

## Article (refereed) - postprint

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Martin, Nicholas A.; Ferracci, Valerio; Cassidy, Nathan; Hook, Josh; Battersby, Ross M.; di Meane, Elena Amico; Tang, Yuk S.; Stephens, Amy C.M.; Leeson, Sarah R.; Jones, Matthew R.; Braban, Christine F.; Gates, Linda; Hangartner, Marcus; Stoll, Jean-Marc; Sacco, Paolo; Pagani, Diego; Hoffnagle, John A.; Seitler, Eva. 2019. **Validation of ammonia diffusive and pumped samplers in a controlled atmosphere test facility using traceable Primary Standard Gas Mixtures.**

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<https://doi.org/10.1016/j.atmosenv.2018.11.038>

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Contact CEH NORA team at  
[noraceh@ceh.ac.uk](mailto:noraceh@ceh.ac.uk)

1 **Validation of ammonia diffusive and pumped samplers in a controlled atmosphere test facility**  
2 **using traceable Primary Standard Gas Mixtures**

3 Nicholas A. Martin<sup>\*a</sup>, Valerio Ferracci<sup>a,†</sup>, Nathan Cassidy<sup>a</sup>, Josh Hook<sup>a</sup>, Ross M. Battersby<sup>a</sup>, Elena  
4 Amico di Meane<sup>a</sup>, Yuk S. Tang<sup>b</sup>, Amy C. M. Stephens<sup>b</sup>, Sarah R. Leeson<sup>b</sup>, Matthew R. Jones<sup>b</sup>, Christine  
5 F. Braban<sup>b</sup>, Linda Gates<sup>c</sup>, Markus Hangartner<sup>d</sup>, Jean-Marc Stoll<sup>d</sup>, Paolo Sacco<sup>e</sup>, Diego Pagani<sup>e</sup>, John A.  
6 Hoffnagle<sup>f</sup>, Eva Seitler<sup>g</sup>

7 <sup>a</sup>National Physical Laboratory (NPL), Chemical, Medical and Environmental Sciences Department,  
8 Hampton Road, Teddington, Middlesex, TW11 0LW, UK

9 <sup>†</sup>Now at the Centre for Environmental and Agricultural Informatics, Cranfield University, College  
10 Road, MK43 0AL, UK

11 <sup>b</sup>Centre for Ecology and Hydrology, Bush Estate, Penicuik, Midlothian, EH26 0QB, Scotland, UK

12 <sup>c</sup>Gradko International Ltd, 77 Wales St, Winchester SO23 0RH, UK

13 <sup>d</sup>Passam AG, Schellenstrasse 44, 8708 Männedorf, Switzerland

14 <sup>e</sup>Istituti Clinici Scientifici Maugeri (ICSM), Via Atene 9, 35010 Vigonza, Italy

15 <sup>f</sup>Picarro Inc, 3015, Patrick Henry Drive, Santa Clara, CA 95054, USA

16 <sup>g</sup>FUB Research Group for Environmental Monitoring AG, Alte Jonastrasse 83, 8640 Rapperswil,  
17 Switzerland

18 **Abstract**

19 We report the determination of ammonia (NH<sub>3</sub>) diffusive sampling rates for six different designs of  
20 commercial diffusive samplers (CEH ALPHA sampler, Gradko diffusion tube, Gradko DIFRAM-400,  
21 Passam ammonia sampler, and ICS Maugeri Radiello radial sampler (blue and white turbulence  
22 barriers)), together with the validation test results for a pumped sampler (CEH DELTA denuder). The  
23 devices were all exposed in the UK's National Physical Laboratory's (NPL) controlled atmosphere test  
24 facility (CATFAC). For each of the seven diffusive sampler exposure tests there were traceable  
25 concentrations of ammonia (in the range 3-25 µg m<sup>-3</sup>) generated under well-defined conditions of  
26 temperature, relative humidity and wind speed, which are applicable to a variety of ambient  
27 monitoring environments. The sampler exposure time at each concentration was 28 days, except for  
28 the radial devices, which were exposed for 14 days. The work relied on the dilution of newly  
29 developed stable Primary Standard Gas Mixtures (PSMs) prepared by gravimetry in passivated gas  
30 cylinders as a method of improving the metrological traceability of ammonia measurements. The  
31 exposed diffusive samplers were sent blind to the participants for analysis and the reported NH<sub>3</sub>  
32 concentrations were then compared against the known reference concentration. From the results  
33 for each sampler type a diffusive sampling rate was calculated and compared against the rate used  
34 routinely by the participants. Some measurement results were in good agreement with the known  
35 traceable reference concentration (particularly for one diffusive sampler design (ALPHA)), while  
36 other devices exhibited over-reading and under-reading (each with a clear bias). The new diffusive  
37 sampling rates determined in the laboratory study were then applied to measurements in a field  
38 comparison campaign, and this was found to deliver an improvement in agreement between the  
39 different devices deployed.

40

41

42 **Key words**

43

44 Diffusive sampling rates, denuders, ammonia, metrological traceability

45 \* Corresponding author.

46 E-mail address: nick.martin@npl.co.uk (N.A. Martin).

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## 49 1. Introduction

50

51 Intensive livestock farming (specifically from cattle, pig, and poultry) and arable farming with the  
52 increased use of synthetic and organic fertilizers are responsible for rises in the amount fraction of  
53 ammonia (NH<sub>3</sub>) detected in ambient air in Europe and other areas during the 20th century. Ambient  
54 concentrations are predicted to increase leading to undesirable environmental effects at the ground  
55 surface, with eutrophication and acidification of land and freshwater leading to a loss of biodiversity,  
56 and in the air, with the formation of secondary particulate matter (PM) (Hornung et al., 1995;  
57 Pitcairn et al., 1998; Erisman et al., 2008; Pinho et al., 2012).

58 The recognition of NH<sub>3</sub> as an important pollutant has led to its inclusion in international  
59 agreements to reduce air pollutant emissions, firstly under the 1999 United Nations Economic  
60 Commission for Europe (UNECE) Gothenburg Protocol and then in the National Emissions Ceilings  
61 Directive (NECD) of the European Union (EU) (Directive 2001/81/EC). The target of both of these  
62 agreements is that NH<sub>3</sub> emissions should not exceed emission ceilings set for individual EU member  
63 states.

64 The revision of both the Gothenburg Protocol (in 2012) and the NEC Directive (Directive  
65 2016/2284/EU) included new, more stringent emission ceilings for 2020 that seek greater  
66 environmental protection and improvement in air quality, including the introduction of an emissions  
67 ceiling for particulate matter (PM). Under the 2012 UNECE Gothenburg protocol, EU member states  
68 must jointly cut their emissions of NH<sub>3</sub> by 6% and particles by 22 % between 2005 and 2020. A  
69 recent study (Bessagnet et al., 2014) employing three chemical transport models found that they  
70 underestimated the formation of ammonium particles and concluded that the role of NH<sub>3</sub> on PM  
71 formation is larger than originally thought. Other work (Vieno et al., 2016) suggested that the most  
72 effective measures to reduce the UK population exposure to PM<sub>2.5</sub> is to reduce ammonia emissions.  
73 According to the European Environment Agency (EEA) ammonia emissions increased in 2015 in  
74 several European Union member states, as well as the EU as a whole, and consequently exceeded  
75 their respective emission limits under the UN Convention (European Environment Agency, 2017).

76 Other legislation to abate ammonia emissions includes the Industrial Emissions Directive (IED)  
77 (Directive 2010/75/EU), which requires pig and poultry farms (above stated size thresholds) to  
78 reduce emissions using “Best Available Techniques” (BATs). The IED repeals the former Integrated  
79 Pollution Prevention and Control (IPPC) Directive, with effect from January 2014.

80 In Germany, the Federal Immission Control Act (TA Luft, 2002a) provides guidance and technical  
81 instructions on air quality control and recommends that at any assessment point the concentration  
82 of ammonia should not exceed 10 µg m<sup>-3</sup> (equivalent to an amount fraction of approximately 14  
83 nmol mol<sup>-1</sup> at ground level), thereby limiting damage to plants and ecosystems.

