sup>

**Figure 4.6 - Results of comparison of Gradko and AMOR: low concentrations**

Figures 4.5 and 4.6 show that for the different concentration regions (means of sampler results 15,3 µg/m<sup>3</sup> for the high levels and 3,7 µg/m<sup>3</sup> for the low respectively) the relative uncertainties are markedly different: for low levels the uncertainty is about 2 times higher. Note that the uncertainties do not include a contribution from the monthly calibration of the sampling rate. It is assumed that this contribution is random in nature, and that, by virtue of the regression being the outcome of an evaluation of 49 months, the contribution will be negligible.

Another factor to consider is the reduction of the above uncertainties due to the use of triplicate samplers. For single results the uncertainty should – in principle – include this reduction. In order to study the magnitude of this contribution, standard deviations and relative standard deviations have been calculated for the triplicate results that have been used for the above evaluations.

The standard deviations obtained have been plotted against the corresponding mean sampler values in Figure 4.7. This shows a large scatter in the relationship between standard deviation and AMOR mean value. The slope of the regression equation forced through zero indicates the pooled relative standard deviation to be around 8 %. When a separation is made between sites with high and low concentrations, the pooled relative standard deviations for individual sites are found to differ considerably (see Table 4.4 -).

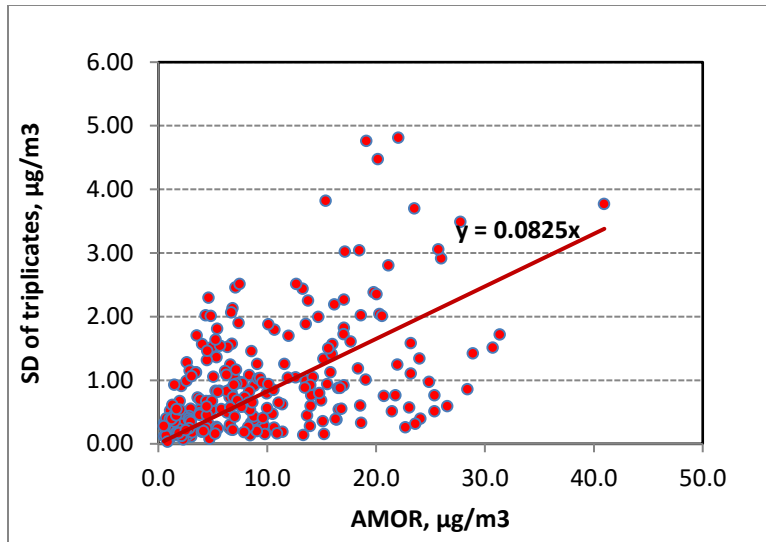


Figure 4.7 - Standard deviations of Gradko triplicates plotted vs. AMOR means

Table 4.4 - Standard deviations of pooled triplicates for individual Dutch sites

Site code	Mean concentration (µg/m <sup>3</sup> )	Standard deviation (µg/m <sup>3</sup> )	Relative standard deviation (%)
131	18,7	2,0	10,5
633	10,3	1,1	10,7
738	15,5	1,6	10,1
444	2,0	0,44	21,8
538	5,2	0,93	17,2
929	5,0	0,99	20,0

For sites with high mean concentrations (>10 µg/m<sup>3</sup>) the relative standard deviation is about 10 %, resulting in a contribution for the use of single samplers of about 6 %. For sites with low mean concentrations, the relative standard deviation is about 20 %, resulting in a contribution for the use of single samplers of about 12 %. However, when results of monthly sampling are averaged, e.g., to form yearly averages, the contribution is reduced by a factor  $1/\sqrt{n}$ , in which  $n$  is the number of monthly results used to form the average. For a yearly average, the contribution from the use of single samplers would reduce to about 1,8 % for sites with high concentrations, and to 3,5 % for sites with low concentrations. In both cases, the contributions are insignificant in comparison to the uncertainty resulting from the comparison with the reference method.

Concluding, the expanded uncertainty of the results of the Gradko sampler is estimated to be:

- $2\sqrt{(11^2 + (10/\sqrt{n})^2)}$  % for high concentrations (mean > 10 µg/m<sup>3</sup>);
- $2\sqrt{(19^2 + (20/\sqrt{n})^2)}$  % for low concentrations.



#### 4.1.7 Known applications

The Netherlands Institute of Public Health and the Environment (RIVM) has been using the short 3,5 cm membrane (Gradko) sampler since 2005 for measuring ammonia in nature areas in the MAN-monitoring system (Monitoring of Ammonia in Nature). The MAN performs a hybrid monitoring system, based on 6 AMOR locations (since 2016 replaced with DOAS equipment) in combination with Gradko samplers on circa 280 locations in 82 nature areas.

Triplicate samplers are also being used on the AMOR sites in order to calibrate the Gradko samplers each month. In this way, the cheap and little demanding Gradko samplers can be adapted to the accuracy of the AMOR measurements, resulting in an improved accuracy on all 280 MAN-sites.

The procedure in the MAN-network is as follows:

- Samplers are produced and delivered by the manufacturer (Gradko) to RIVM;
- Samplers are sent to local nature managers and volunteers accompanied by forms and instructions for the actual deployment. Samplers are exposed for one month *without* any further protection, e.g. shelters, in order to maintain unnoted during performance;
- After exposure, samplers and forms are returned to RIVM by mail;
- RIVM then sends the samplers to the manufacturer for analysis. Results are received in the form of spreadsheets and .pdf for further processing;
- For the calculation of the concentrations measured, RIVM uses a single sampling rate of 152 cm<sup>3</sup>/h is used for all exposure periods, regardless of variations in (e.g.) ambient temperature.

For each AMOR-location the data available consist of:

- Sets of triplicate results for diffusive samplers and blank samplers for each monthly monitoring period;
- Sets of monthly average results for AMORs when the data capture based on hourly values is ≥ 85 %.

The six AMOR-sites represent a wide range (1-16 µg/m<sup>3</sup>) of atmospheric ammonia concentrations. To determine the calibration parameters the ratio between the AMOR-concentration and the mean of the triplicate is determined for each AMOR-station. After that, a linear regression is performed on the five/six ratios against the triplicate means (Equation 12). Then, the determined calibration parameters are applied to the non-calibrated passive samplers.

$$y = a + b * x \tag{12}$$

where

- y is concentration (LML) divided by concentration (passive sampler);
- x is concentration (passive sampler).

The calibration results in a notably decreased deviation between sampler values and AMOR values in the concentration range of 0-10  $\mu\text{g}/\text{m}^3$  (Figure 4.8). The original sampler data suffer from influences of meteorology, especially temperature, which is nearly totally absent in the calibrated sampler results [92].

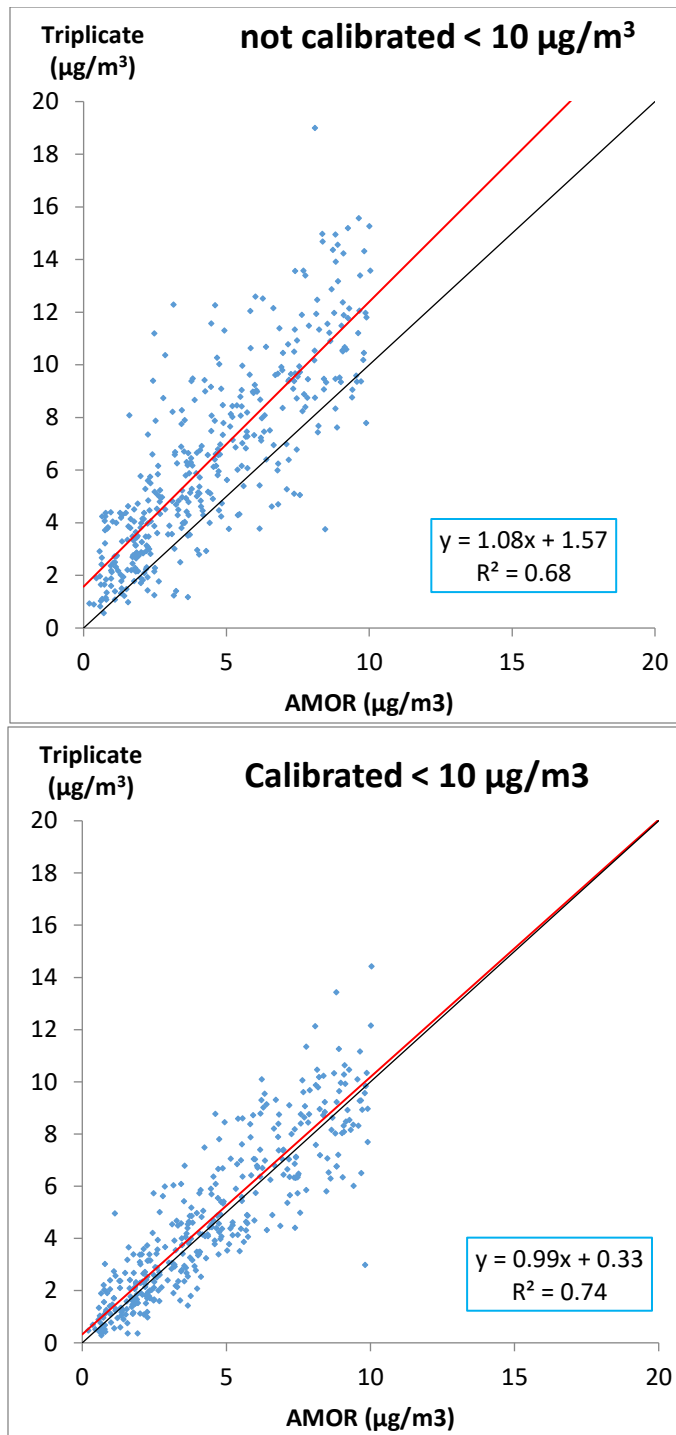


Figure 4.8 - Original and calibrated sampler values against AMOR measurements. The calibration has been performed by successive exclusion of the AMOR location for which the comparison with Gradko-samplers is made

The resulting uncertainties in the sampler measurements have been reported [36], taking also into account the uncertainty of the AMOR-equipment, is shown for different situations in Table 4.5 . These values are for concentrations from 2 to 5  $\mu\text{g}/\text{m}^3$  nearly the same as the standard deviations of pooled triplicates in Table 4.1, although the data here refer to single samplers and include the uncertainty in AMOR measurements. From 10 to 20  $\mu\text{g}/\text{m}^3$  the uncertainties are two times higher than the values in Table 4.5.

**Table 4.5 - Uncertainty in Gradko samplers for different ammonia concentrations, based on single sampler measurements per month. [85]**

Concentration ( $\mu\text{g}/\text{m}^3$ )	Uncertainty absolute ( $\mu\text{g}/\text{m}^3$ )			Uncertainty relative (%)		
	1 Month	3-Month	Year	1 Month	3-Month	Year
1	0,41,	0,24	0,14	41	24	14
2	0,53	0,33	0,22	27	17	11
5	1,1	0,69	0,49	21	14	9,8
10	2,0	1,3	0,96	20	13	9,6

## 4.2 Passam sampler

### 4.2.1 Sampler design

The ammonia diffusive sampler from Passam is a badge-type sampler that collects ammonia molecules onto an absorbent material impregnated with phosphoric acid. Thus,  $\text{NH}_3$  is trapped as ammonium phosphate on the absorbent material. A schematic of the ammonia passive sampler is shown in Figure 4.9. It consists of a polypropylene housing (sampler case) with an inner diameter of 23 mm and a length of 20 mm. The opening is equipped with a wind protection (glass fibre and steel screen) to reduce the effect of wind on the uptake rate. In addition, the samplers shall be installed in a protective shelter to minimise the effects from the environmental factors (e.g. wind, rain, sunlight, etc.), see Figure 4.10.

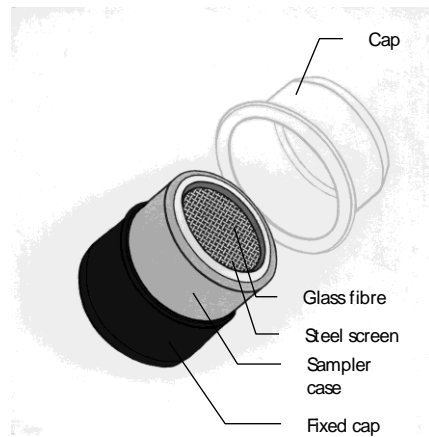


Figure 4.9 – Schematic of ammonia diffusive sampler from Passam



Figure 4.10 - LHS: Protective shelter for NH3 Sampler; RHS: Mounting NH3 Sampler with clips

#### 4.2.2 Extraction and analysis

After the exposure of the samplers (typical exposure times range from 2 to 4 weeks), ammonia is extracted from the absorbent material and its quantity is determined spectrophotometrically at 630 nm using the Indophenol-method. Here, the reaction with phenol and alkaline sodium hypochlorite produces indophenol. The intensity of this blue dye can be easily detected by photometry. The reaction is accelerated by the addition of sodium nitroprusside as a catalyst. Two types of solution may be used:

- Solution I: 10 g of Phenol, 50 mg of sodium nitroprusside, filled up to 1 litre with ultra-high purity water;
- Solution II: 5 g Sodium hydroxide, 4,2 ml sodium hypochlorite (12 % available chlorine) filled up to 1 litre with ultra-high purity water.

#### 4.2.3 Application range and conditions

Performance data are revised each year according to the corresponding quality report. The data are published on the website: [www.passam.ch](http://www.passam.ch) and are available on request.

**Table 4.6 - Performance data of Passam's ammonia diffusion tube**

Sampling rate	31,5 ml/min at 20 °C
Working range	0,5 – 30 µg/m <sup>3</sup> (see also Figure 4.13)
Sampling period	2 – 4 weeks
Detection limit	0,2 µg/m <sup>3</sup> (4-week exposure period)
External influences:	influence of wind speed < 10 % up to 4,5 m/sec
wind speed	using protection shelters
temperature	no influence between 10 to 30 °C
humidity	no influence between 20 to 80 %
Storage	Before use: 4 months After exposure : 2 months
Interferences	Ammonium particles are not collected
Expanded uncertainty*	29,3 % at a level 1 to 5 µg/m <sup>3</sup>

#### 4.2.4 Uptake rate and environmental effects

In the study by Kirchner [93] possible variations of the performance of the passive sampler were examined relating the average bias to the average environmental conditions. The measurements were performed at concentration levels of ammonia between 2 and 8  $\mu\text{g}/\text{m}^3$ . The influence of the temperature and relative humidity on the ammonia concentration is  $< 1 \mu\text{g}/\text{m}^3$ .

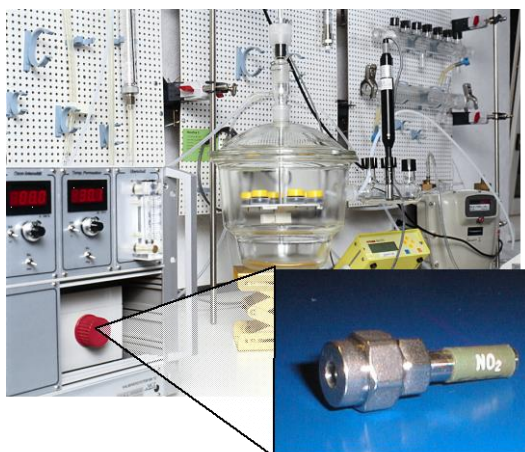
**Table 4.7 Bias due to influence of temperature and relative humidity**

Temperature ( $^{\circ}\text{C}$ )	$< 5$	$5 - 15$	$> 15$
Bias ( $\mu\text{g}/\text{m}^3$ )	-0,78	0,62	0,50
Relative humidity (%)	$< 75$	$75 - 85$	$> 85$
Bias ( $\mu\text{g}/\text{m}^3$ )	-0,26	0,74	-0,58

#### 4.2.5 Validation of sampler performance

##### 4.2.5.1 Laboratory experiments

Passam's laboratory is equipped with a calibration system of Umwelttechnik GmbH, Ober-Mörlen, Germany. Calibration gas is produced by constant emission of substances out of permeation devices in a temperature controlled heating chamber. The airflow was measured by an BIOS Air Flow Meter, the weight loss of  $\text{NH}_3$  was measured repeatedly by a certified analytical balance. All laboratory test were done on this testing set-up which is shown in Figure 4.11.



