



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



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ABSTRACT

We report the determination of ammonia (NH₃) diffusive sampling rates for six different designs of commercial diffusive samplers (CEH ALPHA sampler, Gradko diffusion tube, Gradko DIFRAM-400, Passam ammonia sampler, and ICS Maugeri Radiello radial sampler (blue and white turbulence barriers)), together with the validation test results for a pumped sampler (CEH DELTA denuder). The devices were all exposed in the UK's National Physical Laboratory's (NPL) controlled atmosphere test facility (CATFAC). For each of the seven diffusive sampler exposure tests there were traceable concentrations of ammonia (in the range 3–25 μg m⁻³) generated under well-defined conditions of temperature, relative humidity and wind speed, which are applicable to a variety of ambient monitoring environments. The sampler exposure time at each concentration was 28 days, except for the radial devices, which were exposed for 14 days. The work relied on the dilution of newly developed stable Primary Standard Gas Mixtures (PSMs) prepared by gravimetry in passivated gas cylinders as a method of improving the metrological traceability of ammonia measurements. The exposed diffusive samplers were sent blind to the participants for analysis and the reported NH₃ concentrations were then compared against the known reference concentration. From the results for each sampler type a diffusive sampling rate was calculated and compared against the rate used routinely by the participants. Some measurement results were in good agreement with the known traceable reference concentration (particularly for one diffusive sampler design (ALPHA)), while other devices exhibited over-reading and under-reading (each with a clear bias). The new diffusive sampling rates determined in the laboratory study were then applied to measurements in a field comparison campaign, and this was found to deliver an improvement in agreement between the different devices deployed.

1. Introduction

Intensive livestock farming (specifically from cattle, pig, and poultry) and arable farming with the increased use of synthetic and organic fertilisers are responsible for rises in the amount fraction of ammonia (NH₃) detected in ambient air in Europe and other areas during the 20th century. Ambient concentrations are predicted to

increase leading to undesirable environmental effects at the ground surface, with eutrophication and acidification of land and freshwater leading to a loss of biodiversity, and in the air, with the formation of secondary particulate matter (PM) (Hornung et al., 1995; Pitcairn et al., 1998; Erismann et al., 2008; Pinho et al., 2012).

The recognition of NH₃ as an important pollutant has led to its inclusion in international agreements to reduce air pollutant emissions,

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firstly under the 1999 United Nations Economic Commission for Europe (UNECE) Gothenburg Protocol and then in the National Emissions Ceilings Directive (NECD) of the European Union (EU) (Directive, 2001/81/EC). The target of both of these agreements is that NH_3 emissions should not exceed emission ceilings set for individual EU member states.

The revision of both the Gothenburg Protocol (in 2012) and the NEC Directive (Directive, 2016/2284/EU) included new, more stringent emission ceilings for 2020 that seek greater environmental protection and improvement in air quality, 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 NH_3 by 6% and particles by 22% between 2005 and 2020. A recent study (Bessagnet et al., 2014) employing three chemical transport models found that they underestimated the formation of ammonium particles and concluded that the role of NH_3 on PM formation is larger than originally thought. Other work (Vieno et al., 2016) suggested that the most effective measures to reduce the UK population exposure to $\text{PM}_{2.5}$ is to reduce ammonia emissions. According to the European Environment Agency (EEA) ammonia emissions increased in 2015 in several European Union member states, as well as the EU as a whole, and consequently exceeded their respective emission limits under the UN Convention (European Environment Agency, 2017).

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

In Germany, the Federal Immission Control Act (TA Luft, 2002a) provides guidance and technical instructions on air quality control and recommends that at any assessment point the concentration of ammonia should not exceed $10 \mu\text{g m}^{-3}$ (equivalent to an amount fraction of approximately 14 nmol mol^{-1} at ground level), thereby limiting damage to plants and ecosystems.

Annual mean Critical Levels (“CLs”) of ammonia have also been assessed (Cape et al., 2009) and adopted by the UNECE for protection of sensitive ecosystems; these concentrations are $1 \mu\text{g m}^{-3}$ for lichens and bryophytes and $3 \mu\text{g m}^{-3}$ for other types of vegetation. A monthly critical level of $23 \mu\text{g m}^{-3}$ was retained as a provisional value in order to deal with the possibility of high peak emissions during periods of manure application. There is a German limit of 30 mg m^{-3} that should not be exceeded in the exhaust gas of industrial plants (TA Luft, 2002b). Currently there is no established human exposure level for ambient air, but the US Environmental Protection Agency (EPA) has set a chronic lifetime exposure value equivalent to $100 \mu\text{g m}^{-3}$ (US EPA, 2001).