84 Annual mean Critical Levels (“CLs”) of ammonia have also been assessed (Cape et al., 2009) and  
85 adopted by the UNECE for protection of sensitive ecosystems; these concentrations are 1 µg m<sup>-3</sup> for  
86 lichens and bryophytes and 3 µg m<sup>-3</sup> for other types of vegetation. A monthly critical level of  
87 23 µg m<sup>-3</sup> was retained as a provisional value in order to deal with the possibility of high peak  
88 emissions during periods of manure application. There is a German limit of 30 mg m<sup>-3</sup> that should

89 not be exceeded in the exhaust gas of industrial plants (TA Luft, 2002b). Currently there is no  
90 established human exposure level for ambient air, but the US Environmental Protection Agency  
91 (EPA) has set a chronic lifetime exposure value equivalent to  $100 \mu\text{g m}^{-3}$  (US EPA, 2001).

92 Measurements of ambient ammonia covering a wide geographical area are principally carried out  
93 with low-cost diffusive samplers or by pumped sampling with denuders, with each method  
94 delivering time-integrated values over the monitoring period (from daily up to monthly). The  
95 denuder technique is considered by certain experts to be suitable as an “unofficial” reference  
96 method in the absence of any agreement to select an appropriate continuous analyser with  
97 adequate sensitivity over the required concentration range (Ferm, 1979, Sutton et al., 2001). A  
98 number of national monitoring networks using these low-cost technologies have been implemented  
99 to assess ambient ammonia concentrations and trends, including the National Ammonia Monitoring  
100 Network (NAMN) in the UK (Tang et al., 2018) and the Measuring Ammonia in Nature (MAN)  
101 Network in the Netherlands (van Zanten et al., 2017).

102 Monitoring ammonia poses a number of challenges: there is a lack of regulation regarding which  
103 analytical techniques to employ, no agreement on the required uncertainty of measurements, no  
104 standardised quality control/quality assurance (QA/QC) procedures in place, and there is no  
105 established traceability infrastructure to underpin the measurements. Traceability is a property of  
106 the measurement results (in this case the ammonia amount fraction) that can be related to primary  
107 metrological standards through an unbroken chain of calibrations. Within this chain, the  
108 measurement uncertainty is determined at each step and then combined, in accordance with  
109 international guidelines (ISO-Guide 98-3), thereby ensuring that there can be comparability of  
110 measurements originating from different studies.

111 Passive samplers rely on the diffusion of the target gas ( $\text{NH}_3$ ) onto a surface on which the gas is  
112 chemically captured by a sorbent. Uncertainties in the measurement come from both the sampler  
113 preparation, laboratory analysis and environmental exposure factors (Tang et al., 2001). In larger  
114 networks passive samplers are co-located with active “reference methods” in order to calibrate the  
115 diffusive sampling rate (which may be dependent on many parameters including temperature, and  
116 local meteorology for the region where the measurements are being made). In other cases a  
117 theoretical sampling rate is applied based on the relevant sampler’s dimensions. A recent German  
118 guideline has been developed to cover measurements of ammonia in ambient air with diffusive  
119 samplers (VDI 3869, 2012), but is limited in scope and has not been widely adopted in other  
120 countries. The European Standardization Body, CEN, has recently been charged with developing a  
121 wider measurement protocol through CEN Technical Committee 264 Working Group (WG) 11.

122 The aim of this work was to determine the diffusive sampling rates of a wide range of commonly  
123 employed commercial low cost diffusive samplers and to validate the performance of one type of  
124 denuder sampler design with a view to improving the reliability and accuracy of ambient ammonia  
125 measurements. The study involved carrying out traceable sampler exposure tests in a controlled  
126 atmosphere test facility (CATFAC) developed at the UK’s National Physical Laboratory (NPL). It also  
127 required the development of stable traceable Primary Standard Gas Mixtures (PSMs) of  $\text{NH}_3$   
128 prepared by gravimetry to create well characterised atmospheres of this species, together with the  
129 further development of a cavity ring-down spectrometer (CRDS) for on-line continuous monitoring  
130 of ammonia. The new determinations of the diffusive sampling rates were then applied to  
131 measurements carried out in the field with the goal of improving the comparability of data obtained  
132 from the different samplers.

133

134

## 135 2. Experimental method

### 136 2.1 Laboratory test procedures

137 A modified controlled atmosphere test facility (CATFAC), consisting of a wind tunnel with an  
138 internal volume of approximately 1000 L (Martin et al., 2003; Martin et al., 2014) was employed to  
139 carry out validation tests on simultaneously exposed ammonia diffusive and pumped samplers. Here  
140 a series of test atmospheres at relevant  $\text{NH}_3$  ambient concentrations were generated at nominally:  
141 3, 7, 10, 15, 17, 20 and 25  $\mu\text{g m}^{-3}$ , (where 1  $\mu\text{g m}^{-3}$   $\text{NH}_3$  is equivalent to an amount fraction of 1.41  
142  $\text{nmol mol}^{-1}$  at a reference temperature of 20 °C, or 1.41 ppb (parts per billion)). Figure 1 shows a  
143 photograph of the CATFAC, which is predominantly made of glass with perfluoroalkoxy (PFA) tubing  
144 to minimise potential undesirable wall losses of  $\text{NH}_3$ .

145 The required  $\text{NH}_3$  concentrations were prepared by dynamically blending and diluting traceable  
146 NPL PSMs of this molecule with scrubbed air (Peak Scientific), using an array of calibrated mass flow  
147 controllers (Brooks). The test gas mixtures were continuously replenished, at a known measured rate  
148 of approximately 30  $\text{L min}^{-1}$ , by a freshly generated mixture of the same concentration. This was  
149 carried out in a section of the CATFAC where the flow of gas is turbulent, so as to ensure good  
150 mixing. A stainless steel recirculating blower (Eurotherm Drives) was employed to drive the gas  
151 mixtures through a series of restricting grids designed to reduce the spatial and temporal  
152 fluctuations, and ensure a uniform airflow over the diffusive sampler deployment section of the  
153 facility. Together with continuous gas recirculation, this design delivered accurate and stable  
154 atmospheres at constant concentrations in the test chamber before being exhausted safely to  
155 atmosphere, thus minimising total gas consumption and the cost of its operation.

156 The CATFAC temperature was maintained at a target value of nominally  $(20 \pm 1)^\circ\text{C}$  using a  
157 chiller/heater control system that pumped a mixture of ethylene glycol and water through external  
158 pipe coils made of copper. The facility was further wrapped in a glass fibre insulation jacket to  
159 prevent “cold spots” and potential water condensation on the inside walls. Calibrated temperature,  
160 relative humidity and pressure sensors were employed to monitor the environmental conditions in  
161 the chamber. For each of the seven exposure tests, the relative humidity was maintained at  
162 nominally 70% using a calibrated liquid water pump supplied with de-ionised water and a vaporiser  
163 (developed in-house), which is very typical of ambient conditions found in Northern Europe. The  
164 adjustable air speed was set to approximately 1.2  $\text{m s}^{-1}$ , as measured by a hot wire anemometer,  
165 which is within the range of other diffusive sampler studies.

166 Continuous on-line monitoring of the test atmosphere concentration was achieved by extractive  
167 sampling through PFA pipework into a modified cavity ring down spectrometer (CRDS) (Model  
168 G2103, Picarro Inc), which could detect both ammonia and water vapour. Initially, the spectrometer  
169 was found to be affected by direct and indirect cross-interference from  $\text{H}_2\text{O}$ . The spectrometer  
170 reported concentration based on peak absorption, which was correct for dry  $\text{NH}_3$  atmospheres, but  
171 for humidified atmospheres of this molecule, there was an under reporting due to the broadening of  
172 the  $\text{NH}_3$  spectral feature, resulting in a reduction in peak height. In collaboration with the  
173 manufacturer a correction mechanism (Martin et al., 2016) was developed for the CRDS, which  
174 required new measurements of the collisional broadening due to water vapour of two  $\text{NH}_3$  spectral  
175 lines in the near infrared (6548.6 and 6548.8  $\text{cm}^{-1}$ ). Traceability of the  $\text{NH}_3$  spectrometer  
176 measurements was achieved through the use of NPL’s stable PSMs of  $\text{NH}_3$  to generate dry and  
177 humidified atmospheres at low concentrations. The correction has been incorporated by the  
178 manufacturer in all new CRDS ammonia sensors.