**Figure 4.11 – Test facilities for assessment of sampling rate**

The concentration of the test atmosphere was calculated based on the air flow and weight loss of the permeation tube. It is assumed that the conversion efficiency is 100 % under laboratory conditions. The samplers were rotated in order to have a wind speed of 0,5 m/sec. The following concentration levels were applied.

Samplers were exposed at different times and overlapping periods in various concentrations levels. This resulted in a number of different concentrations as given in Table 4.8. All passive samplers were measured as triplicates.

**Table 4.8 - NH<sub>3</sub> exposure concentration levels for sampler validation  
[Conversion factor 0,67]**

Level	Air flow (l/min)	NH <sub>3</sub> (ppb test atmosphere)	NH <sub>3</sub> (µg/m <sup>3</sup> )	Duration (h)
A	2,43	45,9	30,8	336
B	4,48	21,3	14,3	269
C	8,56	6,0	4,0	336
D	12,17	3,0	2,0	334

**Table 4.9 - Experimental determination of sampling rate at different concentration levels**

Code	Exposure time (min)	Test atmosphere (ug/m <sup>3</sup> )	Dose (mg/m <sup>3</sup> *min)	Amount NH <sub>3</sub> (pg)	Diffusive sampler (µg/m <sup>3</sup> )
1	20175	30,8	621,39	19591	30,8
2	20325	22,5	457,31	14556	22,7
3	36315	23,5	53,40	26880	23,5
4	16140	18,7	301,82	9492	18,7
5	5850	22,4	131,04	4120	22,4
7	26175	20,1	526,12	16533	20,1
8	16140	18,7	301,82	9507	18,7
10	10060	4,0	40,24	2231	7,0
11	20150	4,0	80,60	3770	5,9
12	20185	3,0	60,56	3091	4,9
13	20010	2,0	40,02	1649	2,0
14	9915	2,0	19,83	1066	3,4
15	30245	2,7	81,66	3936	4,1
16	30100	2,7	81,27	3481	3,7
17	40160	3,0	120,48	4609	3,6



The dose was calculated from the exposure time that the sampler was exposed at each of the concentration levels, as detailed in Table 4.9 (column 3: Test atmosphere). The dose is the product of concentration level and the exposure time. The amount of NH<sub>3</sub> is the result of analytical procedure using the spectrophotometric determination (column 5: Amount of NH<sub>3</sub>).

The last column (column 6: Diffusive sampler) shows the result of the passive samplers obtained with the sampling rate of 31,5 ml/min that is valid for passam ammonia samplers. Using this data, the sampling rate was re-evaluated: a sampling rate of 31,8 ml/min was obtained, which is in good agreement with the previously determined sampling rate of 31,5 ml/min. The results are also presented in Figures 4.12 and 4.13, which show the determination of the sampling rate and the comparison of passive samplers with monitor measurements, respectively.

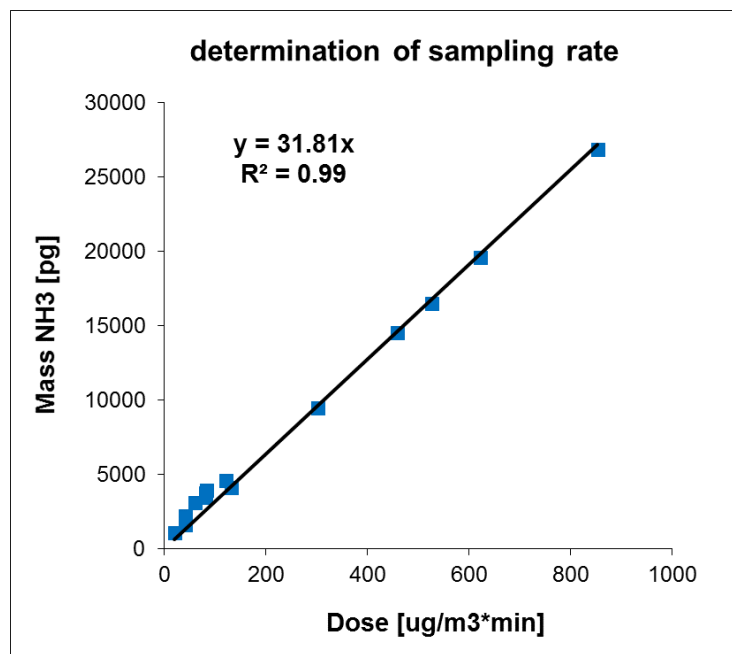


Figure 4.12 – Re-determination of sampling rate in the laboratory

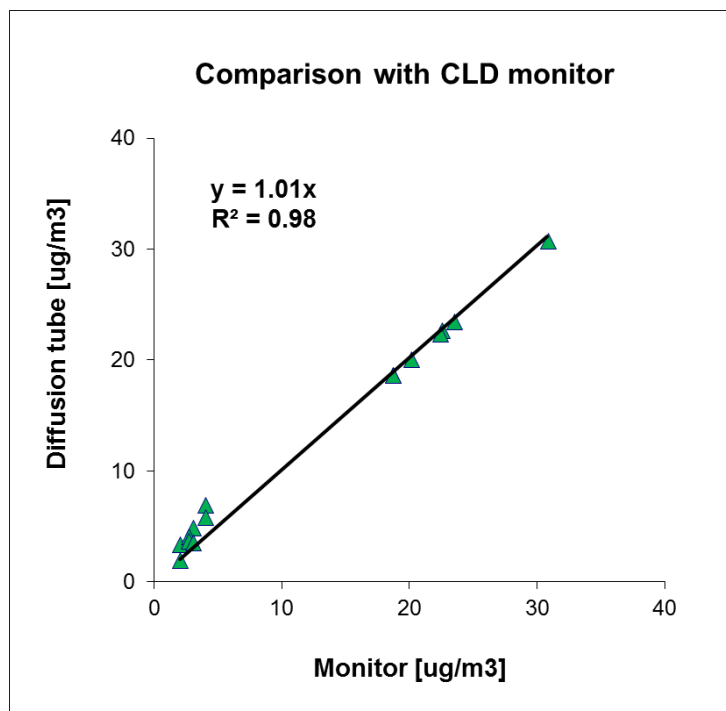


Figure 4.13 – Comparison NH<sub>3</sub> monitor and diffusive samplers using the sampling rate of 31,5 l/min

#### 4.2.5.2 Field experiments

The data of the field experiment of Kirchner were used to recalculate the sampling rate under field conditions. As reference method wet annular denuder system: AMOR was chosen [94, 95]. A sampling rate of 30,2 ml/min was obtained, which is in coincidence with the official sampling rate of 31,5 ml/min.

#### 4.2.6 Measurement uncertainty

The measurement uncertainty was evaluated according to JCGM 100. The whole analytical chain was considered as described in the evaluation of measurement data - Guide to the expression of uncertainty in measurement [96]. Input parameters are calibration records of analytical function, multiple field samples, laboratory and field blanks as well as influence of meteorological factors. The data were evaluated based on the values obtained during 2009.

Table 4.10 - Passam diffusion sampler uncertainties

measuring range $\mu\text{g}/\text{m}^3$	1 - 5	> 5
combined uncertainty	14,7	10,7
expanded uncertainty	29,3	21,4

## 4.3 CEH ALPHA samplers

### 4.3.1 Sampler design

The ALPHA (Adapted Low-cost High Absorption) sampler is a badge-type diffusive sampler developed by the Centre for Ecology & Hydrology in UK (Tang et al. 2001). The ALPHA sampler (Figure 4.14) is made up of a circular polyethylene vial (26 mm height, 27 mm diameter) with one open end. An internal ridge (G, 17 mm height) supports a filter (F, 24 mm diameter). The filter is coated with an acid such as citric acid, which serves to capture the ammonia, and is held in place with a polyethylene ring (E, 6 mm height). The open end is capped with a polyethylene cap with a hole punched out in the centre (D, 23 mm diameter), which holds in place a white PTFE (teflon) membrane (C, 27 mm diameter, 5 µm pore size) allowing gaseous ammonia to diffuse through. This end is positioned facing downwards. The membrane-cap end of the sampler is sealed with a top protective cap (B), which is removed prior to exposure. At the end of exposure, the membrane cap plus membrane are removed and replaced with a replacement solid cap (A).

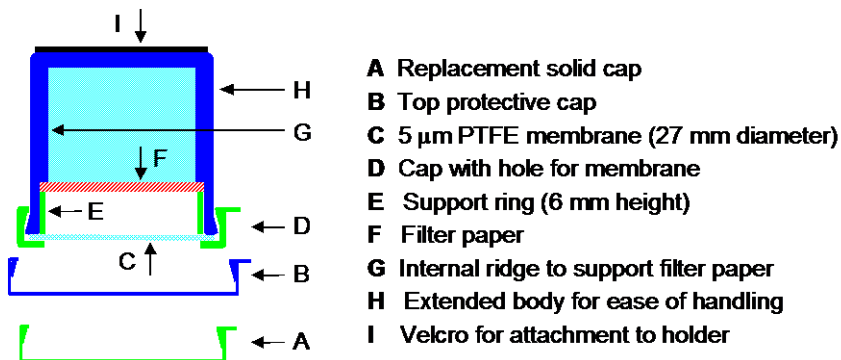


Figure 4.14 - Schematic view of ALPHA sampler

The ALPHA sampler geometry permits an optimised sampling rate for long-term sampling (1 or 2 monthly periods) plus high sensitivity to allow measurements down to low concentrations ( $<1\mu\text{g}/\text{m}^3 \text{NH}_3$ ) in background areas. The membrane inlet is placed directly at the mouth of the sampler, which minimises the formation of a boundary layer in front of the membrane, whilst achieving a stable, turbulent-free diffusion path length behind the membrane.

To make handling easier, the sampler body was extended behind the coated filter. The PTFE membrane + membrane cap are removed at end of exposure and sampler capped with replacement cap provided. This serves to avoid potential contamination arising from possible volatilisation of volatile ammonium salts on the outside of the PTFE membrane during exposure.

### 4.3.2 Extraction and analysis

Exposed samples are stored at 4 °C until analysis. In order to avoid potential contamination during the extraction process, care must be taken in handling the ALPHA samplers and components. Disposable gloves must be worn at all times. This serves to protect the samples from contamination by skin. It is also advised to avoid breathing directly on the samples, as exhaled breath contains ammonia.

### 4.3.3 Extraction of acid coated filter paper

The following steps are used for analyte extraction:

- 1) Using forceps, lift the plastic retainer ring out of the ALPHA sampler.
- 2) Place the open end of the ALPHA sampler over a 20 ml polystyrene pot (or other suitable container) and tap the sampler very gently against the pot until the coated filter paper drops out into the pot. If the paper does not drop out, then use a pair of clean forceps and remove the coated filter paper very carefully.
- 3) Add 3 ml deionised water to the filter paper in the pot. Cap the pot with a clean cap, label with sample name and leave to extract for at least one hour. Repeat this extraction with all of the samples (including a suitable number of ALPHA sampler blanks), noting the time at which the extraction process commenced.
- 4) Using a pair of clean forceps (rinse the forceps with deionised water in between different samples), pinch an edge of the filter paper and dunk it up and down in the extractant a few times to ensure that all the chemical species of interest enters into the extractant, and that the solution is well mixed.
- 5) For analysis on the AMFIA (AMmonia Flow Injection Analysis system), 1,5 ml of extracted solution is decanted into 3 ml autosampler tubes. Care should be taken to ensure that any bits of loose fibres coming off the filter paper are not decanted into the autosampler tubes, which may cause blockage in AMFIA.

### 4.3.4 Analysis of ammonium

#### 4.3.4.1 Flow Injection Conductivity Ammonium Analysers

The extracted samples are analyzed for ammonium on the AMFIA (ECN) and FloRRia system (an updated version of AMFIA; RR mechatronics, <http://www.mechatronics.nl/products/florria/>) at CEH. This analysis system is based on selective dialysis of ammonium across a membrane at high pH with subsequent analysis of conductivity. The calibration range normally used is 0 - 10 ppm (0,1 ppm, 1 ppm and 10 ppm calibration standards), and the QC's used are 0,2 ppm (low QC), 0,9 ppm (high QC), 2 (low QC) and 9 ppm (high QC). It may be necessary to dilute the extracted samples and repeat the analysis if they are outside the calibration range.

Measuring characteristics

- Dynamic range 5 ppb – 30 000 ppb;
- Resolution 5 ppb;
- Accuracy 5 %.



Figure 4.15 -FloRRia Flow Injection Ammonium Analyser

#### 4.3.4.2 Spectrophotometry

##### **A. The salicylate method [97]**

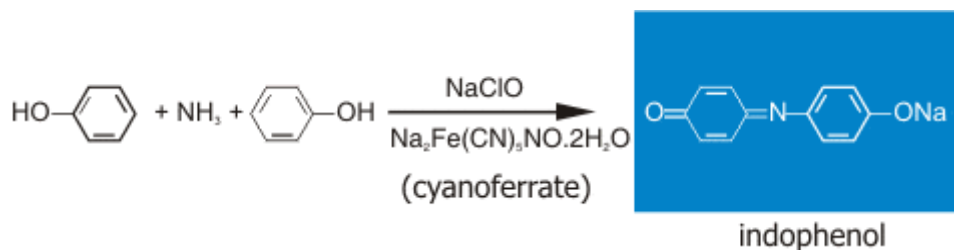
Ammonia reacts with salicylate and hypochlorite in a buffered alkaline solution in the presence of sodium nitroferricyanide (pH 12,8 - 13) to form the salicylic acid analog of indophenol blue. The blue-green color produced is measured at 660 nm. A rapid segmented flow analyzer: RFA 300 (Alpkem - USA), based on Continuous Flow Analysis techniques. (pers. Commun)

##### **B. Berthelot microplate method for ammonium**

Berthelot's reagent is an alkaline solution of phenol and hypochlorite. Ammonia reacts with Berthelot's reagent to form a blue product which is used in a colorimetric method for determining ammonia. Phenol in the Berthelot reagent can be replaced by a variety of phenolic reagents, the most common being sodium salicylate, which is significantly less toxic [98]. Replacement of phenol by 2-phenylphenol reduces interferences by a variety of soil and water constituents and improves color stability at slightly lower pH (Rhine et al. 1998 [99]). Berthelot's reagent has been used in a range of situations. It is often used in colorimetric methods, through an auto-analyser, spectrophotometer, or multiwell plate spectrophotometer. The reagent lacks sensitivity in situations where there may be amines as well as ammonia, however this can be overcome in part by the use of 2-phenylphenol to replace phenol.

##### **C. Indophenol method**

Ammonium ion is quantified by visible spectrometry as indophenol: at basic buffered pH, ammonium ion reacts with phenol and sodium hypochlorite, with pentacyanonitrosylferrate catalysis (in the following *cyanoferrate*), to form indophenol. The reaction product is intensely coloured in blue, and its absorbance measured at 635 nm.



#### 4.3.4.3 Ion Chromatography

Ion chromatography can be used (and is recommended in the EMEP manual [100] for the determination of the ammonium ions in the extracts of impregnated filters. See also Chapter 8: Radiello sampler details. A small volume of the sample, typically less than 0,5 ml, is introduced into the injection system of an ion chromatograph. The sample is mixed with an eluent and pumped through a guard column, a separation column, a suppressor device and a detector, normally a conductivity cell.

The separation column is an ion exchange column which has the ability to separate the ions of interest. The separation column is often preceded by a shorter guard column of the same substrate as in the separation column to protect the separation column from overloading and particles. Different types of separation columns, eluents and suppression devices have to be used for anions and cations respectively. Each ion is identified by its retention time within the separation column. The sample ions are detected in the detection cell, and the signals produced (chromatograms) displayed on a strip chart recorder or a PC equipped with the necessary software for measurement of peak height or area. The ion chromatograph is calibrated with standard solutions containing known concentrations of the ions of interest. Calibration curves are constructed from which the concentration of each ion in the unknown sample is determined.

#### 4.3.5 Application range and conditions

The limit of detection for 1 month exposure ~ 0,03 µg/m<sup>3</sup> using flow injection conductivity analysis or colorimetry (salicylic acid). The range of meteorological conditions where the use of the ALPHA sampler is applicable is given in Table 4.11.

**Table 4.11 - Application range of NH<sub>3</sub> ALPHA sampler**

Parameter	Range where no effect on uptake rate is observed
Temperature	-10 to 35 °C.
Relative humidity	10 to 100 %.
Wind speed	0 to 40 m/s
Sampling duration	24 hours to 3 months

According to the manufacturer, the samplers are stable for at least 6 months before and after exposure, if kept refrigerated at ~ 4 °C in an ammonia-free environment. 10 % of a batch of samples should be kept as blanks.