179 *2.2 Primary standard gas mixtures: preparation, validation and statistical analysis of stability*  
180 *measurements*

181 Stable PSMs were specifically developed for the exposure tests in the CATFAC in order to improve  
182 the current state-of-the-art metrological traceability and validation of ambient ammonia  
183 measurements by providing new diffusive sampling rate measurements for some of the devices  
184 tested. The PSMs used in this work were prepared gravimetrically using the method outlined in  
185 guide ISO 6142 (2001) from pure ammonia (Air Products, VLSI, 99.999% purity) and nitrogen (Air  
186 Products, BIP+, 99.99995% purity). A more detailed account on the development of the PSMs has  
187 been given previously (Martin et al., 2016; Pogány et al., 2015; Pogány et al., 2016). Mixtures of 100  
188  $\mu\text{mol mol}^{-1}$   $\text{NH}_3$  in nitrogen were prepared in Spectra-Seal™ (BOC plc) and Aculife IV™ (Air  
189 Liquide/Scott)-treated 10 L cylinders, whilst mixtures at 10  $\mu\text{mol mol}^{-1}$  were prepared in 10 L  
190 Spectra-Seal™ cylinders and in 3.785 L stainless-steel cylinders (Swagelok) coated with the  
191 SilcoNert™2000 treatment (SilcoTek, Inc).

192 As the exposure test programme took place over relatively long timescales (generally 4 weeks for  
193 each of the seven ammonia concentrations described above), it was crucial that the PSMs employed  
194 were stable over extended periods of time to ensure that the ammonia concentrations delivered to  
195 the CATFAC were constant and internally consistent. Ammonia PSMs, as those of other reactive  
196 gases, can be prone to instability if cylinders without the suitable passivation technique are  
197 employed; this issue was highlighted by the lack of consensus between National Metrology Institutes  
198 (NMIs) in an international key comparison (CCQM-K46) carried out in 2006-2007 (van der Veen et al.,  
199 2010). The long term stability of these mixtures was monitored by periodically validating the PSMs  
200 against freshly prepared mixtures in the same cylinder type at the same nominal amount fraction (or  
201 concentration). The ammonia amount fraction of all mixtures was measured with a non-dispersive  
202 infra-red (NDIR) analyser (ABB, Uras26) using a known-unknown validation routine that has been  
203 described in detail previously (Martin et al, 2016).

204 Once a time series of ammonia amount fraction in the cylinders under test was obtained, a  
205 significance analysis was therefore invoked to establish whether the trends observed were  
206 statistically significant in the light of the uncertainties associated with the data points; this type of  
207 analysis is described in detail elsewhere (Ferracci et al., 2015). Ordinary least squares (OLS) fits to  
208 the plots of ammonia amount fraction against time were performed using NPL's XLGENLINE software  
209 (Smith, 2010) (described in detail in Section 3.2). The values of the gradients obtained and their  
210 associated uncertainties were then analysed: if the expanded uncertainty interval for the gradient of  
211 each plot encompassed zero, then the trend in the dataset could be said to be insignificant.

212 The results of these stability studies are described in Section 3.1 below.

213 *2.3 Samplers tested*

214  
215 There are numerous passive samplers on the market including tube-, badge- and radial-types,  
216 with designs having advantages and disadvantages depending on the ammonia concentration range  
217 being measured and deployment exposure time (Tang et al., 2001). A recent review was available to  
218 assist in the selection of devices to test in this study where the prior art knowledge was without  
219 commercial restrictions and for which well-defined performance characteristics were published and  
220 publically accessible (Braban et al., 2018). The samplers employed in the CATFAC exposure tests  
221 were from the Centre for Ecology and Hydrology, CEH (CEH ALPHA sampler and CEH DELTA  
222 denuder), Gradko International Ltd (Gradko diffusion tube and Gradko DIFRAM-400), Istituti Clinici

223 Scientifici Maugeri, ICS Maugeri (Radiello radial sampler with blue outer cylinder turbulence barrier  
 224 (#RAD1201)), Passam AG (Passam ammonia sampler), and FUB AG (Radiello radial sampler from the  
 225 ICS Maugeri, but with white outer cylinder turbulence barrier (#RAD120)). There is no difference in  
 226 porosity between the white (#RAD120) and blue diffusive bodies (#RAD1201). The blue type was  
 227 developed by ICS Maugeri with the aim of protecting photo-sensitive reagents and/or products,  
 228 before, during and/or after sampling from sunlight (ICS Maugeri, 2018). The devices were randomly  
 229 distributed inside the section of the exposure chamber perpendicular to the direction of gas flow.  
 230 The diffusive samplers were exposed to each relevant atmosphere for 28 days, with the exception of  
 231 Radiello samplers: these were dosed for periods of 14 days as recommended by the manufacturer.  
 232 The denuders actively sampled through separate perfluoroalkoxy (PFA) ports in the CATFAC for  
 233 either 14 or 28 days. The DELTA denuder is less prone to cross interference by particulate capture  
 234 due to the laminar air flow conditions (Sutton et al, 2001).

235 After exposure all samplers were sealed and returned to each participant for wet chemical  
 236 analysis. The ICS Maugeri processed their own radial samplers, but FUB AG (which had used ICS  
 237 Maugeri devices) carried out their own chemical extraction and analysis. FUB AG provides this  
 238 combination to an extensive set of clients and our study tests this particular combination.

239 Using their own in-house validated/accredited procedures, the participants employed de-ionised  
 240 water to extract the ammonia chemically captured by their samplers, which in the aqueous phase, is  
 241 in the form of ammonium ( $\text{NH}_4^+$ ). As an example of the procedure, the  $\text{NH}_3$  captured on the acidified  
 242 filter paper of the ALPHA diffusive sampler and on the acid coated DELTA denuders (20 cm long  
 243 borosilicate glass tubes) was extracted into 3 mL and 5 mL deionised water, respectively. The  
 244 extracts were analysed for ammonium using an AMFIA (ammonia flow injection) system, which is  
 245 based on the selective dialysis of ammonium across a membrane, at high pH, with subsequent  
 246 analysis by conductivity (Wyers et al. 1993). The results from all participants were reported to NPL as  
 247 a concentration in the conventional units of  $\mu\text{g m}^{-3}$ .

248 For the redetermination of the diffusive sampling rates,  $\vartheta$ , a knowledge of the traceable  
 249 concentrations in the CATFAC, the measured exposure times, and the analysed masses of ammonia  
 250 reported by each manufacturer were employed, as described in Section 2.4. Lack of fit plots were  
 251 generated using XLGENLINE, which is a generalized least-squares (GLS) Microsoft Excel-based  
 252 software package for low-degree polynomial fitting developed at NPL (Smith, 2010).

253 XLGENLINE employed a user-defined input file: this required values of  $x$  and  $u(x)$  (respectively the  
 254 known  $\text{NH}_3$  input concentration multiplied by the exposure time and the combined standard  
 255 uncertainty);  $y$  and  $u(y)$  (respectively the reported mean mass of ammonia and the combined  
 256 uncertainty). The software package performed a first-order polynomial GLS fit, in this case, forced  
 257 through zero, and the gradient of the regression lines delivered the new values of the diffusive  
 258 sampling rates in units of  $\text{m}^3 \text{h}^{-1}$ , together with their uncertainties.

259

#### 260 *2.4 Diffusive sampling rate and pumped denuder sampler calculations*

261

262 The sampling mechanism for the passive devices employed in this work is described by Fick's first  
 263 law of diffusion, which has been discussed extensively in a number of publications (Martin et al.,  
 264 2014). Very briefly, the ambient concentration of ammonia,  $[\text{NH}_3]$ , either in a test chamber or in the  
 265 field, may be determined from Equation (1):

266

$$267 \quad [\text{NH}_3] [\mu\text{g m}^{-3}] = m [\mu\text{g}] / (\vartheta [\text{m}^3 \text{h}^{-1}] \cdot t [\text{h}]) \quad (1)$$

268  
269 where  $m$  is the measured mass of  $\text{NH}_3$  (after correction for the laboratory blank value),  $\vartheta$  is the  
270 diffusive sampling rate and  $t$  is the exposure time.