#### 4.3.6 Uptake rate and environmental effects

The effective volume of air sampled ( $V$ , m<sup>3</sup>) is given by:

$$V = DA t / L \quad (13)$$

where

$t$  is the time of exposure (s), for NH<sub>3</sub>,  $D = 2,09 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  at 10°C

The air concentration of ammonia ( $\chi$ , e.g.  $\mu\text{g m}^{-3}$ ) can then be calculated as:

$$\chi = (m_e - m_b) / V \quad (14)$$

where

$m_e$  is the amount of ammonia collected on an exposed sample (e.g.  $\mu\text{g}$ );

$m_b$  is the amount of ammonia in the blank sample (e.g.  $\mu\text{g}$ ).

The theoretical uptake rate, based on sampler dimensions =  $4,34 \times 10^{-3} \text{ m}^3/\text{h}$ . It is noted that the theoretical uptake rate is substantially higher than the values measured in laboratory and field studies. Results from the comparison of the ALPHA samplers against the DELTA system at 12 (up to 2014) and 9 (2014 onwards) intercomparison sites across the UK (lowest concentration- $100 \mu\text{g}/\text{m}^3$ ) were used to derive an effective uptake rate for the ALPHA sampler and also to ascertain linearity of response. Based on field calibration against the DELTA system, the effective uptake rate (with Swiftlab 5 $\mu\text{m}$  pore size PTFE membrane inlet) was derived as:

$$V (\text{m}^3) = 0,00324 \text{ m}^3 \times t (\text{h}) \quad (15)$$

#### 4.3.7 Validation of sampler performance

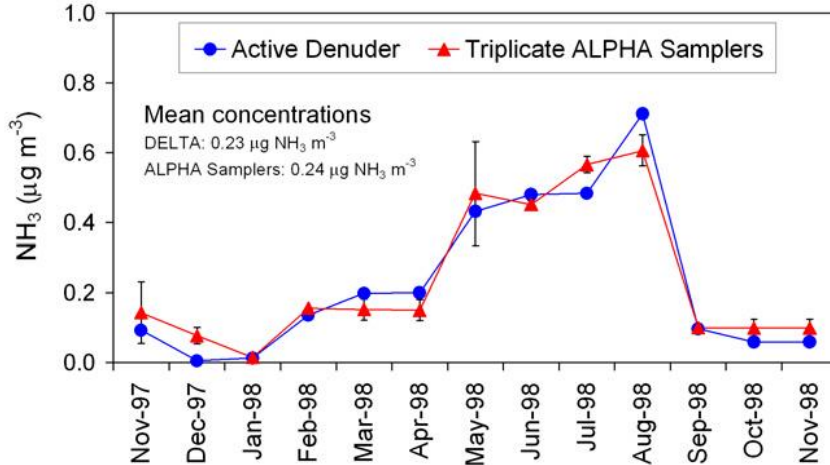
##### 4.3.7.1 Laboratory experiments

The ALPHA sampler has not been tested by CEH under laboratory conditions, however the samplers participated in the MetNH<sub>3</sub> chamber. The results for this are described in Section 8.

##### 4.3.7.2 Field experiments

###### *EC Ecomont*

The ALPHA samplers have been tested within the EC ECOMONT project at several U.K. and European sites (Sutton et al. 2001 [18]) against the CEH DELTA system. Results from an intercomparison between the ALPHA samplers and an active denuder (CEH DELTA) system at Monte Bondone in Northern Italy are shown in Fig. 6. Even with a 9-month average concentration of around  $0,2 \mu\text{g}/\text{m}^3$ , the mean estimates agreed within 5 %, while the results show a very close agreement of individual monthly results.

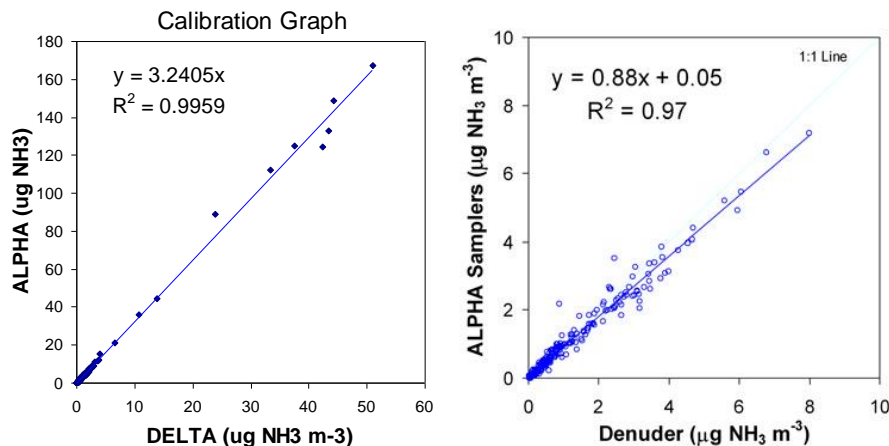


**Figure 4.16 - Intercomparison of  $\text{NH}_3$  measurement results by ALPHA sampler and active denuder system at Monte Bondone, Italy (ECOMONT project). Each data point for the ALPHA sampler results represent the mean  $\pm$  SD of replicate samples ( $n=3$ ).**

The results of the ALPHA samplers yielded good agreement with the reference denuder method ( $r^2 = 0,97$ ). The regression plot of the intercomparison is given in Figure 4.16. The method is sensitive enough to resolve low concentrations ( $< 1 \mu\text{g}/\text{m}^3$ ) in background areas. In tests in source regions, the method has also been demonstrated to be suitable for monitoring up to  $500 \mu\text{g}/\text{m}^3$  for exposure period of 1 month.

**UK intercomparison sites**

To provide an ongoing validation of the ALPHA sampler, its performance is continuously assessed at nine UK sites (historically 12 until 2013) within the NAMN. The comparison shown in Fig. 6.4 demonstrates good agreement of the ALPHA samplers, while the intercept is also small ( $0,05 \mu\text{g}/\text{m}^3$ ). The non-unity slope may be attributed to the additional resistance due to the membrane and boundary layer. This regression is used to calibrate the ALPHA sampler data



**Figure 4.17 - Relationship between monthly values from parallel DELTA (denuder) and ALPHA sampling at 9 sites in the UK.**



### US intercomparison

An intercomparison of three passive sampling devices (Radiello, Ogawa and ALPHA) was performed by Puchaliski et al. [101], with all samplers including the ALPHA performing well.

### AMOR-DELTA-ALPHA

An intercomparison of ammonia measurements by the RIVM AMOR system and the CEH DELTA (DENuder for Long-Term Atmospheric) sampling system have been carried out at the Zegveld site in the Netherlands since 2003. Zegveld (site number 633) is one of eight sites in the Dutch air monitoring network that uses the AMOR system, a wet annular denuder method operated by RIVM, to provide atmospheric ammonia concentrations at hourly resolution.

Two DELTA systems were operated in parallel alongside the hourly AMOR measurements. The replicated DELTA measurements showed good agreement, demonstrating high reproducibility in the method (slope = 1,00,  $R^2 = 0,91$ ) (Figure 4.18). A comparison of the mean of the paired DELTA monthly measurements with the AMOR hourly results (averaged to the corresponding DELTA monthly periods) over the period September 2003 to December 2015 also gave good agreement (slope = 0,96,  $R^2 = 0,69$ ) (Figure 4.18).

Since September 2012, monthly ALPHA measurements (deployed in triplicate) have also been added. The results of the intercomparison of the monthly ALPHA with the monthly averaged AMOR data over the period September 2012 to December 2015 are shown in Figure 4.18, with good agreement (slope = 1,03,  $R^2 = 0,87$ ).

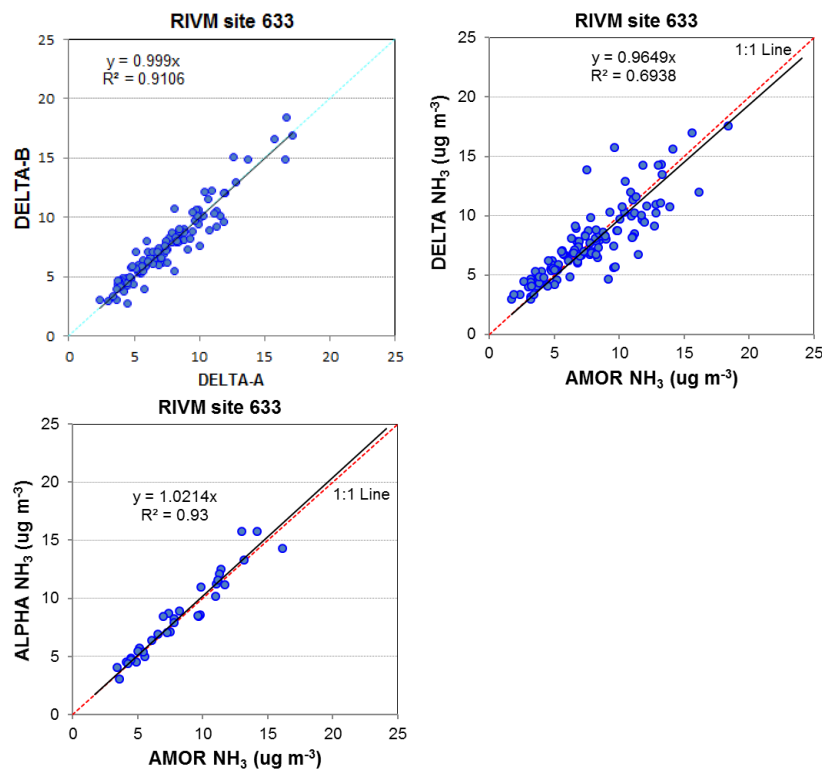


Figure 4.18 - ALPHA and DELTA AMOR intercomparison

#### 4.3.8 Measurement uncertainty

A total of 34 valid data pairs were collected between the period September 2012 to December 2015 at Zegveld for monthly ALPHA sampler measurements (averaged of triplicate samplers) and “reference” (AMOR) measurements (averaged to the corresponding ALPHA monthly period). The data pairs are compared by orthogonal regression according to the procedure laid down in GDE [91], as described in section 4.1.6. From this, the uncertainty of the results of the ALPHA sampler was calculated using a CEH derived uptake rate. In this calculation the input uncertainty of the reference measurement results is 5 % (k=1). The results of the regression and uncertainty evaluation for the full dataset are given below. The relative uncertainty of the results of the ALPHA sampler for the full dataset is 16,8 %. The mean value of the sampler is 8,4  $\mu\text{g}/\text{m}^3$ , equal to the mean “reference” value of 8,2  $\mu\text{g}/\text{m}^3$  (AMOR).

The measurement uncertainty of the ALPHA samplers have also been derived in a controlled laboratory chamber exposure study (see section 5).

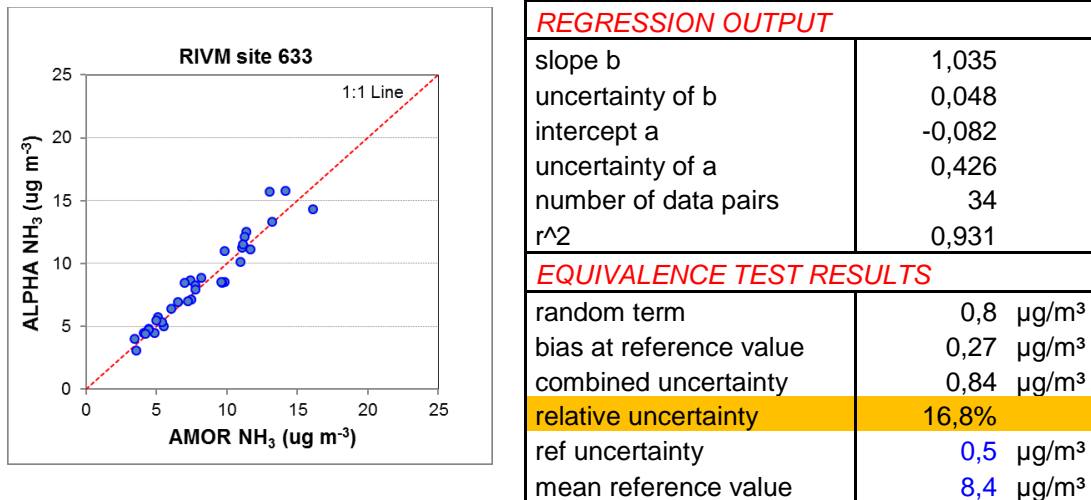
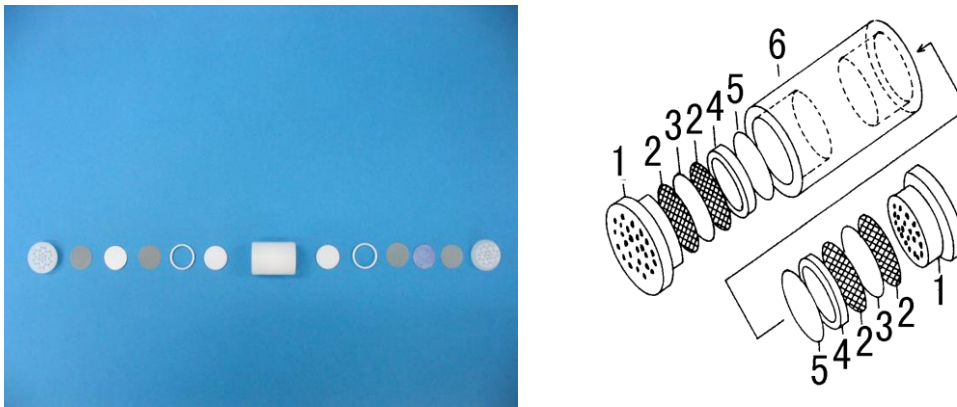


Figure 4.19 Relationship between monthly values from parallel AMOR (denuder) and ALPHA sampling

## 4.4 The Ogawa sampler

### 4.4.1 Sampler design

The Ogawa sampler [102] is a badge-type sampler that can be equipped with a sampling filter on either side of the sampler body (see). Sampling filters consist of glass-fibre. Both filters can be coated with citric acid for the sampling of ammonia, although in other studies other substrates have been used (phosphoric acid [103], boric acid [104], phosphorous acid [105]). Coated filters are supplied by the manufacturer. Filters may also be coated by users themselves; a procedure is described in [40]



**Figure 4.19 - Ogawa sampler; 1. Diffuser end cap; 2. Stainless steel mesh; 3. Sampling filter (14,5 mm  $\phi$ ); 4. Teflon ring; 5. Teflon disk; 6. Body (15 mm ID; 19 mm OD; 6 mm length)**

The presence of a second filter permits:

- Doubling the mass of ammonia sampled when combining both filters for analysis;
- Determining the precision of the sampling and analysis by analyzing both filters separately.

### 4.4.2 Extraction and analysis

The manufacturer describes a procedure for the determination of the collected ammonia by ion chromatography after extraction with water. [102] The procedure used is as follows:

- 1) One or two sampling pads (if pads from both ends are combined) are put into a 25-ml test tube. To the tube 8 mL of deionized water is added;
- 2) The pads are extracted using ultrasonic vibration for 30 min after which the tube is shaken to homogenize the extract;
- 3) The extract is analyzed using ion chromatography.

Various analytical procedures are described in the references ([40, 43, 66, 101, 106, 107] [104], [105] based wither on IC or colorimetry

#### 4.4.3 Application range and conditions

The manufacturer gives no recommendations for minimum and maximum exposure periods or for minimum and maximum concentrations feasible in measurement practice. In practical studies exposure periods vary from 5 minutes when measuring ammonia near sources [40] up to 3 weeks [106]. Detection limits calculated in practical studies 0,18  $\mu\text{g}/\text{m}^3$  for a 3-week exposure [106] and increases nearly linearly with reduces exposure periods [40]. The detection limit is affected by the cleanliness of preparation, handling and storage of samplers. [103] The upper concentration limits encountered in practice are around 100  $\mu\text{g}/\text{m}^3$  for a 7-day exposure [43] and around 8000  $\mu\text{g}/\text{m}^3$  for a 5-minute exposure [40]. When sampling at such high concentrations the capacity of the sampler is limited by diffusion and sorption into the filter pad. The estimated maximum load of ammonia under such conditions is about 12  $\mu\text{g}$  [40].