271  
272 The theoretical diffusive sampling rate may be calculated from a knowledge of the sampler  
273 dimensions:

$$274 \quad \vartheta [\text{m}^3 \text{h}^{-1}] = D [\text{m}^2 \text{h}^{-1}] \cdot A [\text{m}^2] / L [\text{m}] \quad (2)$$

275  
276 where  $D$  is the diffusion constant,  $A$  is the cross sectional area, and  $L$  is the diffusion length (where  $1$   
277  $\text{m}^3 \text{h}^{-1}$  is equivalent to  $277.78 \text{ cm}^3 \text{s}^{-1}$ ). However this method does not take into account any biases  
278 that may be present from a particular sampler design (e.g. additional resistance to gas diffusion by  
279 turbulence damping membranes), or introduced in the wet chemical analysis carried out by each of  
280 the laboratories.

281  
282 The value of the diffusion constant of  $\text{NH}_3$  in air is stated as  $0.1978 \text{ cm}^2 \text{s}^{-1}$  at  $273 \text{ K}$ ,  $101.3 \text{ kPa}$   
283 (Massman, 1998), obtained from an earlier study (Wintergerst, 1930), while its temperature  
284 dependence is given by (ISO: 16339:2013):

$$285 \quad D_T = D_{273\text{K}} \cdot (T/273)^{1.81} \quad (3)$$

286  
287 where  $D_T$  is the diffusion constant at a given temperature  $T$ ,  $D_{273\text{K}}$  is the diffusion constant at  $273\text{K}$ ,  
288 and  $T$  is the temperature of the gas components in  $\text{K}$ . The approach taken in this study was to  
289 measure the diffusive sampling rates under reference conditions of  $20^\circ\text{C}$  ( $293 \text{ K}$ ), which are normally  
290 employed for the reporting of ambient measurements (e.g., Directive, 2008/50/EC). For instances  
291 where temperature data in the field is available then the diffusive sampling rate could be modified  
292 using Equation (4):

$$293 \quad \vartheta_T = \vartheta_{T_{\text{Ref}}} \cdot (T/T_{\text{Ref}})^{1.81} \quad (4)$$

294  
295 In the case of pumped sampling with the DELTA denuder then the concentration of ammonia is  
296 given by:

$$297 \quad [\text{NH}_3] [\mu\text{g m}^{-3}] = m [\mu\text{g}] / V [\text{m}^3] \quad (5)$$

298  
299 where  $V$  is the calibrated volume of air sampled.

300  
301  
302  
303  
304

## 305 2.5 Treatment of uncertainties

306  
307 The combined standard uncertainty,  $u_\vartheta$ , for each determination of the diffusive sampling rate is  
308 given by Equation (6):

$$309 \quad u_\vartheta = ((u_{\text{cfinal}})^2 + (u_r)^2 + (u_{\text{an}})^2 + (u_{\text{sr}})^2 + (u_t)^2)^{1/2} \quad (6)$$

310  
311 where  $u_{\text{cfinal}}$  is the combined standard uncertainty of each  $\text{NH}_3$  concentration introduced into the  
312 CATFAC,  $u_r$  is the repeatability standard uncertainty of on-line  $\text{NH}_3$  measurements recorded with the  
313 CRDS,  $u_{\text{an}}$  is the calculated analytical analysis standard uncertainty from information reported by  
314 each laboratory,  $u_{\text{sr}}$  is the repeatability standard uncertainty of the recovered analyte from the  
315 samplers, and  $u_t$  is the standard uncertainty for the relevant sampler exposure time.

316  
317



318 For the orthogonal regression analysis described in Section 3.2 the combined uncertainties for the  
319 first two components in Equation (6) are associated with the generation of the ammonia test  
320 atmospheres (through the traceable dilution of a PSM, on-line measurements, and the exposure  
321 time period) i.e.,  $u(x)$ , while the last two terms are associated with contributions from the analysis of  
322 the exposed samplers by each manufacturer, i.e.,  $u(y)$ .

323  
324 The uncertainty calculation for the delivery of the  $\text{NH}_3$  concentration,  $u_{\text{Cfinal}}$ , for each exposure has  
325 been described previously (Martin et al, 2016), and follows a standard international method (ISO  
326 6145-7:2010). The sources of uncertainty identified in the exposure concentration include the  $\text{NH}_3$   
327 concentration of the parent cylinder, individual repeatability standard deviations in the mass flow  
328 rates, mass flow controller temperature dependencies, gravimetric water calibration (including  
329 balance drift), mass flow meter calibrations, and time. A 'sensitivity' was then assigned to each of  
330 these components by differentiating the concentration with respect to each component, followed by  
331 summation in quadrature, together with the repeatability uncertainty of the on-line CRDS  
332 measurements.

333  
334 The analytical analysis standard uncertainty,  $u_{\text{an}}$ , is associated with the determination of the mass  
335 of ammonium in a sample, and was calculated from information supplied by each laboratory in  
336 accordance with their established accredited procedures. This took into account contributions from  
337 the uncertainty of the mass of ammonium in the liquid calibration standards, the lack of fit of the  
338 calibration function, the analytical repeatability, the response drift between calibrations, and blanks,  
339 following similar principles applied to  $\text{NO}_2$  diffusive samplers in EN 16339:2013-11. It is noted that  
340 systematic method or extraction errors by a laboratory would not be captured in this study as there  
341 was no agreed central analytical laboratory. All laboratories participating are either accredited or  
342 participate in analytical comparisons.

## 343 344 2.6 Field Procedures

345 A field study was carried out in Scotland (Stephens et al. 2017) where there is a facility in place for  
346 controlled releases of  $\text{NH}_3$  on a peatland site (Leith et al, 2004, Whim Bog, 2016). Ammonia was  
347 released at a known rate of  $0.2 \text{ kg h}^{-1}$ , when the wind in the preceding minute was in a particular  $30^\circ$   
348 wind sector. Over two consecutive 4-week exposure periods in summer 2016, measurements of  
349 ammonia were taken of the ambient background, and at 12.5 m, 32 m and 60 m from the source  
350 release. The exposed diffusive samplers were treated in a similar manner to those employed for the  
351 laboratory tests.

## 352 353 3. Results and discussion

### 354 355 3.1 Stability of $\text{NH}_3$ primary standard gas mixtures

356  
357 The stability of the PSMs was monitored over a period ranging from approximately 10 months  
358 (Aculife IV™) to 19 months (Spectra-Seal™ and SilcoNert™2000); the certified ammonia content of  
359 each mixture as a function of time is shown in Figure 2a for the  $100 \mu\text{mol mol}^{-1}$  mixtures and Figure  
360 3a for the  $10 \mu\text{mol mol}^{-1}$  mixtures. At the  $100 \mu\text{mol mol}^{-1}$  level there were no obvious signs of  
361 instability within the given analytical uncertainty ( $< 2\%$ ) for any of the mixtures under test. This was  
362 also the case for the  $10 \mu\text{mol mol}^{-1}$  mixtures in SilcoNert™2000-treated cylinders, whereas the  $10$   
363  $\mu\text{mol mol}^{-1}$  mixtures in Spectra-Seal™ cylinders exhibited a decrease in ammonia content.

364  
365 The outcome of the significance analysis is shown in Figures 2b and 3b for the  $100$  and  $10 \mu\text{mol mol}^{-1}$   
366 mixtures respectively. In both diagrams all the gradients of the stability plots overlap with zero  
367 within the given uncertainty at the  $k = 2$  level (corresponding to a 95 % confidence level), indicating

368 no statistically significant sign of instability within the ammonia PSMs. However the downward  
369 trend in ammonia amount fraction observed in the 10  $\mu\text{mol mol}^{-1}$  mixtures in Spectra-Seal™ is  
370 statistically significant at the  $k = 1$  level. This, along with the elevated gas consumption rate  
371 associated with using PSMs at low amount fractions, led to the use of the 100  $\mu\text{mol mol}^{-1}$  mixtures  
372 for the exposure tests described here.