The manufacturer gives no recommendations as to ranges of temperature and relative humidity for which the sampler may be used. None of the studies reported here provides any further information about ranges of environmental conditions for which the sampler is suitable.

The sampler should always be exposed with a shelter as provided by the manufacturer. The manufacturer specifies the following conditions for storage of coated filters, samplers and sampled filters upon refrigeration:

- Coated filters sealed in original glass vial with aluminium pouch: 90 days
- Sampler loaded with coated filter(s) placed in bag in sealed brown vial: 90 days
- Exposed sampler placed in bag in sealed brown vial: 14 days\*
- Filter extract in sealed amber glass vial: 90 days

\* Filters should be analyzed as soon as possible after exposure.

#### 4.4.4 Uptake rate and environmental effects

The Ogawa Protocol gives a sampling rate of 32,3  $\text{cm}^3/\text{min}$  for 2-sided exposure without specifying (potential effects of variations in) concentration, temperature or relative humidity. Tate [103] first calculates the sampling rate to be 33,2  $\text{cm}^3/\text{min}$  for 2-sided exposure using a diffusion coefficient value for ammonia of 0,249  $\text{cm}^2/\text{s}$ . After revisiting the dimensions of the sampler he recalculates the sampling rate to be 36,4  $\text{cm}^3/\text{min}$ . Roadman [40] calculates the sampling rate to be 31,1  $\text{cm}^3/\text{min}$  for 2-sided exposure. However, the value of the diffusion coefficient used is 0,232  $\text{cm}^2/\text{s}$  at 25 °C. This value and similar values, have been used in the other studies cited above.

## 4.4.5 Validation of sampler performance

### 4.4.5.1 Laboratory experiments

The only laboratory experiments with Ogawa samplers were reported by Gartman et al. [108] in a conference poster which does not appear to have led to a publication. In the abstract, preliminary results of the laboratory validation of three samplers were described: the Alpha, Radiello and Ogawa. Samplers have been exposed to a concentration of ammonia of 13,6 µg/m<sup>3</sup> for 10 days. The Ogawa sampler has been exposed in triplicate, yielding a mean concentration of 15,5 µg/m<sup>3</sup> with a standard deviation of 1,4 µg/m<sup>3</sup>, i.e., a systematic deviation of +14 %. It is recommended that this data is treated with caution.

### 4.4.5.2 Field experiments

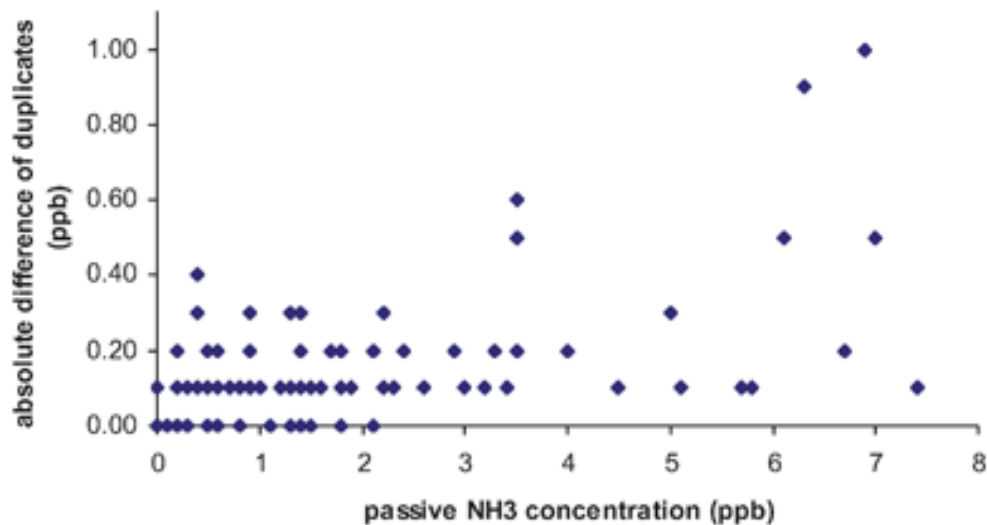
A number of publications have described the verification/validation of (elements of) sampler performance. Most of these give practical values for sampler precision and detection limits. The number of publications in which actual validation (determination of accuracy) of the sampler by comparison with an independent method has been performed is limited. Tate [103] has determined the precision of the Ogawa ammonia sampler from duplicate exposures. Early results revealed relatively high precision; only at ammonia loads on the sampler are above 10 µg (corresponding to about 13 µg/m<sup>3</sup> for a 2-week exposure) the coefficient of variation of duplicate results (CV) is below 10 %. After improvement of the sampler cleaning procedure the CV dropped to 5 % for levels above 0,6 µg of ammonia (0,76 µg/m<sup>3</sup> for a 2-week exposure). Comparisons have been performed against URG annular denuders (ADS) inside a sludge collection plant. When using a sampling rate of 38,8 cm<sup>3</sup>/min the relationship for all data is given by:

$$ogawa = 1,24 \cdot ADS \quad (16)$$

It is noted that ammonia levels measured are very high and not variable (only 2 levels measured by the ADS). The positive bias of the Ogawa – even when using a sampling rate that is much higher than those typically used (see above) – suggests to the author that the ADS does not quantitatively capture the ammonia present in the ambient air. Their conclusion is that the accuracy of the Ogawa sampler is ± 30 %. Tanner [104] has compared results obtained using the Ogawa sampler (1-week exposure) with those obtained using honeycomb denuders. Mean average concentrations over the period of comparison are 0,72 µg/m<sup>3</sup> for the denuder and 0,93 µg/m<sup>3</sup> for the diffusive sampler.

Roadman et al [40] has measured the precision of the sampler from replicate results at varying exposure periods. The CV is reported to be between 5 % and 10 % for masses of ammonia sampled ranging from detection to saturation limits. The accuracy of the results of the Ogawa sampler has been determined by comparison with results from impingers containing an aqueous solution of phosphoric acid. Results show that the Ogawa sampler gives results comparable to those of the impingers, but systematically produces lower results at high concentrations (inside poultry houses). Roadman attributes this to the fact that the impinger will also collect particles containing ammonium salts.

In the Four-Corners Study [106] Sather et al. have determined the precision of the sampler over a period of one year from 124 duplicate results. The exposure period is 3 weeks. The absolute differences between duplicates are shown in Figure 4.20.



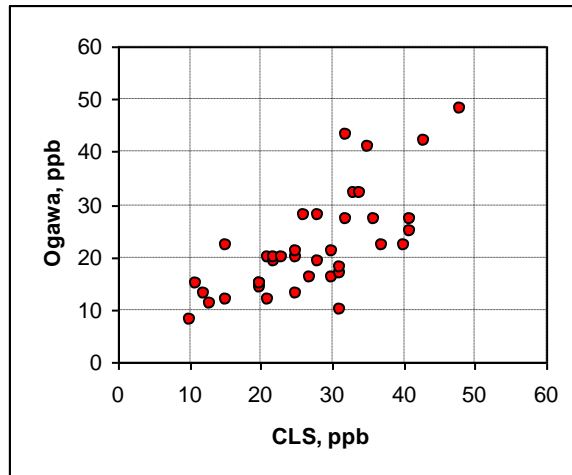
**Figure 4.20 - Absolute differences for duplicates as a function of ammonia concentrations [98]**

From all results Sather has calculated the median absolute difference to be  $0,07 \mu\text{g}/\text{m}^3$ . From the figure the CV of the duplicate results may be estimated by “eye-ball” statistics to be about 5 % to 10 % for levels above  $0,7 \mu\text{g}/\text{m}^3$ . The results of the Ogawa have been compared with those obtained using a photo-acoustic spectrometry analyzer. Mean concentrations found over the one-year study period are  $1,9 \mu\text{g}/\text{m}^3$  for the analyzer and  $1,3 \mu\text{g}/\text{m}^3$  for the Ogawa. The differences are not significantly different, and may have been caused by release of ammonia from particle filters employed with the analyzer. The observation that after approximately 6 months of deployment the analyzer systematically produces high results supports this suggestion.

Meng et al. [66] in their study into ammonia levels in China, have determined the precision of the Ogawa, expressed as the median CV for all duplicate results, to be 9,1 % for a 10-day exposure period. The levels of ammonia measured (annual means) range from about 2 to  $9,9 \mu\text{g}/\text{m}^3$ . A limited comparison (8 results) with a chemiluminescence (CLS) analyzer equipped with an ammonia converter reveals a ratio between Ogawa and CLS results of 0,76. As above, the difference may be explained by the use of particle filters to protect the analyzer from contamination. In a second publication [43]. Meng et al. have again determined precision and accuracy of Ogawa ammonia samplers. Samplers have been exposed in Beijing at an urban and a rural site, leading to a range of concentrations from 0,7 to 85 ppb for exposure periods of 7 and 10 days, respectively. CVs for duplicate samplers are calculated to be 9,9 % for the urban site and 6,5 % for the rural site. Comparison with results obtained using a converter-equipped chemiluminescence analyzer (CLS) yields a relationship (forced through (0,0)) of:

$$ogawa = 0,83 \cdot CLS \quad (17)$$

When unforced orthogonal regression is applied to an emulation of the dataset the slope of the relationship is close to 1. However, the scatter of the results is considerable ( $r^2 = 0,5$ ), see Figure 4.21.



**Figure 4.21 - Relationship between results of Ogawa and chemiluminescence analyzer. Data have been reproduced from the original graph by hand**

Reese [109] has compared the performance of the Ogawa with a number of instrumental methods when measuring ammonia emissions from area sources within dairies. The exposure period of the samplers is 12 hours, measured concentrations range from approximately 100 to 1400 ppb. The instrumental methods include:

- Annular denuders;
- FTIR;
- DOAS.

The latter two methods are open-pathway methods. Results of the comparisons indicate that the passive samplers tend to yield higher concentrations relative to both the ADS and FTIR. The difference between results for Ogawa and FTIR may be explained by the fundamental difference between single-point and path-integrated measurements. Differences between results for Ogawa and ADS are less pronounced. The author attributes some of the high results for Ogawa to high wind velocities (> 5 m/s) during particular exposure periods.

Puchalski et al. [101] have summarized results of comparisons of 3 samplers: the Alpha, Radiello and Ogawa. The overall precision of the Ogawa is 6 % for duplicate samplers over a very limited range of concentrations (0 to about 3  $\mu\text{g}/\text{m}^3$ ). As in Sather et al.[106] the accuracy has been studied by comparison with photo-acoustic spectrometry (PAS). For the limited concentration range given the Ogawa is found to underestimate the results of the PAS by about 37 %. It is noted that the dataset used here includes the data used in a previous study [105] Hence, the additional value of this observation is limited. In addition, the conclusion may not be entirely fair towards the Ogawa sampler. The same publication reports the bias of the Alpha sampler to be -2,4 %, while both samplers show similar biases in the laboratory study. [108]. Scudlark et al. [107] report the precision based on results of paired samplers to be 18 % for concentrations < 1,5  $\mu\text{g}/\text{m}^3$  ammonia and 7 % for a mean concentration of 6,2  $\mu\text{g}/\text{m}^3$  (14-day exposure).

#### **4.4.6 Other information about performance characteristics**

Other publications reporting the use of Ogawa samplers for the measurement of ammonia in ambient air have been identified [110-115]. However, none provides further information on the performance of the Ogawa sampler for the measurement of ammonia.

#### **4.4.7 Measurement uncertainty**

No information has been found in the literature of (systematic) assessments of measurement uncertainties associated with the use of the Ogawa sampler, e.g., performed according to the Guide to the Expression of Uncertainty in Measurement. The limited amount of information available from comparisons does not allow for a direct estimation of uncertainties. One author attributes this finding to insufficient sampling capacity of the annular denuders. Comparison with open-path FTIR leads to higher results for Ogawa. No information has been found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

The Ogawa badge-type diffusive sampler has been used both for short- and for long-term monitoring of ammonia near sources and in ambient air in a limited number of studies. Exposure periods from 5 minutes [5] up to 3 weeks [6] have been reported. The lower detection limit for a 3-week exposure is reported to be 0,18  $\mu\text{g}/\text{m}^3$ . Values provided for the precision of replicate samples are internally consistent, yielding CVs between 5 % and 10 % for concentrations up to 85 ppb (120  $\mu\text{g}/\text{m}^3$  at 20 °C, 101 kPa).

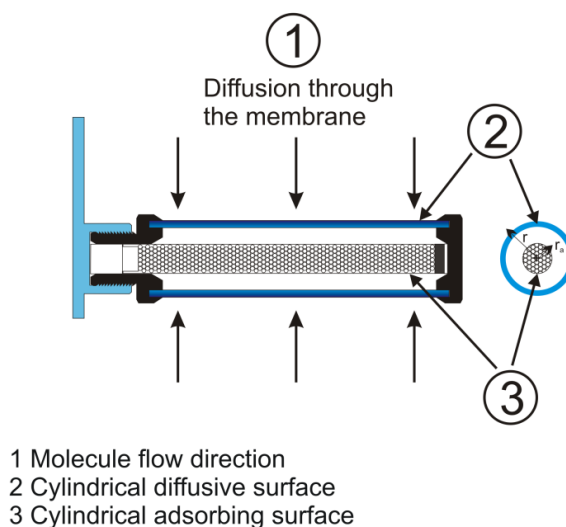
Information provided about the comparability of the results of the Ogawa sampler with independent, mostly instrumental, methods is rather incoherent and may be affected by the presence of ammonium salts, either in the sampled air or on filters used to protect the instrumental equipment and the use of open-path methods for comparison. Comparison with direct-reading closed-path instruments (photo-acoustic spectrometry; chemiluminescence) generally shows the Ogawa samples lower concentrations. The comparisons reported with annular denuders show the Ogawa to yield higher ammonia concentrations



## 4.5 The Radiello sampler

### 4.5.1 Sampler design

The Radiello sampler is a radial-type of diffusive sampler and is developed by Fondazione Salvatore Maugeri in Italy. [116] It has a cylindrical outer surface acting as a diffusive membrane (60 x 16 mm diameter; 1,7 mm thickness;  $25 \pm 4,8 \mu\text{m}$  average porosity). The gaseous molecules move axially parallel towards a cylindrical adsorbent bed (60 x 4,8 mm) and coaxially to the diffusive surface as described in literature on the Radiello webpage [117] and illustrated in Figure 4.22.



**Figure 4.22 Radiello Sampler design**

According to manufacturer's instructions, exposure for a long time to rain generally does not affect the sampling performances of the Radiello sampler. Nevertheless, the sorption of large quantities of water by the cartridges can affect the sampler performance. Therefore a shelter is important to protect Radiello samplers from rain. For outdoor exposures, a mountable polypropylene shelter is available (Figure 4.23). It is designed to be mounted easily without any tool in the field. The shelters are open on 3 sides.



**Figure 4.23 Radiello Sampler shelter**

Once assembled, it ensures the best compromise between protection against rain and wind. It can house up to four samplers and is able to fit a wide range of pole diameters. The diffusive body can be fitted on a supporting plate either in a vertical or horizontal position as shown in Figure 4.24. The cartridge designed to collect NH<sub>3</sub> is made of microporous polyethylene and impregnated with phosphoric acid. Ammonia is adsorbed as ammonium ion. It is very important to prevent touching the microporous portion of the cartridge with fingers, since sweat contains ammonium ions. The manufacturer states that airborne ammonium salts dispersed as particulate matter do not cross the diffusive membrane of Radiello.



Figure 4.24 Radiello sampler supporting plate

The concentration of ammonia (C) in µg/m<sup>3</sup> is obtained according to the equation:

$$c = 0.994 \frac{m}{235t} 1,000,000 \quad (18)$$

where

- m is the mass of ammonium ion in µg found onto the cartridge;
- t is exposure time in minutes;
- 235 is the sampling rate in ml/min at 298 K (25 °C) and 1013 hPa;
- 0,944 is the numerical factor necessary to convert ammonium ion into ammonia.

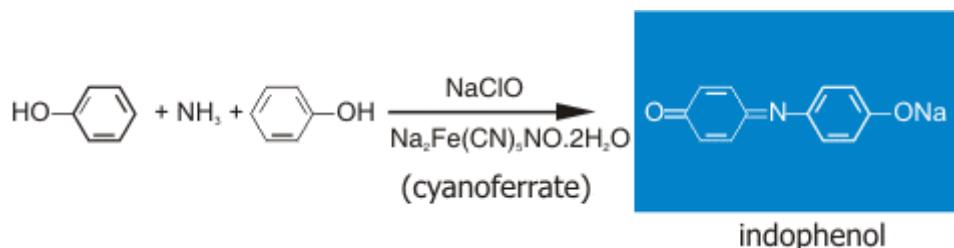
#### 4.5.2 Extraction and analysis

In order to avoid contamination during extraction, care must be taken whenever handling Radiello passive diffusion gas samplers, testing tubes and caps. Wearing laboratory gloves is required when extracting. There are several analytical methods available as described in previous chapter. Spectrophotometry and flow injection analysis specifically applied to Radiello samplers are discussed below.

##### **Spectrophotometry**

It is the method described by the manufacturer on the company website (link above) Ammonium ion is quantified by visible spectrometry as indophenol: at basic buffered pH (around 12,6), ammonium ion reacts with phenol and sodium hypochlorite, with pentacyanonitrosylferrate catalysis (referred to as cyanoferrate), to form indophenol. Explicit details about the solutions and their concentrations can be found on the

manufacturer's website. The reaction product is intensely coloured in blue, and its absorbance measured at 635 nm.



For exposure value higher than 500,000  $\mu\text{g}/\text{m}^3\cdot\text{min}$  the absorbance value is no longer linear: it is thus necessary to dilute a known fraction of the coloured solution with the buffer (and not with water: the pH value is critical in the determination of the colour intensity). Calibration curves are conveniently prepared with ammonium chloride solutions in the range from 0,5 to 10  $\text{mg}/\text{l}^1$  as ammonium ion. The manufacturer states that generally, the blank value does not exceed 0,040 absorbance units. However, results have shown that blank values are in practice higher (AIR LR tubes analysed by the manufacturer itself)

#### **Flow injection analysis**

This method, used in the United States and in Switzerland, is known for improving the blanks. Through flow injection analysis (FIA), aqueous ammonium solutions can be determined using fewer chemicals, quickly (about 70 s per measurement), cost-effectively, fully automatically and quantitatively. The total measuring system is commercially available. For analysis, the samples and the reagents shall be at room temperature.

The sample is injected into a continuously flowing carrier stream (ultrapure water), with which a sodium hydroxide stream (reagent solution I) is mixed. In the resultant alkaline stream, gaseous ammonia is formed, which diffuses through a gas-permeable membrane into a carrier stream, or indicator stream (reagent solution II). It can then be detected with different systems of detection (conductimetry, ion chromatography or colorimetry, where for instance indophenol can be used as an indicator). The content of ammonium in the sample shall lie within the calibration range. If required, the sample shall thus be diluted with a solution of the same matrix. The extraction should be performed 24 hours before the analysis.

#### **4.5.3 Application range and conditions**

According to the manufacturer, the uptake rate of  $\text{NH}_3$  is constant in the range from 2 000  $\mu\text{g}/\text{m}^3\cdot\text{min}$  to  $20 \times 10^6 \mu\text{g}/\text{m}^3\cdot\text{min}$ . The detection limit of the method depends on the detection sensitivity of the analytical method used:

- Spectrophotometry: the limit of quantification after 1 day exposure is  $1 \mu\text{g}/\text{m}^3$  (manufacturer specified);
- Flow injection analysis : in the VTI report [118], the limit of detection is  $0,2 \mu\text{g}/\text{m}^3$  for a 14-day exposure period using flow injection analysis followed by UV detection.

Literature review [118] mentioned in the German standard (VDI 3869-4) shows that Radiello tubes exposed 14 days at a mean concentration of 4 µg/m<sup>3</sup> have a limit of detection of 0,2 µg/m<sup>3</sup>, which is similar to that reported in the US AMON network [119].

The range of meteorological conditions where the use of the Radiello sampler is applicable is given in table 4.12.

**Table 4.12 - Manufacturer specified application range of NH<sub>3</sub> Radiello sampler**

Parameter	Range where no effect on uptake rate is observed
Temperature	2 to 39 °C (effect negligible : <0,1 %/°C)
Relative humidity	10 to 90 %
Wind speed	0,1 to 10 m/s
Sampling duration	1 hour to 14 days

According to the manufacturer the cartridges are stable for at least 12 months before and after exposure, if kept at room temperature in an ammonia-free environment. Expiry date is printed on the plastic bag. At least two cartridges belonging to the same lot should be kept as blanks.

#### 4.5.4 Uptake rate and environmental effects

The uptake rate was determined by the manufacturer as 235 cm<sup>3</sup>/min at 25 °C and 1013 hPa. A report by VITO for Gradko [120] has found sampling rates of :

- 214 cm<sup>3</sup>/min at 12 °C and 63 % of relative humidity;
- 218 cm<sup>3</sup>/min at 15 °C and 62 % of relative humidity.

According to the manufacturer, sampling rate is invariant with wind speed between 0,1 and 10 m/s.

According to the manufacturer, the effect of temperature on sampling rate is negligible (<0,1 %/°C) in the range from 275-312 K (2-39 °C). According to the VITO report [120] the effect of temperature on sampling rate is +1,5 cm<sup>3</sup>/min.K from -5 to 30 °C.

According to the manufacturer, sampling rate is invariant with humidity in the range 10-90 %. And in the VITO study, the effect of humidity on sampling rate is – 1,1 cm<sup>3</sup>/min. RH from 45 % to 80 %

#### 4.5.5 Validation of sampler performance

##### 4.5.5.1 Laboratory experiments

An AMoN special study was reported in a conference poster and focused on the test of 3 different passive sampler types (Radiello, Ogawa and ALPHA) in an environmental chamber, compared to a URG-type annular glass denuder. The tests conditions were 13,62 µg/m<sup>3</sup> of ammonia (which corresponds to the 99<sup>th</sup> percentile concentration of AMoN), and the tubes were exposed during 10 days. The preliminary results of this chamber studies – as well as field studies run simultaneously; see paragraph 8.5.2.1) – indicate that Radiello samplers have the lowest measurement variability of the 3 passive

samplers tested and that they are biased low (biased:  $-1,75 \mu\text{g}/\text{m}^3$  related to a concentration of  $13,62 \mu\text{g}/\text{m}^3$ ). See Figure 4.25 below.

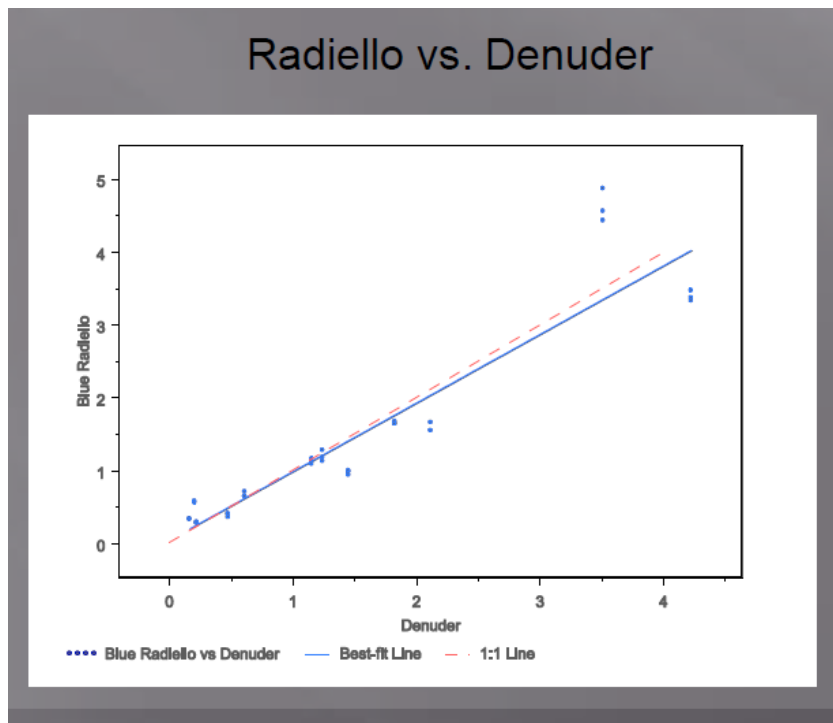
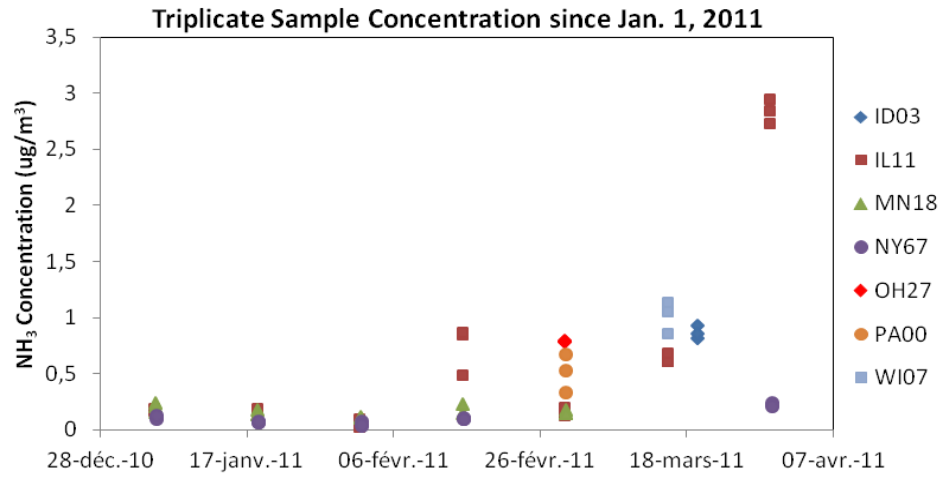


Figure 4.25 - Field experiments Radiello versus Denuders (AMON study)

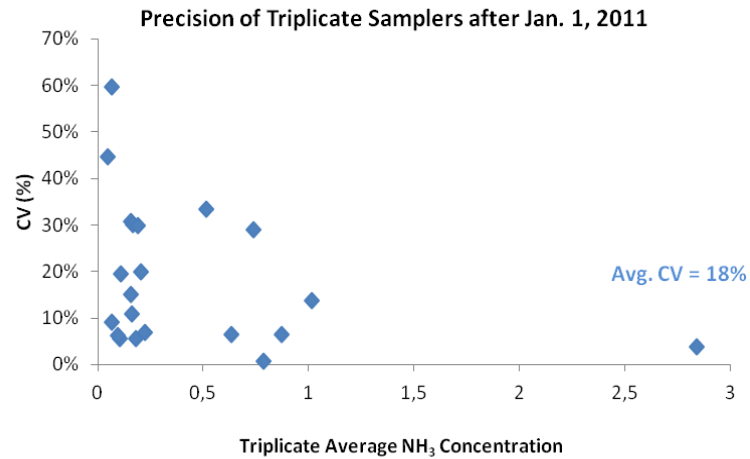
#### 4.5.5.2 Field studies

In a study in Germany, the average coefficient of variation between 18 duplicates exposed during 14 days at concentrations between 2 and 8  $\mu\text{g}/\text{m}^3$  was 8,8 % (see VDI 3869-4, <https://www.beuth.de/de/technische-regel/vdi-3869-blatt-4/146660579>). In the United States, the AMoN network runs triplicates Radiello tubes (14 days exposure) on 3 sites (at random), analysed by Flow Injection Analysis. The differences within each triplicate since the beginning of year 2011 are shown on the following graphs (Figure 4.26 and Figure 4.27). Within the ammonia range of 0-4  $\mu\text{g}/\text{m}^3$ , the average coefficient of variation is 18 % ranging from 0 to 60 %. All the results and data are available online [121]

In France, AIR LR has run a comparison to assess the expanded uncertainty, according to the ISO 20988 standard. [122] During 16 weeks, duplicates were exposed on 1 industrial site and analysed by spectrophotometry; the  $[\text{NH}_3]$  range was 6 to 180  $\mu\text{g}/\text{m}^3$ . The coefficient of correlation between the 16 duplicates was 0,9934, and the standard deviation 4 %.



**Figure 4.26 - Triplicate Radiello in AMON study**



**Figure 4.27 - Precision of Triplicate Radiello samples in AMON study**

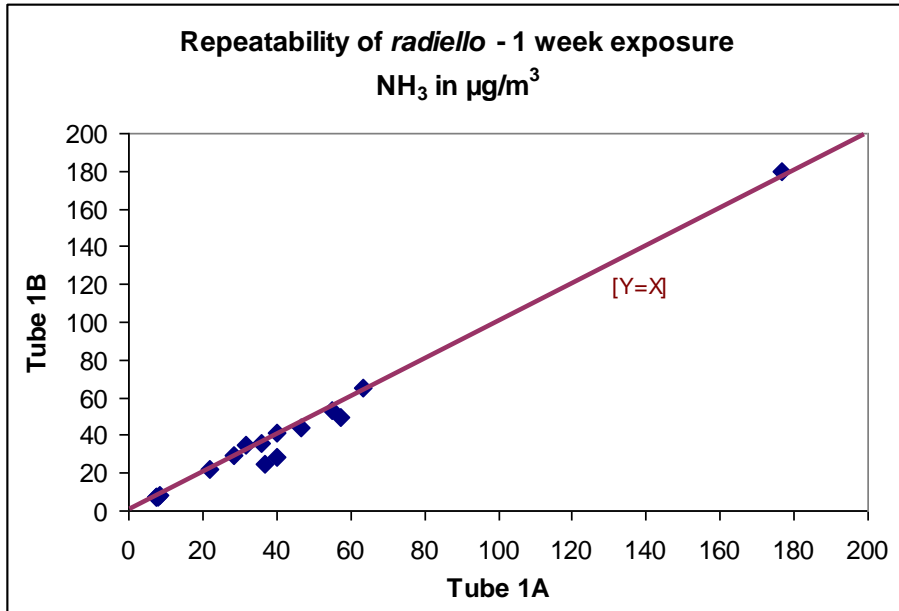


Figure 4.28 - Repeatability of Radiello (AIR LR study)

Between 2007 and 2011 59 laboratory blanks (stored in the fridge) were sent by AIR LR to the Istituti Clinici Scientifici Maugeri (ICS Maugeri) (formally Fondazione Maugeri) for analysis by spectrophotometry. The average NH<sub>3</sub> mass on the cartridge was 3,6 µg, ranging from 1,0 to 8 µg (see Figure 4.29), which corresponds – for a one-week exposure – to 0,3 to 2,5 µg/m<sup>3</sup>. Within the US AMoN network, there was, in 2013, one "travel blank" per sampling period per site; the blank average is approximately 0,2 µg/m<sup>3</sup>. To avoid contamination, it was shown to be essential to transport them in a **glass** vial instead of a **plastic** shipping vial. It appears that travel blanks stored in a cool environment are very stable.

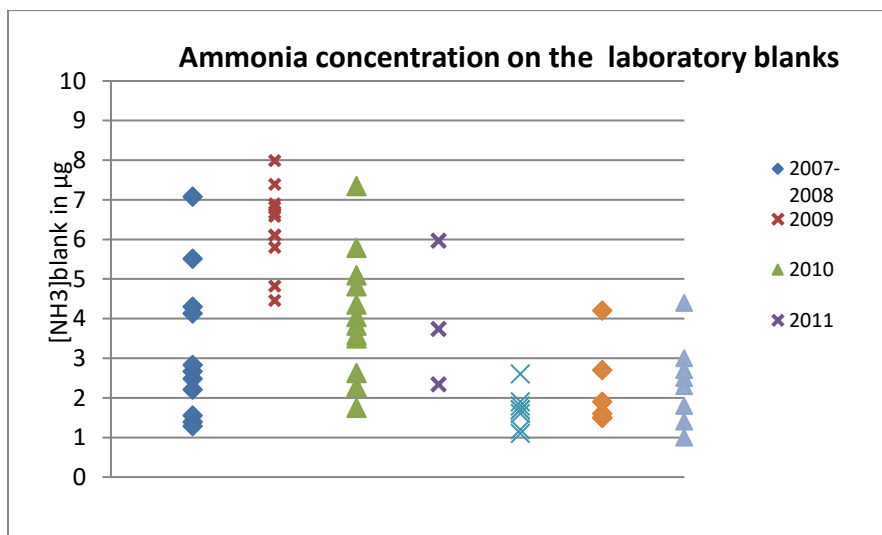


Figure 4.29 - Laboratory blanks in AIR LKR study

#### 4.5.6 Measurement uncertainty

According to the manufacturer, the uncertainty at  $2\sigma$  is 6,5 % within the application range. In France, AIR LR has run a comparison to assess the expanded uncertainty, according to the ISO 20988 standard. [122] During 16 weeks, duplicates were exposed on 1 industrial site ; the  $[\text{NH}_3]$  range was 6 to  $180 \mu\text{g}/\text{m}^3$ . At an average ammonia concentration on this site of  $41 \mu\text{g}/\text{m}^3$ , the expanded uncertainty corresponds to 8,7 %, which is the same order of magnitude as the uncertainty mentioned by the manufacturer.