373  
374 The 10  $\mu\text{mol mol}^{-1}$  mixtures prepared in SilcoNert™2000-treated cylinders showed no sign of  
375 instability at both the  $k = 1$  and  $k = 2$  levels. While this result confirmed the suitability of this  
376 treatment for applications involving ammonia (along with the positive outcome of the decant tests  
377 described by Pogány et al. (Pogány et al., 2016)), the use of these mixtures in the exposure tests was  
378 limited by the small gas volume accommodated in the treated cylinders (3.785 L) compared to the  
379 larger ones available (10 L).

380  
381 The results of the stability measurements provided confidence to the use of the 100  $\mu\text{mol mol}^{-1}$   
382 PSMs in the exposure tests as they demonstrated that the samplers were exposed to ammonia  
383 atmospheres that were stable throughout the duration of the entire test programme. The  
384 development of new PSMs of ammonia will be further exploited in a forthcoming international key  
385 comparison for ammonia (CCQM-K117), scheduled to be carried out 2018, to establish whether  
386 progress by all NMIs has been achieved since CCQM-K46.

387

388

### 389 *3.2 Experimental determination of the NH<sub>3</sub> diffusive sampling rates*

390

391 Figure 4 shows the initial assessment of the CATFAC exposure study data for both diffusive and  
392 pumped samplers. The results are based on the application of the relevant manufacturers' historical  
393 diffusive sampling rates, analysis procedure, and calibrations, which in many cases may not have  
394 been extensively validated prior to this study. The ordinate axis shows the results reported by each  
395 participant, expressed as the mean percentage deviation from the known ammonia reference  
396 concentrations introduced into the CATFAC. The nominal values of the seven traceable NH<sub>3</sub>  
397 reference concentrations are detailed in the legend.

398

399 In general, for each type of device tested, the mean concentration values were calculated from six  
400 diffusive sampler measurements (eight in the case Radiello devices analysed by ICSM and three for  
401 those from FUB), and four for the pumped samplers, while the error bars shown in the figure  
402 represent the calculated repeatability uncertainty (one sigma standard deviation) of the mean  
403 values. Even though the devices were randomly distributed in the CATFAC, and were exposed  
404 simultaneously to the various test atmospheres, the results indicate a considerable variation in the  
405 reported concentrations (by design type). Some measurement results were in good agreement with  
406 the known traceable reference concentration (particularly for one diffusive sampler design (ALPHA)),  
407 while other devices exhibited over-reading and under-reading (each with a clear bias).

408

409

410 Figure 5 shows the lack of fit plots for each sampler type tested while Table 1 contains the  
411 summary of the diffusive sampling rates, as calculated by XLGENLINE, together with their combined  
412 expanded standard uncertainties (with a coverage factor  $k = 2$ ), providing a coverage probability of  
413 approximately 95%. Table 1 also contains the  $R^2$  of the linear fits, which are all effectively = 0.99.  
414 For comparison, the diffusive sampler data originally employed by each manufacturer are included,  
415 together with the reference temperature (in °C). In the cases where the sampling rates were  
416 originally reported at either 25°C or 10°C then Equation (4) was employed to adjust the  
417 manufacturers' values to a reference temperature of 20°C. We kept the results from ICS Maugeri  
418 separate from FUB since the two diffusive sampling rates did not overlap within their measurement

419 uncertainties. We cannot decouple the effects of the body types and the potential analysis  
420 differences from the two different laboratories. The strong linear behaviour over the concentration  
421 range tested shown in Figure 5 indicates all that all the samplers design work well and that biases  
422 (where found in the original diffusive sampling rates) can be corrected.

423

424 For the pumped CEH DELTA denuder samplers, a first order lack of fit plot was generated by  
425 XLGENLINE using the reported concentrations (ordinate axis) and the known traceable delivered  
426 concentrations (abscissa axis). These data are shown in Figure 6 (with one outlier removed),  
427 together with the linear equation and the value of  $R^2$ , which is effectively equal to 0.99. The  
428 delivered concentrations are traceable to the ammonia PSMs developed in this work, and the  
429 measured concentrations are derived from a completely separate and independent wet chemical  
430 analysis technique. There is good agreement between the two, to within 1%; it provides separate  
431 comparison data for the ammonia pumped sampling technique, and is also not dependent on a  
432 value of a diffusive sampling rate to provide the quantification. For the concentration range tested,  
433 the expanded uncertainty for the denuder was found to be  $\pm 11\%$ .

434

435 A worked example calculation of the relative expanded uncertainty estimation for ammonia  
436 measurements ( $k=2$ ) is provided in Table 2 for an annual critical level of  $1 \mu\text{g m}^{-3}$ . The results shown  
437 are for the ALPHA sampler incorporating the measured diffusive sampling rate determined in this  
438 work (in  $\text{m}^3 \text{h}^{-1}$ ). This rate was used to calculate the volume of gas sampled,  $V$  (together with  
439 contributions from the sampling time, pressure and temperature). Finally, Table 3 contains a  
440 summary of the data for all the diffusive sampler designs tested covering annual critical levels of  
441 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  
442 period of 28 days (14 days for Radiello samplers). The measurement uncertainties are different for  
443 the various sampler designs tested with the radial type being the poorest. Nevertheless, the  
444 expanded relative uncertainty values for the  $\text{NH}_3$  critical levels are consistent with the typical  
445 indicative measurements requirements of  $\pm 25\%$  (for nitrogen dioxide) and  $\pm 30\%$  (benzene)  
446 detailed in EU Air Quality Directives (Directive 2008/50/EC).

447

### 448 3.3 Field Tests

449

450 The CATFAC study delivered new values of the diffusive sampling rates; these were applied to the  
451 field comparison results to determine whether there was improved agreement between the  
452 different types of samplers. Figure 7 shows the field measurement results obtained by employing  
453 the original diffusive sampling rates from each manufacturer to the data, and also using the new  
454 determinations obtained from the CATFAC study. In all cases the mean  $\text{NH}_3$  concentration values are  
455 displayed for each type of sensor (Passam-; ALPHA-, Gradko DIFRAM-400-, Gradko 3.5 cm diffusion  
456 tube-, ICSM Radiello, and FUB Radiello-), and the error bars represent the repeatability uncertainty  
457 (one sigma standard deviation) at each location from the release source for both exposure periods.  
458 Three diffusive samplers of each type were deployed at each of the four locations from the release  
459 point.

460 The coefficients of variation (COVs) (i.e., ratio of one sigma standard deviation and the mean  $\text{NH}_3$   
461 concentration of samplers multiplied by 100%) have also been calculated for all results of all  
462 samplers using diffusive sampling rates provided by the manufacturers and those from the  
463 laboratory tests described; the COVs provide evidence (Table 4) that the agreement between the  
464 results improves when diffusive sampling rates from this study are used. This is particularly evident  
465 for the higher concentration locations, but less so at background levels.

466 This is particularly evident for the higher concentration locations, but less so at background levels.  
467 Sampler types should be suitably matched to the measurement requirements. The low diffusive

468 sampling rates of some tube-type samplers make them too uncertain to use at background  
469 concentrations  $< 1 \mu\text{g m}^{-3}$  where it seems they can significantly overestimate concentrations (Tang et  
470 al., 2001). Instead, badge- or radial-type samplers can be used to monitor low concentrations of  $\text{NH}_3$   
471 in background areas, but then they may be less suitable for monitoring in source regions for longer-  
472 term exposures due to potential saturation problems. . Clearly there are also other factors which  
473 can affect the variability of the measurements including wind speed, temperature range, dust  
474 deposition on turbulence barrier, location in the plume of gas and the laboratory analysis.

475  
476

#### 477 **4. Conclusions**

478

479 New values of the diffusive sampling rates for a range of commercial low cost diffusive samplers,  
480 commonly employed for ambient monitoring of ammonia, have been determined (as summarised in  
481 Table 1) in a controlled atmosphere test facility, together with validation of pumped denuder  
482 samplers. The work required the development of stable ammonia Primary Standard Gas Mixtures  
483 (PSMs) to generate known concentrations of this species for the laboratory exposure tests. It also  
484 required a water cross-interference correction mechanism to be applied to a commercial cavity ring-  
485 down spectrometer to enable continuous on-line measurements of ammonia to be carried out. For  
486 certain of the devices tested there is good agreement with previous determinations of the diffusive  
487 sampling rates, but new data is also presented in the cases where there was poorer agreement with  
488 historical values of these rates. This study has provided sampler manufacturers and end users with  
489 the tools to improve the metrological traceability and accuracy of low concentration ambient  
490 measurements of ammonia.