Reference [118] shows that Radiello tubes exposed 14 days at a mean concentration of  $4 \mu\text{g}/\text{m}^3$  have a relative uncertainty of 11 %, and that it decreases to 6 % around the TA Luft value of  $10 \mu\text{g}/\text{m}^3$  [123] In Germany, the VTI report shows that the uncertainty calculated from the parallel measurement results using ISO 20988 standard is 5 %.

#### 4.5.7 Known applications

In 2013, the following operational networks in Europe using Radiellos are two:

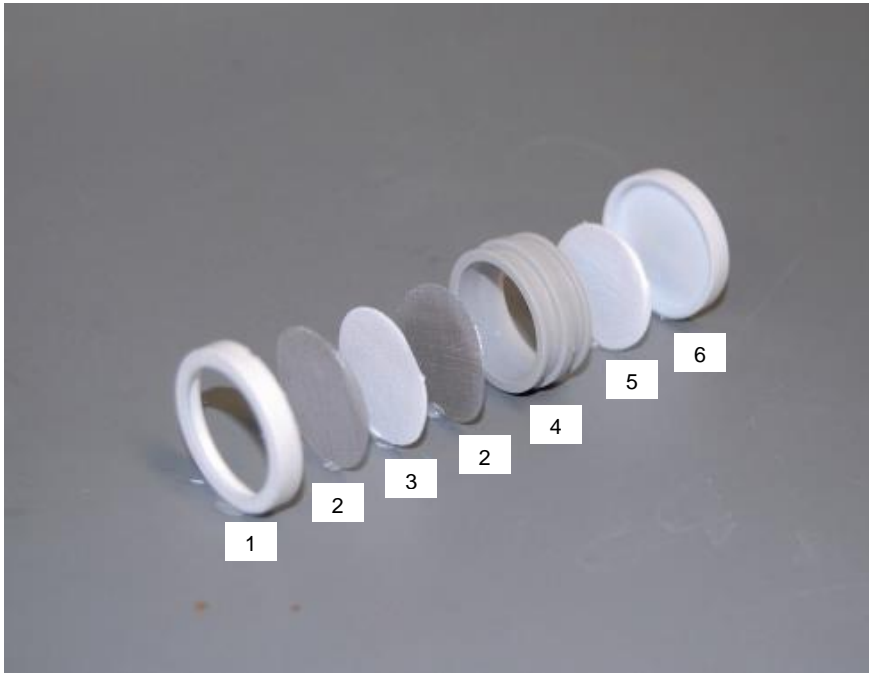
In **Switzerland**, the Federal Office for the Environment, the FUB (research group for environmental monitoring, Rapperswill) and several Swiss cantons have run a permanent Radiello ammonia monitoring network since 2002 on more than 50 sites (rural, rural near from agricultural sources of ammonia, urban and alpine sites). The aim is to estimate the N-input to sensitive ecosystems, to compare the  $\text{NH}_3$  concentrations to the critical loads and thus to work on measures to reduce the emissions. On each site, there are triplicates and time exposure is 2 or 4 weeks (which is higher than the range of application provided by the manufacturer). On some sites, other methods (e.g. active denuders) are used to provide a comparison with the Radiello device. The highest  $\text{NH}_3$  concentration were found on sites with intensive cattle and pig farming, whereas in urban areas, the average concentrations are the same order of magnitude than sites with extensive cattle farming or crop farming.

In **France**, Radiello tubes are sometimes used in temporary surveys to assess  $\text{NH}_3$  concentration around waste water facilities, relating to bad odours. The only French permanent network of ammonia using passive devices is run by AIR LR around a facility which performs the first stage of conversion of uranium-bearing concentrates from mining sites for nuclear industry and emits  $\text{NH}_3$ . The  $\text{NH}_3$  annual averages (based on 52 weekly means) ranges from 1 to  $69 \mu\text{g}/\text{m}^3$  in 2014, decreasing with the distance to the facility.



## 4.6 The Ferm type sampler

### 4.6.1 Sampler design



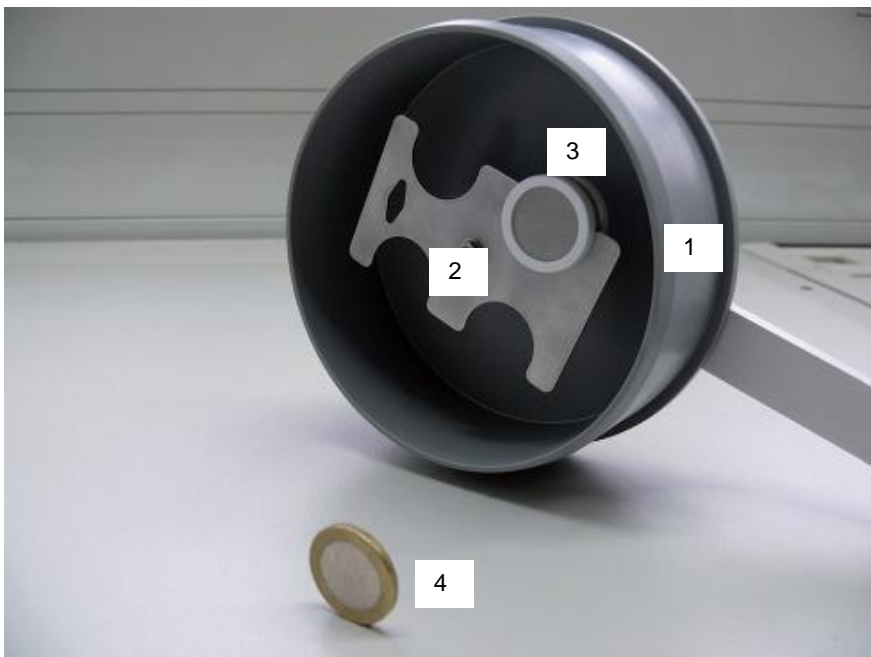
**Figure 4.30 - IVL sampler design: 1. Diffuser end cap (polyethylene); 2. Stainless steel mesh; 3. Membrane filter (turbulence barrier); 4. Sampler body (polypropylene, 10 mm length, 20 mm ID); 5. Sampling filter; 6. End cap (polyethylene)**

The IVL sampler [50] is a badge-type sampler equipped with a PTFE membrane or quartz-fibre filter turbulence barrier and a filter usually coated with citric acid [118, 124] although the use of phosphoric acid has been reported. A number of procedures for preparing the sampling filter have been found in the literature:

- Application of 125  $\mu\text{l}$  of a 3 % w/v citric acid solution in 50/50 v/v ethanol/water onto a non-specified filter type<sup>1</sup>;
- Application of 50  $\mu\text{l}$  a 2 % citric acid solution in acetone on a pre-washed, dried cellulose filter [93, 125-128]
- Application of a 5 % citric acid solution on a glass-fibre filter (solvent unspecified) [129]
- Application of an unspecified volume of 2 % citric acid in methanol [130].

Since the VDI standard [124] is based on previous findings reported it is assumed that the procedure reported herein is the optimum procedure. It is recommended that the sampler is used with a protective cover. A cover used in Dammgen [118], the VDI standard [124] and [129] is shown in Figure 4.31.

<sup>1</sup> It is assumed that this is a cellulose filter.



**Figure 4.31 - Ferm-like sampler protective cover; 1:Protective cover; 2: Holder for 4 samplers; 3: Exposed sampler; 4: End cap for sealing.**

No quantitative information has been found in the literature about the stability of the coated, unexposed, samplers. The VDI report [124] states the sampler to be stable for “several months” if stored airtight at ambient conditions. For the protection of exposed samplers, the addition of a citric-acid coated filter paper to the container is recommended [118, 124]. This procedure may probably also be applied for unexposed samplers. The ammonia sampled is released as ammonium, using 5 ml water and shaking or ultrasonic extraction. The determination of the mass concentration of ammonium in the extract may be performed by:

- Spectrophotometry - after reaction with hypochlorite and salicylate in the presence of sodium nitroprusside to a blue-green indophenol dye;
- Flow injection analysis – after conversion of the ammonium to ammonia, which diffuses through a permeable membrane into a carrier solvent stream – using conductivity detection or spectrophotometry;
- Ion chromatography.

Procedures for the performance of the analyses by the above techniques have been described earlier and are also covered in the references above.

#### **4.6.2 Application range and conditions**

The sampler is typically exposed for a period of 7, 14 or 28 days. The operating range of the sampler is given in [1] as 1 to 150  $\mu\text{g}/\text{m}^3$  for a one-month exposure period. Higher concentrations may be measured by reducing the exposure period. Dammgen [118] reports that, based on laboratory experiments, for a one-hour exposure the maximum concentration should not exceed 1 ppm (700  $\mu\text{g}/\text{m}^3$ ). However the VDI report [124]

mentions the use of a modified sampler geometry without specifying the modification. Consequently, this assessment should be interpreted with care.

The detection limit of the sampler is inversely proportional to the exposure period. In the literature several reports of detection limits have been found, mostly determined as three times the standard deviation of results of blank samplers. Table 4.13 gives the figures found as a function of the exposure period. Letters between parentheses report the analytical method used (see above).

**Table 4.13 - Detection limits of the IVL-sampler**

Exposure period (d)	Detection limit ( $\mu\text{g}/\text{m}^3$ )	Reference
14	1,3 1,6	[124]
7	0,8	[125]
28	1	[129]
14	1	[127]
28	0,5	[118]

The manufacturer gives no recommendations as to ranges of temperature and relative humidity for which the sampler may be used. None of the studies reported here provides any further information about ranges of environmental conditions for which the sampler is suitable. Kirchner [125] reports weekly average temperatures for which samplers have been exposed between ca.  $-3\text{ }^\circ\text{C}$  and  $+18\text{ }^\circ\text{C}$ , with daily extremes between  $-10\text{ }^\circ\text{C}$  and  $+27\text{ }^\circ\text{C}$ . No mention has been made of any adverse effects of extreme temperatures on the performance of the sampler.

#### **4.6.3 Uptake rate and environmental effects**

No information has been found in the literature on sampling rates of the IVL sampler. The reason for this is that the sampling rate is dependent upon the type of turbulence barrier (membrane) used and that therefore the sampling rate has to be determined through comparative measurements with a reference methodology (see Chapter 2). When ignoring the presence of a turbulence barrier, the theoretical sampling rate, based on Fick's first law of diffusion and the sampler dimensions, using the diffusion coefficient for ammonia reported by Massman [131], is  $43,9\text{ cm}^3/\text{min}$  at  $25\text{ }^\circ\text{C}$ , and  $40,0\text{ cm}^3/\text{min}$  at  $10\text{ }^\circ\text{C}$ . The practical sampling rate is expected to be lower because of the presence of the turbulence barrier. No report has been found in the literature about any limiting environmental conditions for the application of the sampler.

#### **4.6.4 Validation of sampler performance**

##### **4.6.4.1 Laboratory experiments**

Apart from the results reported in the VDI report for laboratory experiments with a modified sampler (*modification unknown*) no other results of laboratory experiments have been found. This is most likely due to the fact that the sampler has to be calibrated/validated in field experiments.

#### 4.6.4.2 Field experiments

A number of publications have described the verification/validation of (elements of) sampler performance. Most of these give practical values for sampler precision and detection limits. Sampler precisions have been reported as given in

Table 4.14 for the concentrations indicated.

**Table 4.14 - Precision of the IVL-sampler**

Exposure period (d)	Level ( $\mu\text{g}/\text{m}^3$ )	Precision (%)	Reference
14	3,8	6,2	[125]
28	4,0	2,6	[125]
14	5,4	6,0	[124]
14	Various	$\approx 10$	[118]
14	Various	$\approx 10$	[127]
28	1 – 4	0,15 – 0,20 $\mu\text{g}/\text{m}^3$	[118]

The number of publications in which actual validation (determination of accuracy) of the sampler by comparison with an independent method has been performed is limited. The most comprehensive reports on sampler validations are in the references listed in Table 4.14. Long-term field experiments in which samplers are compared to reference denuders are reported and evaluated. Kircher et al. [125] have presented results for parallel measurements with FUB denuders and IVL samplers for an exposure period of 2 weeks, from June to December 1997. When examining the results (31 data pairs) using orthogonal regression [12], the following relationship is obtained:

$$IVL = 1,05(0,09) \cdot FUB + 0,01(0,33) \quad (19)$$

Note, the numbers in parentheses are standard uncertainties. The scatter of the regression is approximately  $0,4 \mu\text{g}/\text{m}^3$  for an average concentration of  $3,6 \mu\text{g}/\text{m}^3$ , but is strongly affected by one suspect result (see Figure 4.32). Removal of the suspect data pair does not significantly affect the relationship but reduces the scatter to about  $0,25 \mu\text{g}/\text{m}^3$ .

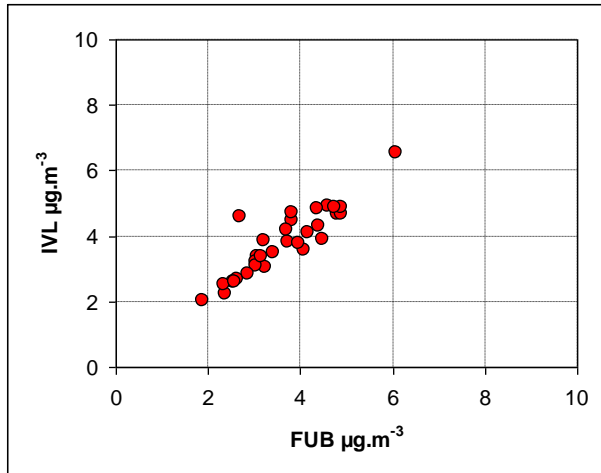


Figure 4.32 - Plot of results for IVL and FUB samplers (2-week exposure) in Dammgen [118]

Kirchner et al. [125] presents results from a comparison between various denuders and two diffusive samplers: Radiello and IVL. A relatively large dataset from January 2007 to October 2008 is available for comparison of the IVL sampler with the KAPS denuder. For this denuder a large amount of information is available from parallel measurements with two systems with a relatively large range of concentrations (up to 20 µg/m³ for a 60-h measurement period and 10 µg/m³ for a 14-d measurement period), showing a good internal consistency and uncertainty. Two types of IVL samplers have been used: one constructed by FAL (Braunschweig) and one by LUBW (Karlsruhe). When combining the results of both IVL samplers available, comparing the results of the IVL sampler (2-week exposure) with those of the KAPS denuder yields the following relationship:

$$IVL = 1,02(0,07) \cdot KAPS - 0,08(0,34) \tag{20}$$

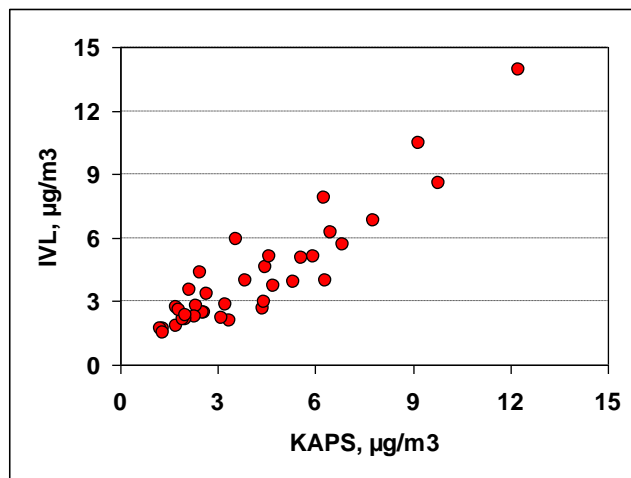


Figure 4.33 - Plot of results for IVL and KAPS samplers (2-week exposure) Kirchner et al. [125].