491

#### 492 **Acknowledgements**

493

494 We gratefully acknowledge the funding received from the Chemical and Biological Metrology  
495 Programme of the UK Department for Business, Energy and Industrial Strategy (BEIS), and the  
496 European Metrology Programme (EMRP) of the European Union. The EMRP is jointly funded by the  
497 EMRP participating countries within EURAMET and the European Union. We sadly report the demise  
498 of Markus Hangartner in 2017.

499

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501 Printer for Scotland.

502

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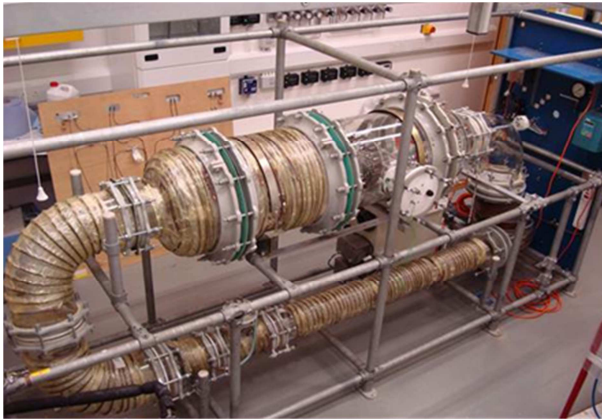
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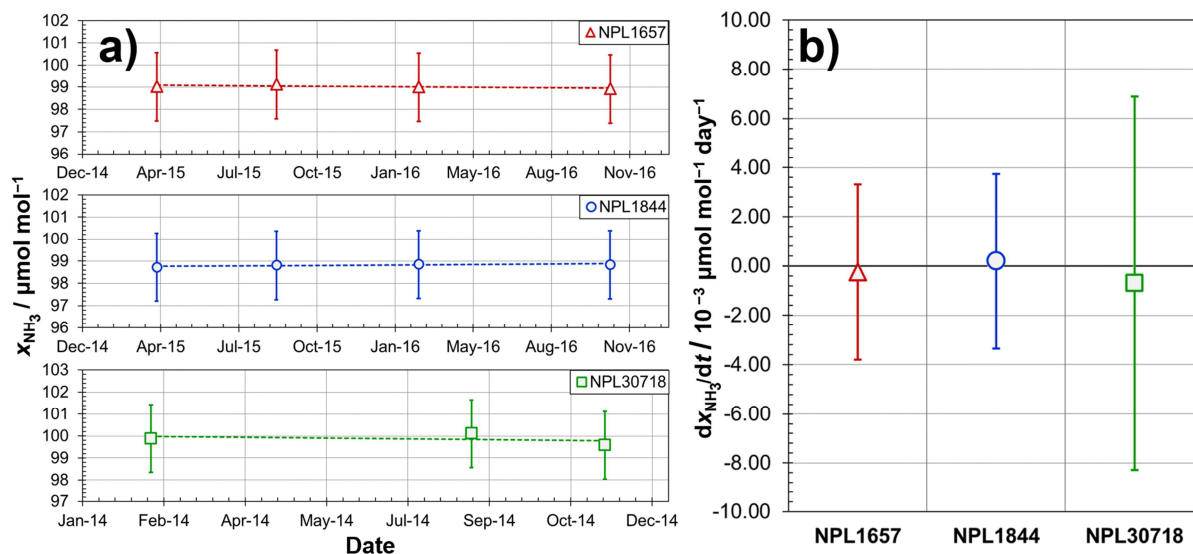


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**Fig. 1.** Controlled Atmosphere Test Facility without insulation.



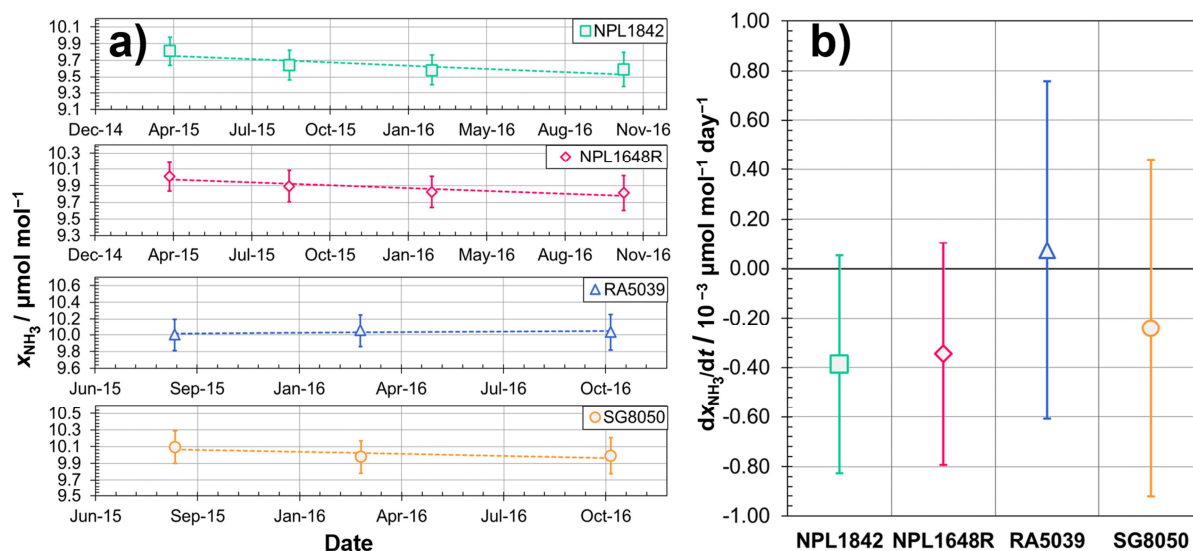
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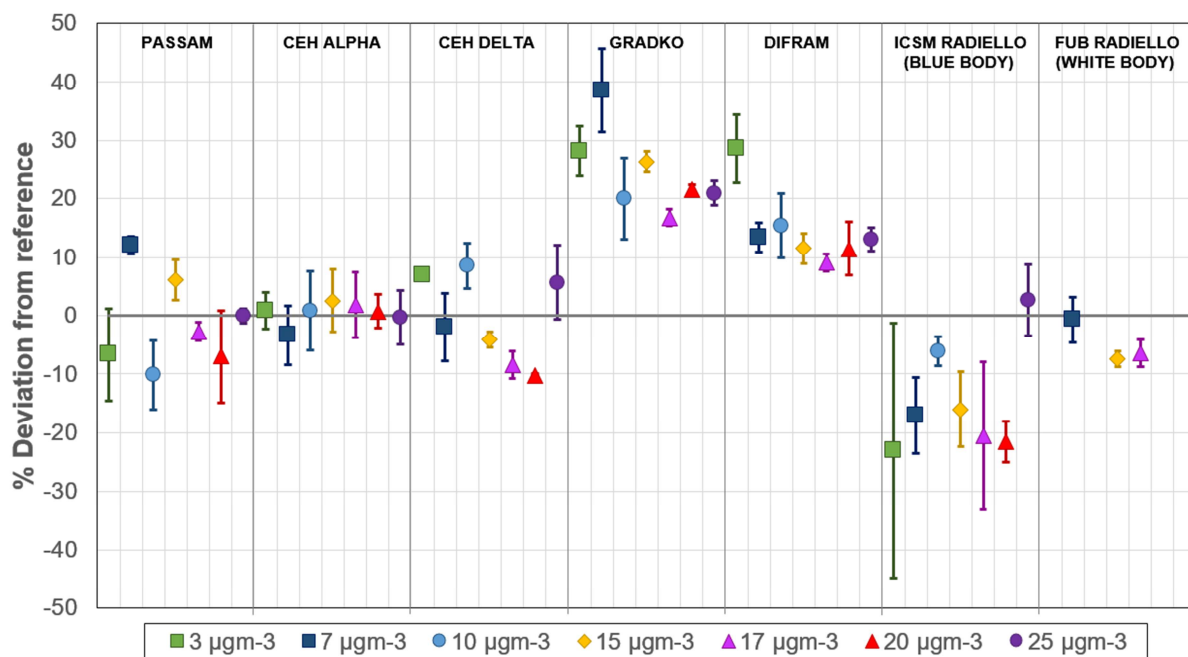
**Fig. 2.** Plots showing results of the long-term stability tests of three PSMs of  $100 \mu\text{mol mol}^{-1} \text{NH}_3$  in  $\text{N}_2$ . Panel a) shows the periodic measurements of the ammonia amount fraction,  $x_{\text{NH}_3}$ , of the PSMs: two prepared in Spectra-Seal™ (BOC plc) cylinders (NPL1657 and NPL1844) and one in an Aculife IV™ (Air Liquide/Scott) cylinder (NPL30718). Panel b) illustrates the significance analysis (see text for details) of the gradients of the stability plots. An overlap of the error bars ( $k = 2$ ) with zero indicates no statistically significant change in  $x_{\text{NH}_3}$  with time.