The scatter of the regression is approximately  $1,0 \mu\text{g}/\text{m}^3$  for an average concentration of  $4,2 \mu\text{g}/\text{m}^3$ . It is noteworthy that the relationship between IVL and denuder results in both studies is close to 1:1. However, when splitting the results into sets for both IVL types, a marked difference is observed in the relationships of the individual samplers and the denuder:

$$IVL(LUBW) = 0,80(0,08) \cdot KAPS + 0,34(0,40) \quad (21)$$

$$IVL(FAL) = 1,13(0,08) \cdot KAPS - 0,08(0,40) \quad (22)$$

Kirchner et al. provides information about the internal consistency for the IVL sampler and its resulting measurement uncertainty, the latter based on calculations using EN-ISO 20988 [122]. These are summarized in Tables 4.15 and 4.16 for both sampler types where the expanded uncertainty (U) and the = relative expanded measurement uncertainty (W) are summarised.

**Table 4.15 - Internal consistency of IVL-FAL, based on quadruplicate exposure, separated by ammonia levels, for a 28-d exposure**

Nr. of data	Mean c(NH <sub>3</sub> ) ( $\mu\text{g}/\text{m}^3$ )	U ( $\mu\text{g}/\text{m}^3$ )	W (%)
38	1,8	0,4	22
33	5,1	0,9	18
39	14,4	1,9	13
39	39	6	16

**Table 4.16 - Internal consistency of IVL-LUBW, for a 14-d exposure**

Nr. of data	Mean c(NH <sub>3</sub> ) ( $\mu\text{g}/\text{m}^3$ )	U ( $\mu\text{g}/\text{m}^3$ )	W (%)
18	4,3	1,0	24

Although the internal consistency of the IVL sampler is good, its comparability with the KAPS denuder appears to depend highly on the type of IVL sampler. When using further data from comparisons of KAPS denuders and IVL-FAL, the resulting expanded measurement uncertainty of the IVL sampler is  $3,2 \mu\text{g}/\text{m}^3$  for an average concentration of  $4,1 \mu\text{g}/\text{m}^3$ . The high uncertainty is caused by the bias between the results of the denuder and IVL sampler. In order to correct for this, FAL uses a correction factor of 0,8333.

The VDI report shows the results of the calibration of the IVL sampler, followed by the determination of its measurement uncertainty, both through comparison measurements with denuders. The exposure period is 14 days. In the calibration phase, IVL samplers have been found to over-estimate ammonia concentrations by a factor of 1,19. This factor has subsequently been used to correct the original sampling rate. The measurement uncertainty has been determined using calculation method A5, case 2, of EN-ISO 20988 [122] from 23 data pairs obtained in a subsequent comparison with the calibrated sampling

rate. The expanded uncertainty is calculated to be  $0,9 \mu\text{g}/\text{m}^3$  for a mean concentration of  $3,5 \mu\text{g}/\text{m}^3$ .

When examining the results using orthogonal regression [91], the following relationship is obtained ( ):

$$IVL = 0,96(0,05) \cdot DENUDER + 0,12(0,19) \quad (23)$$

Or, when forcing the regression through the origin:

$$IVL = 0,98(0,02) \cdot DENUDER + 0,02(0,08) \quad (24)$$

In both cases the standard uncertainty at a level of  $10 \mu\text{g}/\text{m}^3$  is  $0,3 \mu\text{g}/\text{m}^3$ , and the expanded uncertainty is  $0,7 \mu\text{g}/\text{m}^3$ .

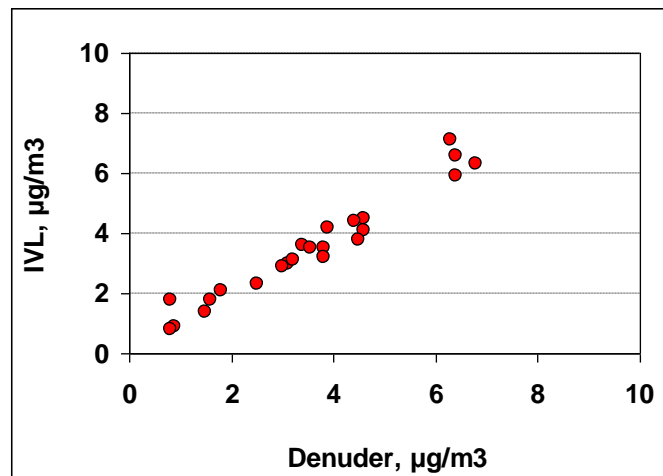


Figure 4.34 - Plot of results for IVL (calibrated) and denuder from VDI report

#### 4.6.5 Other information about performance characteristics

One further publication reporting the use of an IVL-type sampler for the measurement of ammonia in ambient air has been identified in a field study looking at seabird emissions [132]. Because of the lack of information of the nature of the modification of the sampler, no information from this study has been included.

#### 4.6.6 Measurement uncertainty

As describe above, a number of studies have been performed in/from which the uncertainty in the application of the IVL-sampler has been evaluated through comparisons with results obtained using reference denuders. Summarizing, the findings of these references show that, after calibration of the samplers, it is possible to reach expanded uncertainties in the range of 20 to 40 % at the mean levels observed in the studies.

#### **4.7 Other samplers**

The purpose of this review was to provide the background and evidence to underpin the development of a European Standard for ambient ammonia passive sampler protocols.

It is noted that there are several other commercial and non-commercial, passive samplers which have been developed, or adapted, for use in the measurement of ambient ammonia which are not covered in this review.



## 5. MetNH<sub>3</sub> chamber study

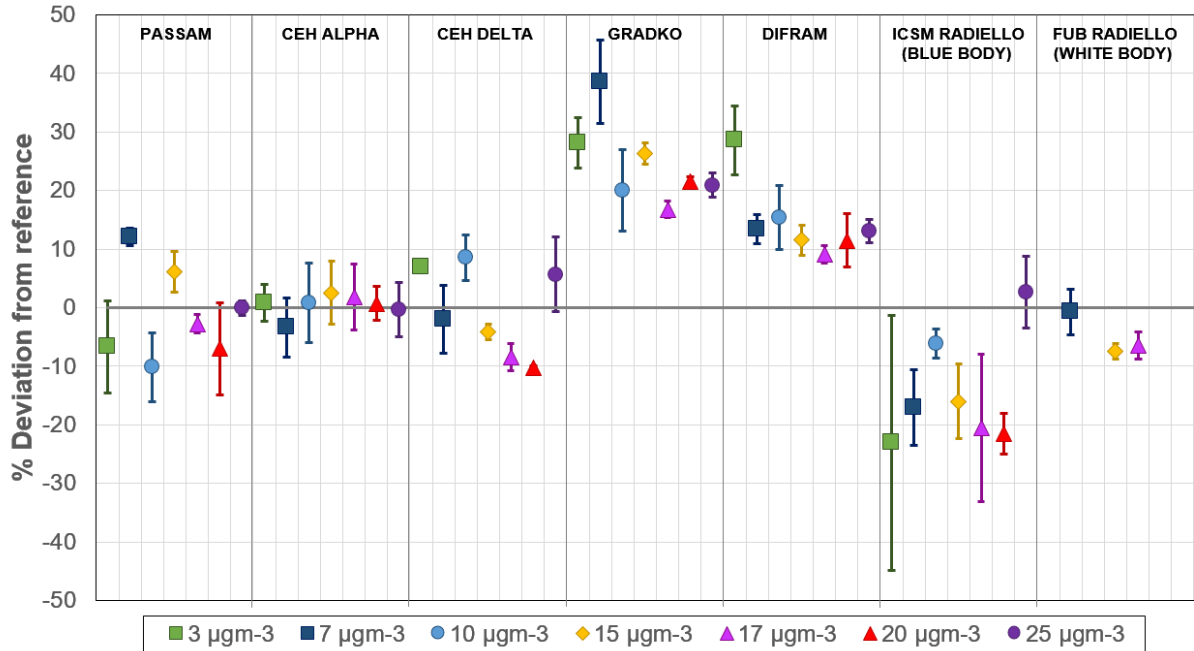
### 5.1 Controlled atmosphere test facility study

The goal of the MetNH<sub>3</sub> study was to improve the reliability and accuracy of ambient ammonia measurements for a range of commonly available commercial low cost diffusive and pumped denuder samplers. The work involved carrying out traceable sampler validation tests in a specialised controlled atmosphere test facility (CATFAC) developed at the National Physical Laboratory (NPL), UK [133-139]. It also required the development of stable traceable Primary Standard Gas Mixtures (PSMs) of NH<sub>3</sub> prepared by gravimetry, together with the further development of a cavity ring-down spectrometer (CRDS) for on-line continuous monitoring of ammonia [49]

The samplers employed in the CATFAC exposure tests were from the Centre for Ecology and Hydrology, CEH (CEH ALPHA sampler and CEH DELTA denuder), Gradko International Ltd (Gradko diffusion tube and Gradko DIFRAM-400), Istituti Clinici Scientifici Maugeri, ICS Maugeri (Radiello radial sampler with blue outer cylinder turbulence barrier), Passam AG (Passam ammonia sampler), and FUB AG (Radiello radial sampler from the ICS Maugeri, but with white outer cylinder turbulence barrier). The devices were randomly distributed inside the section of the exposure chamber perpendicular to the direction of gas flow.

Traceable concentrations (in the range 3-25 µg/m<sup>3</sup>) of humidified NH<sub>3</sub> were introduced into the CATFAC under a wide range of conditions that are relevant to ambient monitoring in the field, and the sensors under test (both passive and active) were simultaneously exposed in the facility for either 28 days or 14 days (dependent on sampler type). The CATFAC temperature was maintained at nominally (20 ± 1) °C at a relative humidity of 70 % and air speed of approximately 1,2 m/s.

After the tests, each manufacturer extracted the captured ammonia in their exposed samplers in the form of ammonium (NH<sub>4</sub><sup>+</sup>) using their own accredited traceable wet chemical techniques, and then reported data based on their historical diffusive sampling rates. There was a considerable variation in the reported results (expressed as either a positive or negative bias) when compared to each of the known amount fractions generated, which demonstrated the need for such validation work to be carried out. Figure 5.1 shows a summary of the results obtained.



**Figure 5.1 - Summary of the mean of the reported NH<sub>3</sub> concentrations for diffusive and pumped samplers tested in the CATFAC, expressed as a percentage deviation from the reference values**

For the redetermination of the diffusive sampling rates,  $\vartheta$ , a knowledge of the traceable concentrations in the CATFAC, the measured exposure times, and the analysed masses of ammonia reported by each manufacturer were employed in a rearrangement of Equation 25:

$$[\text{NH}_3] [\mu\text{g}/\text{m}^3] = m [\mu\text{g}] / (\vartheta [\text{m}^3/\text{h}] \cdot t [\text{h}]) \quad (25)$$

Lack of fit plots were generated using XLGENLINE, which is a generalized least-squares (GLS) Microsoft Excel-based software package for low-degree polynomial fitting developed at NPL [140]

XLGENLINE employed a user-defined input file: this required values of  $x$  and  $u(x)$  (respectively the known NH<sub>3</sub> input concentration multiplied by the exposure time and the combined standard uncertainty);  $y$  and  $u(y)$  (respectively the reported mean mass of ammonia and the combined uncertainty). The software package performed a first-order polynomial GLS fit, in this case, forced through zero, and the gradient of the regression lines delivered the new values of the diffusive sampling rates in units of  $\text{m}^3 \text{h}^{-1}$ , together with their uncertainties.

Figure 5.2 shows the lack of fit plots for each sampler type tested while Table 5.1 contains the summary of the diffusive sampling rates, as calculated by XLGENLINE, together with their combined expanded standard uncertainties (with a coverage factor  $k = 2$ ), providing a coverage probability of approximately 95 %. Table 5.1 also contains the  $R^2$  of the linear fits, which are all effectively = 0,99. For comparison, the diffusive sampler data originally employed by each manufacturer is included, together with the reference temperature (in

°C). In the cases where the sampling rates were originally reported at either 25 °C or 10 °C then Equation 1 was employed to adjust the manufacturers' values to a reference temperature of 20 °C.

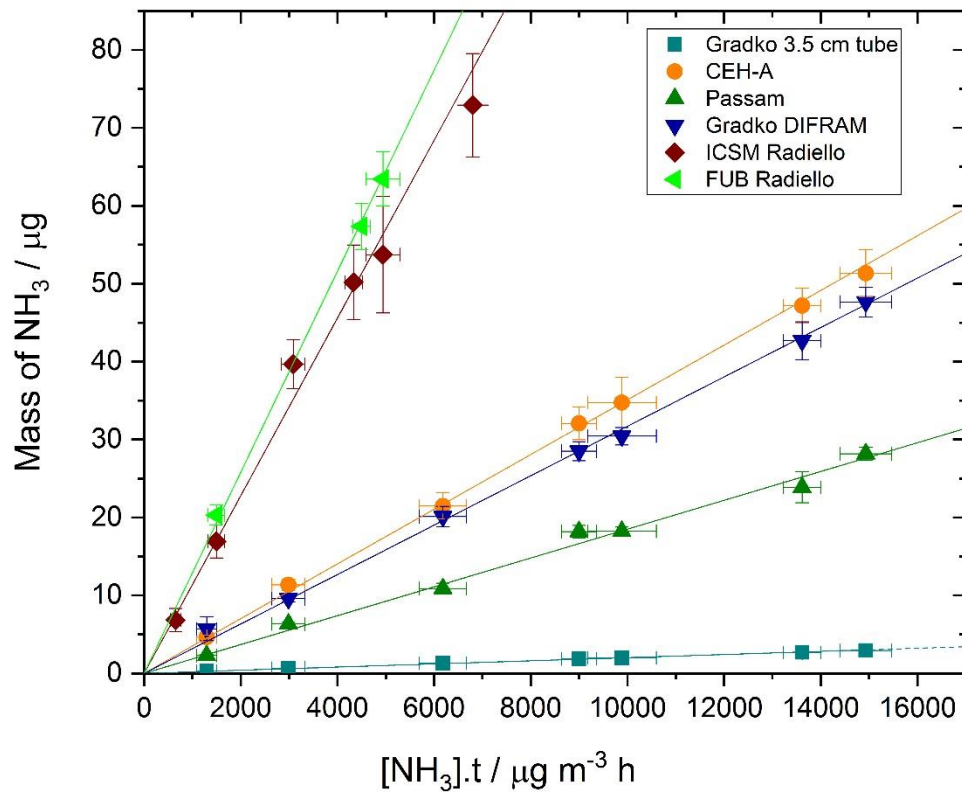


Figure 5.2 - Lack of fit plots for the diffusive samplers tested in the CATFAC laboratory study

**Table 5.1 - Summary of diffusive sampling rate data determined at NPL**

Manufacturer	Diffusive sampler	Sampling rate this work (m <sup>3</sup> /h)	R <sup>2</sup> Value	Reference T this work (°C)	Sampling rate manufacturer (m <sup>3</sup> /h)	Reference T manufacturer (°C)
CEH	ALPHA sampler	$(3,51 \pm 0,23) \times 10^{-3}$	0,999	20 ± 1	$3,45 \times 10^{-3}$ $3,24 \times 10^{-3}$	20 10
Gradko	3,5 cm diffusion tube	$(2,01 \pm 0,11) \times 10^{-4}$	0,997	20 ± 1	$1,62 \times 10^{-4}$	20
Gradko	DIFRAM-400	$(3,17 \pm 0,18) \times 10^{-3}$	0,997	20 ± 1	$2,82 \times 10^{-3}$	20
PASSAM	Passam ammonia sampler	$(1,85 \pm 0,16) \times 10^{-3}$	0,990	20 ± 1	$1,89 \times 10^{-3}$	20
Istituti Clinici Scientifici Maugeri (ICS Maugeri)	Radiello sampler (standard blue body)	$(1,14 \pm 0,12) \times 10^{-2}$	0,986	20 ± 1	$1,37 \times 10^{-2}$ $1,41 \times 10^{-2}$	20 25
FUB	Radiello sampler from ICS Maugeri (white body)	$(1,29 \pm 0,13) \times 10^{-2}$	0,999	20 ± 1	$1,37 \times 10^{-2}$ $1,41 \times 10^{-2}$	20 25