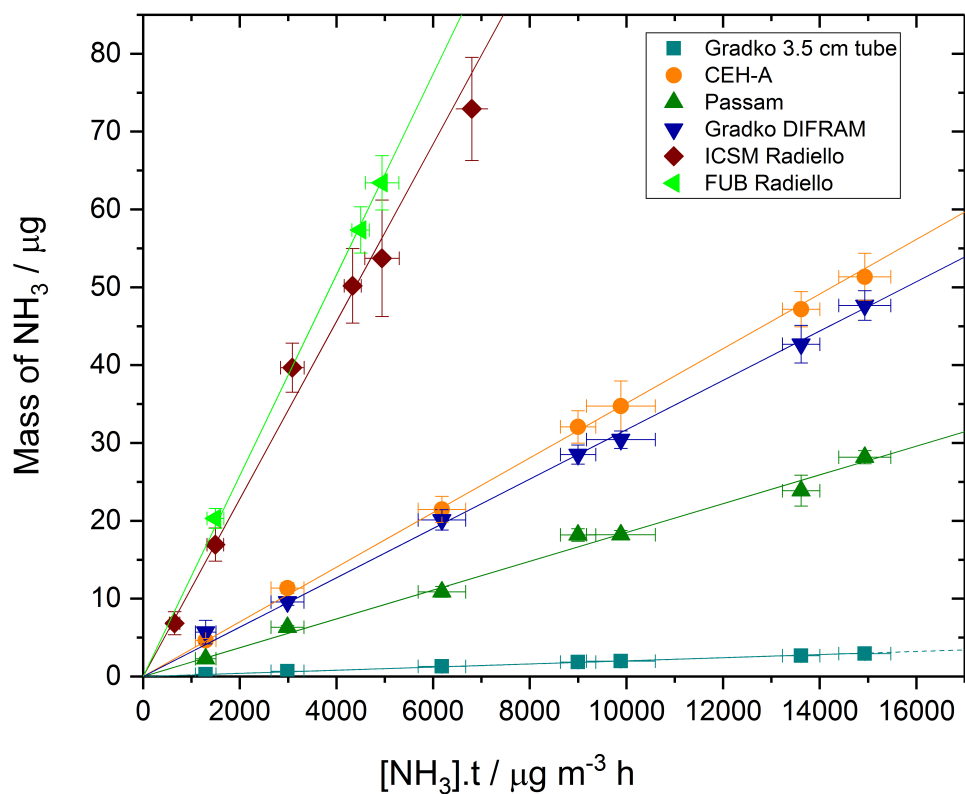
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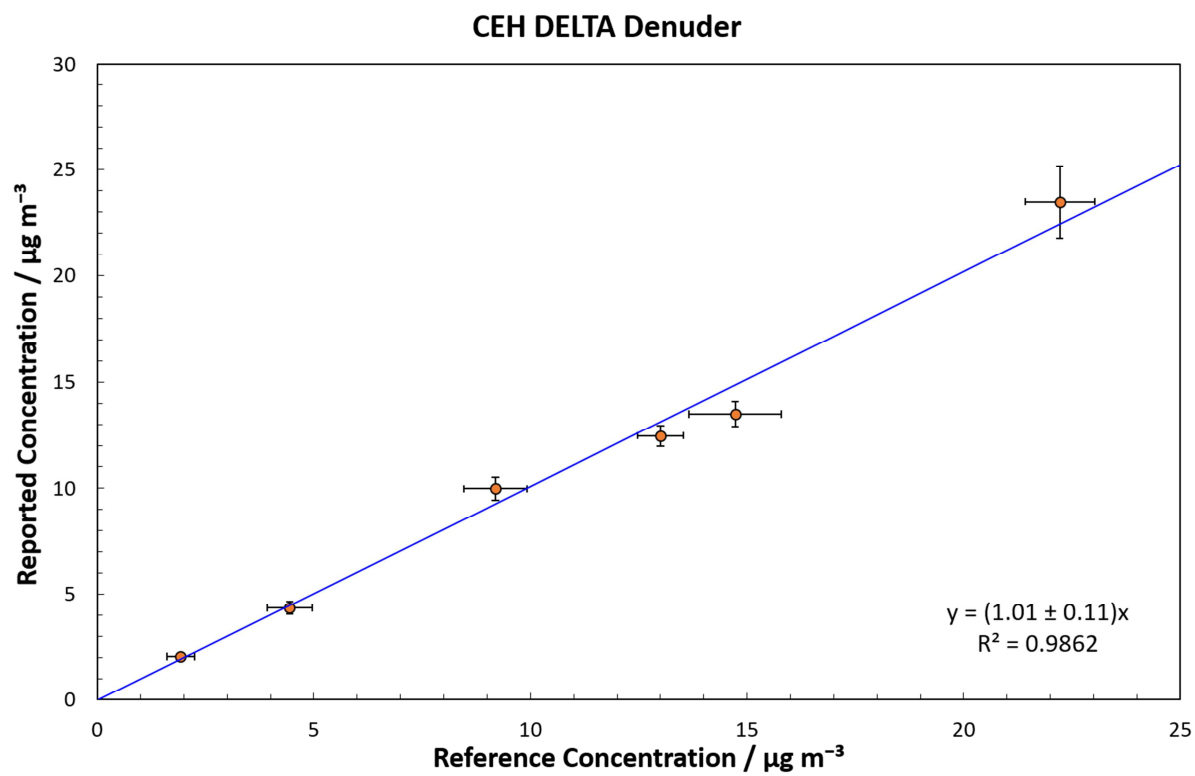
**Fig. 3.** Plots showing results of the long-term stability tests of four PSMs of  $10 \mu\text{mol mol}^{-1} \text{NH}_3$  in  $\text{N}_2$ . Panel a) shows the periodic measurements of the ammonia amount fraction,  $x_{\text{NH}_3}$ , of the PSMs: two prepared in Spectra-Seal™ (BOC plc) cylinders (NPL1842 and NPL1648R) and two in SilcoNert™2000-treated (SilcoTek Inc) stainless steel cylinders (RA5039 and SG8050). Panel b) illustrates the significance analysis (see text for details) of the gradients of the stability plots. An overlap of the error bars ( $k = 2$ ) with zero indicates no statistically significant change in  $x_{\text{NH}_3}$  with time.