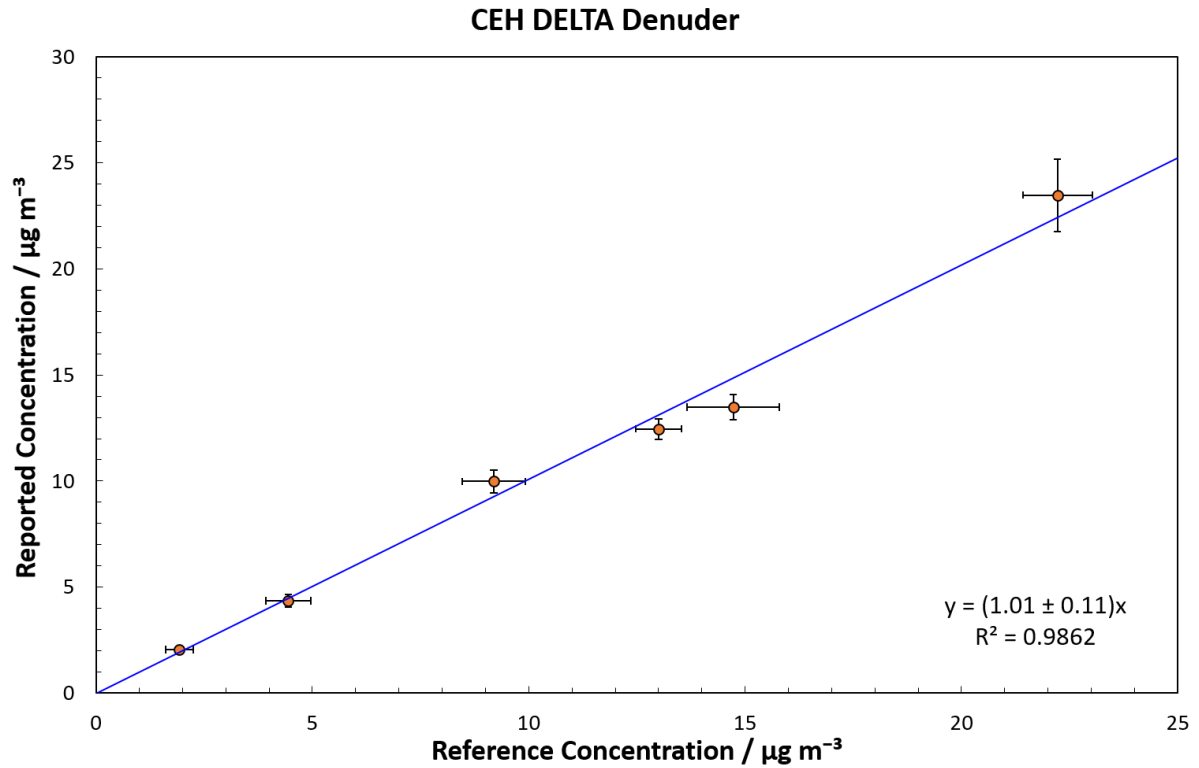
For the pumped CEH DELTA denuder samplers, a first order lack of fit plot was generated by XLGENLINE using the reported concentrations (ordinate axis) and the known traceable delivered concentrations (abscissa axis). This data is shown in Figure 5.3 together with the linear equation and the value of R<sup>2</sup>, which is effectively equal to 0,99. The concentration of ammonia is given by Equation 26:

$$[\text{NH}_3] [\mu\text{g}/\text{m}^3] = m [\mu\text{g}] / V [\text{m}^3] \quad (26)$$

where

V is the calibrated volume of air sampled.

The delivered concentrations are traceable to the ammonia PSMs developed in this work, and the measured concentrations are derived from a completely separate and independent wet chemical analysis technique. There is good agreement between the two, to within 1 %; it provides separate intercomparison data for the ammonia pumped sampling technique, and is also not dependent on a value of a diffusive sampling rate to provide the quantification. For the concentration range tested, the expanded uncertainty for the denuder was found to be ±11 %.



**Figure 5.3 - Lack of fit plot for CEH DELTA denuder**

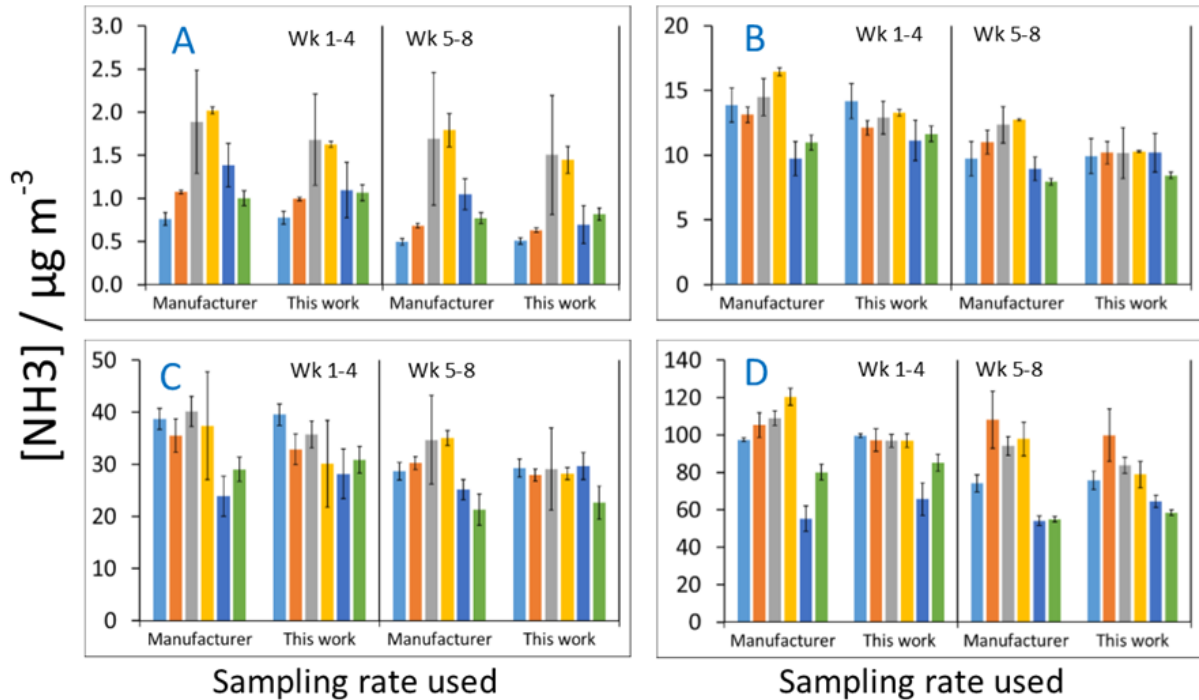
## 5.2 Field Study

A field study was carried out in Scotland [141] where there is a facility in place for controlled releases of  $\text{NH}_3$  on a peatland site. [142, 143] Ammonia was released at a known rate of 0,2 kg/h, when the wind in the preceding minute was in a particular  $30^\circ$  wind sector. Over two 4-week exposure periods in summer 2016, measurements of ammonia were taken of the ambient background, and at 12,5 m, 32 m and 60 m from the source release. The exposed diffusive samplers were treated in a similar manner to those employed for the laboratory tests. Figure 5.4 shows a photograph of the site, together with some of the devices deployed. The CATFAC study delivered new values of the diffusive sampling rates; these were applied to the field intercomparison results to determine whether there was improved agreement between the different types of samplers.



**Figure 5.4 - Field trial deployment of ammonia samplers at Whim Bog in Scotland**

Figure 5.5 shows the field measurement results obtained by employing the original diffusive sampling rates from each manufacturer to the data, and also using the new determinations obtained from the CATFAC study. In all cases the mean  $\text{NH}_3$  concentration values are displayed for each type of sensor (Passam-; ALPHA-, Gradko DIFRAM-400-, Gradko 3.5 cm diffusion tube-, ICSM Radiello, and FUB Radiello-), and the error bars represent the repeatability uncertainty (one sigma standard deviation) at each location from the release source for both exposure periods.



**Figure 5.5 - Summary of  $\text{NH}_3$  concentrations measured by passive samplers in field intercomparison for two four-week periods, using both the manufacturer provided uptake rate and the uptake rate derived in this work. Ammonia concentrations measured away from line source at distances of A: 83m (background); B: 60 m; C: 32m; D:12m; Bars: Light Blue: Passam; Orange: ALPHA Samplers; Grey: Gradko DIFRAM; Yellow: Gradko diffusion tube; Dark Blue: ICSM Radiello; Green: FUB Radiello**

There is evidence that the well characterised traceable diffusive sampling rates determined in this work delivered improved agreement between the different device types in the field tests, as demonstrated by the reduction in the overall spread of results. This data is summarised in Table 5.2 and is expressed as the coefficient of variation (COV) of the mean measured concentration of all the samplers (i.e., ratio of one sigma standard deviation and the mean  $\text{NH}_3$  concentration of samplers multiplied by 100 %). Clearly there are also other factors which can affect the measurements including wind speed, wind direction, solar radiation, temperature range, aerosol deposition on turbulence barrier and location relative to the emission source

**Table 5.2 - Summary of the coefficient of variation (COV) of the mean measured ammonia concentration of all diffusive samplers at each distance from source release**

Distance from source release (m)	83		60		32		12	
Exposure period (weeks)	1-4	5-8	1-4	5-8	1-4	5-8	1-4	5-8
COV (diffusive sampling rates from manufacturers' data) (%)	37	50	19	18	19	18	25	29
COV (diffusive sampling rates from this work) (%)	30	46	9	7	13	9	15	19

### 5.3 Treatment of uncertainties

The combined standard uncertainty,  $u_{\theta}$ , for each determination of the diffusive sampling rate is given by Equation 27:

$$u_{\theta} = ((u_{C_{final}})^2 + (u_r)^2 + (u_{an})^2 + (u_{sr})^2 + (u_t)^2)^{1/2} \quad (27)$$

where

$u_{C_{final}}$  is the combined standard uncertainty of each  $NH_3$  concentration introduced into the CATFAC;

$u_r$  is the repeatability standard uncertainty of on-line  $NH_3$  measurements recorded with the CRDS;

$u_{an}$  is the calculated analytical analysis standard uncertainty from information reported by each laboratory;

$u_{sr}$  is the repeatability standard uncertainty of the recovered analyte from the samplers;

$u_t$  is the standard uncertainty for the relevant sampler exposure time.

For the orthogonal regression analysis described in Section 5.1 the combined uncertainties for the first two components in Equation 27 are associated with the generation of the ammonia test atmospheres (through the traceable dilution of a PSM, on-line measurements, and the exposure time period) i.e.,  $u(x)$ , while the last two terms are associated with contributions from the analysis of the exposed samplers by each manufacturer, i.e.,  $u(y)$ .

The uncertainty calculation for the delivery of the  $NH_3$  concentration,  $u_{C_{final}}$ , for each exposure follows a standard international method [144] The sources of uncertainty identified in the exposure concentration include the  $NH_3$  concentration of the parent cylinder, individual repeatability standard deviations in the mass flow rates, mass flow controller temperature dependencies, gravimetric water calibration (including balance drift), mass flow meter calibrations, and time. A 'sensitivity' was then assigned to each of these components by differentiating the concentration with respect to each component, followed by summation in quadrature, together with the repeatability uncertainty of the on-line CRDS measurements.

The analytical analysis standard uncertainty,  $u_{an}$ , is associated with the determination of the mass of ammonium in a sample, and was calculated from information supplied by each laboratory in accordance with their established accredited procedures of each laboratory. This took into account contributions from the uncertainty of the mass of ammonium in the liquid calibration standards, the lack of fit of the calibration function, the analytical repeatability, the response drift between calibrations, and blanks, following similar principles applied to  $\text{NO}_2$  diffusive samplers in [48, 145]

A worked example calculation of the relative expanded uncertainty estimation for ammonia measurements ( $k=2$ ) is provided in Table 5.3 for an annual critical level of  $1 \mu\text{g m}^{-3}$ . The results shown are for the ALPHA sampler incorporating the measured diffusive sampling rate determined in this work (in  $\text{m}^3 \text{h}^{-1}$ ). This rate was used to calculate the volume of gas sampled,  $V$  (together with contributions from the sampling time, pressure and temperature). Finally, Table 5.4 contains a summary of the data for all the diffusive samplers tested covering annual critical levels of ammonia of 1 and  $3 \mu\text{g/m}^3$ , and the monthly critical level of  $23 \mu\text{g/m}^3$ , using an exposure period of 28 days (14 days for Radiello samplers). The expanded relative uncertainty values for the  $\text{NH}_3$  critical levels are consistent with the typical indicative measurements requirements of  $\pm 25\%$  (for nitrogen dioxide) and  $\pm 30\%$  (benzene) detailed in EU Air Quality Directives [145]



**Table 5.3 - Uncertainty budget of ALPHA diffusive sampler for measurements of ammonia at a critical level of 1 µg/m<sup>3</sup>**

<b>Reference concentration</b>	1	µg/m <sup>3</sup>				
Mole mass NH <sub>3</sub>	17,03	g/mol				
Mole mass NH <sub>4</sub> <sup>+</sup>	18,03	g/mol				
<b>Volume of air sampled</b>						
<i>Uncertainty component</i>	<i>Symbol</i>	<i>Value</i>	<i>Unit</i>	<i>Divisor</i>	<i>Relative uncertainty</i>	<i>Variance</i>
- sampling rate	ϑ	<b>3,51x10<sup>-3</sup></b>	m <sup>3</sup> /h	1	3,28 x 10 <sup>-2</sup>	1,07 x 10 <sup>-3</sup>
- sampling time	t	672	h	1	1,49 x 10 <sup>-3</sup>	2,21 x 10 <sup>-6</sup>
- air pressure	P	101	kPa	1	2,0 x 10 <sup>-2</sup>	4,0 x 10 <sup>-4</sup>
- air temperature	T	293	K	1	2,0 x 10 <sup>-2</sup>	4,0 x 10 <sup>-4</sup>
Sampled volume at STP	V <sub>stp</sub>	2,37	m <sup>3</sup>		4,3 x 10 <sup>-2</sup>	1,9 x 10 <sup>-3</sup>
<b>Mass of ammonium determined</b>		<b>Sample</b>				
<i>Uncertainty component</i>	<i>Symbol</i>	<i>Value</i>	<i>Unit</i>			
- concentration in calibration standards	m <sub>cs</sub>	2	%	1		4,0 x 10 <sup>-3</sup>
- lack-of-fit of calibration function	l	0,2	% max	3		1,33 x 10 <sup>-6</sup>
- response drift between calibrations	D	0,9	% max	3		2,7 x 10 <sup>-5</sup>
- analytical precision	R	3	%	1		9,0 x 10 <sup>-4</sup>
Mass of ammonium in sample	m <sub>s</sub>	2,61	µg			1,3 x 10 <sup>-3</sup>
Uncertainty	u(m <sub>s</sub> )	0,095	µg			3,6 x 10 <sup>-2</sup>
<b>Mass of ammonium determined</b>		<b>Blank</b>				
Mass of ammonium in blank	m <sub>b</sub>	0,10	µg			
Uncertainty	u(m <sub>b</sub> )	0,003	µg			
<b>Net mass of ammonium</b>		2,51	µg			
<b>Uncertainty</b>		0,095	µg			
<b>Relative uncertainty</b>		0,038				
<b>Mass of ammonia</b>		2,37	µg			
<b>Concentration of ammonia</b>		<b>1,0</b>	<b>µg/m<sup>3</sup></b>			
<b>Relative uncertainty</b>		0,058				
<b>Expanded relative uncertainty</b>		<b>11,5</b>	<b>%</b>			

**Table 5.4 - Summary of expanded uncertainties of diffusive samplers**

<b>Sampler type</b>	<b>Reference concentration (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>Expanded uncertainty (%)</b>
CEH ALPHA	1	11,5
	3	11,4
	23	11,3
Gradko 3,5 cm diffusion tube	1	11,6
	3	10,7
	23	10,4
Gradko DIFRAM-400	1	10,9
	3	10,7
	23	10,6
PASSAM ammonia sampler	1	12,5
	3	11,9
	23	11,7
Istituti Clinici Scientifici Maugeri (ICS Maugeri Radiello Sampler, blue body)	1	23,0
	3	18,6
	23	17,2
FUB Radiello (ICS Maugeri sampler, white body)	1	15,8
	3	15,1
	23	15,0

## **6. Summary and future directions**

This review has summarised the state of the art passive sampling technology available with sufficient publication record for quality assessment.

It is noted that there is continual innovation and developments in environmental monitoring however many of the quality assurance calibrations and tests presented herein will be of use for researchers and sampler users.

A clear and correct treatment of uncertainties associated with ambient ammonia measurement using passive samplers is essential to provide confidence in the measurements and apply reasonable, traceable uncertainty assessments.

Both temperature, environmental conditions and sampler handling are key to performing high quality ammonia measurements and applications of methods described in this report.

The information presented herein will underpin the draft CEN standard for measuring ammonia with passive samplers and future quality assurance programmes.

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