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749750 **Fig. 4.** Summary of the mean of the reported  $\text{NH}_3$  concentrations for diffusive and pumped samplers  
751 tested in the CATFAC, expressed as a percentage deviation from the reference values.752  
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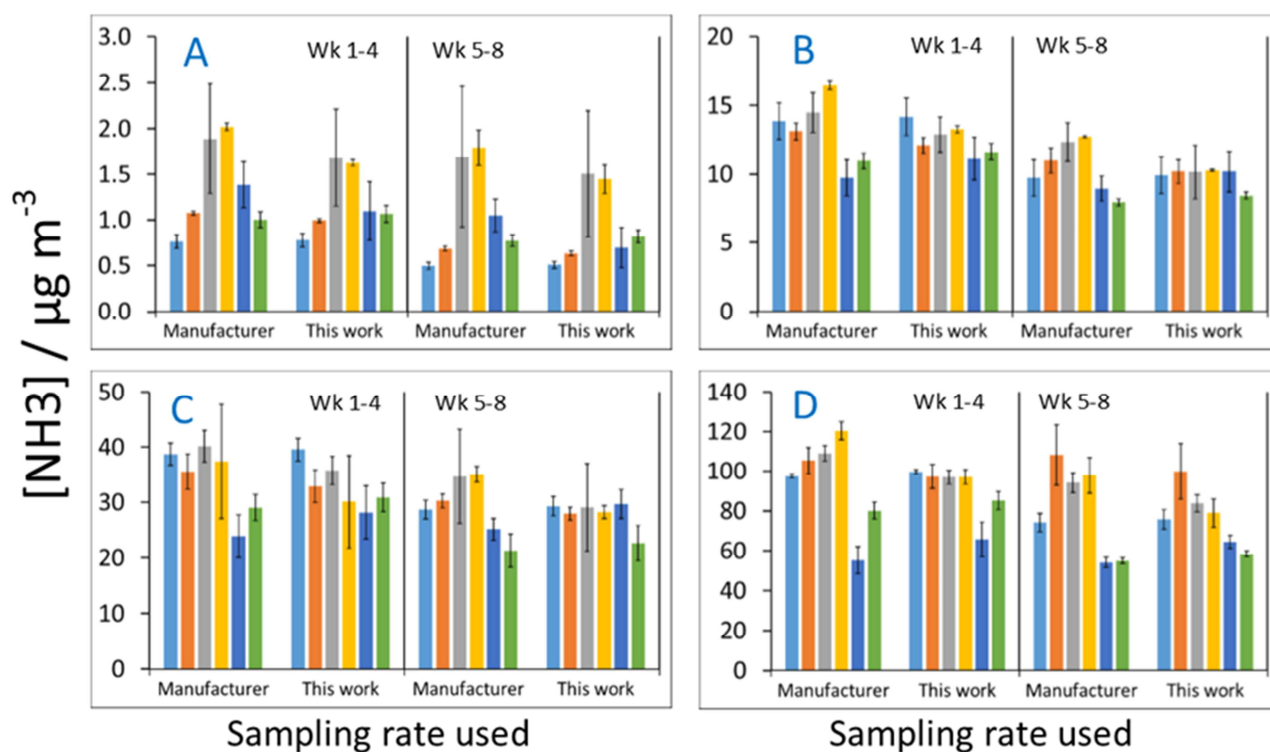
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Fig. 5. Lack of fit plots for the diffusive samplers tested in the CATFAC laboratory study.



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Fig 6. Lack of fit plot for CEH DELTA denuder.



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**Fig. 7.** Summary of  $\text{NH}_3$  concentrations measured by passive samplers in field comparison for two four-week periods, using both the manufacturer provided uptake rate and the uptake rate derived in this work (see Table 1 for details). 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

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**Table 1: Summary of diffusive sampling rate data determined at NPL.**

(T) tube-type sampler (with membrane), (B) badge-type sampler, (R) radial-type sampler

Manufacturer	Diffusive sampler	Sampling Rate (this work), $\vartheta / \text{m}^3 \text{h}^{-1}$	R <sup>2</sup> Value	Reference temp. (this work), /°C	Sampling rate (manufacturer data), $\vartheta / \text{m}^3 \text{h}^{-1}$	Reference temp. (manufacturer data)/ °C
CEH	ALPHA Sampler (B)	$(3.51 \pm 0.23) \times 10^{-3}$	0.999	20 ± 1	$3.45 \times 10^{-3}$ $3.24 \times 10^{-3}$	20 10
Gradko	3.5 cm diffusion tube (T)	$(2.01 \pm 0.11) \times 10^{-4}$	0.997	20 ± 1	$1.62 \times 10^{-4}$	20
Gradko	DIFRAM-400 (B)	$(3.17 \pm 0.18) \times 10^{-3}$	0.997	20 ± 1	$2.82 \times 10^{-3}$	20
PASSAM	Passam ammonia sampler (B)	$(1.85 \pm 0.16) \times 10^{-3}$	0.990	20 ± 1	$1.89 \times 10^{-3}$	20
Istituti Clinici Scientifici Maugeri (ICS Maugeri)	Radiello sampler (standard blue body) (R)	$(1.14 \pm 0.12) \times 10^{-2}$	0.986	20 ± 1	$1.37 \times 10^{-2}$ $1.41 \times 10^{-2}$	20 25
FUB	Radiello sampler from ICS Maugeri (white body) (R)	$(1.29 \pm 0.13) \times 10^{-2}$	0.999	20 ± 1	$1.37 \times 10^{-2}$ $1.41 \times 10^{-2}$	20 25

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835**Table 2: Uncertainty budget of ALPHA diffusive sampler for measurements of ammonia at a critical level of  $1 \mu\text{g m}^{-3}$ .**

<b>Reference concentration</b>	1	$\mu\text{g m}^{-3}$				
Mole mass $\text{NH}_3$	17.03	$\text{g mol}^{-1}$				
Mole mass $\text{NH}_4^+$	18.03	$\text{g mol}^{-1}$				
<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	$\vartheta$	$3.51 \times 10^{-3}$	$\text{m}^3 \text{h}^{-1}$	1	$3.28 \times 10^{-2}$	$1.07 \times 10^{-3}$
- sampling time	t	672	h	1	$1.49 \times 10^{-3}$	$2.21 \times 10^{-6}$
- air pressure	P	101	kPa	1	$2.0 \times 10^{-2}$	$4.0 \times 10^{-4}$
- air temperature	T	293	K	1	$2.0 \times 10^{-2}$	$4.0 \times 10^{-4}$
Sampled volume at STP	$V_{\text{stp}}$	2.37	$\text{m}^3$		$4.3 \times 10^{-2}$	$1.9 \times 10^{-3}$
<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	$m_{\text{cs}}$	2	%	1		$4.0 \times 10^{-3}$
- lack-of-fit of calibration function	l	0.2	% max	3		$1.33 \times 10^{-6}$
- response drift between calibrations	D	0.9	% max	3		$2.7 \times 10^{-5}$
- analytical precision	R	3	%	1		$9.0 \times 10^{-4}$
Mass of ammonium in sample	$m_s$	2.61	$\mu\text{g}$			$1.3 \times 10^{-3}$
Uncertainty	$u(m_s)$	0.095	$\mu\text{g}$			$3.6 \times 10^{-2}$
<b>Mass of ammonium determined</b>	<b>Blank</b>					
Mass of ammonium in blank	$m_b$	0.10	$\mu\text{g}$			
Uncertainty	$u(m_b)$	0.003	$\mu\text{g}$			
<b>Net mass of ammonium</b>		2.51	$\mu\text{g}$			
<b>Uncertainty</b>		0.095	$\mu\text{g}$			
<b>Relative uncertainty</b>		0.038				
<b>Mass of ammonia</b>		2.37	$\mu\text{g}$			
<b>Concentration of ammonia</b>		<b>1.0</b>	$\mu\text{g m}^{-3}$			
<b>Relative uncertainty</b>		0.058				
<b>Expanded relative uncertainty</b>		<b>11.5</b>	%			

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839 **Table 3: Summary of expanded uncertainties of diffusive samplers.**  
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Sampler type	Reference concentration / $\mu\text{g m}^{-3}$	Expanded uncertainty /%
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

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869 **Table 4: Summary of the coefficient of variation (COV) of the mean measured ammonia**  
 870 **concentration of all diffusive samplers at each distance from source release.**

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Distance from source release	83 m		60 m		32 m		12 m	
Exposure period	Weeks 1-4	Weeks 5-8	Weeks 1-4	Weeks 5-8	Weeks 1-4	Weeks 5-8	Weeks 1-4	Weeks 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%

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**Highlights**

- Development of Primary Standard Gas Mixtures of ammonia prepared by gravimetry
- Exposure of pumped and diffusive samplers in a controlled atmosphere test facility
- New ammonia diffusive sampling rates for wide range of commercial samplers
- Improved traceability and accuracy of ambient measurements of ammonia in the field

## COMPETING INTERESTS STATEMENT

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and that there are no impediments to publication, including the timing of publication, with respect to intellectual property. In so doing we confirm that we have followed the regulations of our institutions concerning intellectual property.

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