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

Monitoring ammonia poses a number of challenges: there is a lack of regulation regarding which analytical techniques to employ, no agreement on the required uncertainty of measurements, no standardised quality control/quality assurance (QA/QC) procedures in place, and there is no established traceability infrastructure to underpin the measurements. Traceability is a property of the measurement results (in

this case the ammonia amount fraction) that can be related to primary metrological standards through an unbroken chain of calibrations. Within this chain, the measurement uncertainty is determined at each step and then combined, in accordance with international guidelines (ISO-Guide 98-3), thereby ensuring that there can be comparability of measurements originating from different studies.

Passive samplers rely on the diffusion of the target gas (NH_3) onto a surface on which the gas is chemically captured by a sorbent. Uncertainties in the measurement come from both the sampler preparation, laboratory analysis and environmental exposure factors (Tang et al., 2001). In larger networks passive samplers are co-located with active “reference methods” in order to calibrate the diffusive sampling rate (which may be dependent on many parameters including temperature and local meteorology for the region where the measurements are being made). In other cases a theoretical sampling rate is applied based on the relevant sampler’s dimensions. A recent German guideline has been developed to cover measurements of ammonia in ambient air with diffusive samplers (VDI 3869, 2012), but is limited in scope and has not been widely adopted in other countries. The European Standardization Body, CEN, has recently been charged with developing a wider measurement protocol through CEN Technical Committee 264 Working Group (WG) 11.

The aim of this work was to determine the diffusive sampling rates of a wide range of commonly employed commercial low-cost diffusive samplers and to validate the performance of one type of denuder sampler design with a view to improving the reliability and accuracy of ambient ammonia measurements. The study involved carrying out traceable sampler exposure tests in a controlled atmosphere test facility (CATFAC) developed at the UK’s National Physical Laboratory (NPL). It also required the development of stable traceable Primary Standard Gas Mixtures (PSMs) of NH_3 prepared by gravimetry to create well characterised atmospheres of this species, together with the further development of a cavity ring-down spectrometer (CRDS) for on-line continuous monitoring of ammonia. The new determinations of the diffusive sampling rates were then applied to measurements carried out in the field with the goal of improving the comparability of data obtained from the different samplers.

2. Experimental method

2.1. Laboratory test procedures

A modified controlled atmosphere test facility (CATFAC), consisting of a wind tunnel with an internal volume of approximately 1000 L (Martin et al., 2003; Martin et al., 2014) was employed to carry out validation tests on simultaneously exposed ammonia diffusive and pumped samplers. Here a series of test atmospheres at relevant NH_3 ambient concentrations were generated at nominally: 3, 7, 10, 15, 17, 20 and $25 \mu\text{g m}^{-3}$, (where $1 \mu\text{g m}^{-3}$ NH_3 is equivalent to an amount fraction of $1.41 \text{ nmol mol}^{-1}$ at a reference temperature of 20°C , or 1.41 ppb (parts per billion)). Fig. 1 shows a photograph of the CATFAC, which is predominantly made of glass with perfluoroalkoxy (PFA) tubing to minimise potential undesirable wall losses of NH_3 .

The required NH_3 concentrations were prepared by dynamically blending and diluting traceable NPL PSMs of this molecule with scrubbed air (Peak Scientific), using an array of calibrated mass flow controllers (Brooks). The test gas mixtures were continuously replenished, at a known measured rate of approximately 30 L min^{-1} , by a freshly generated mixture of the same concentration. This was carried out in a section of the CATFAC where the flow of gas is turbulent, so as to ensure good mixing. A stainless steel recirculating blower (Eurotherm Drives) was employed to drive the gas mixtures through a series of restricting grids designed to reduce the spatial and temporal fluctuations, and ensure a uniform airflow over the diffusive sampler deployment section of the facility. Together with continuous gas recirculation, this design delivered accurate and stable atmospheres at

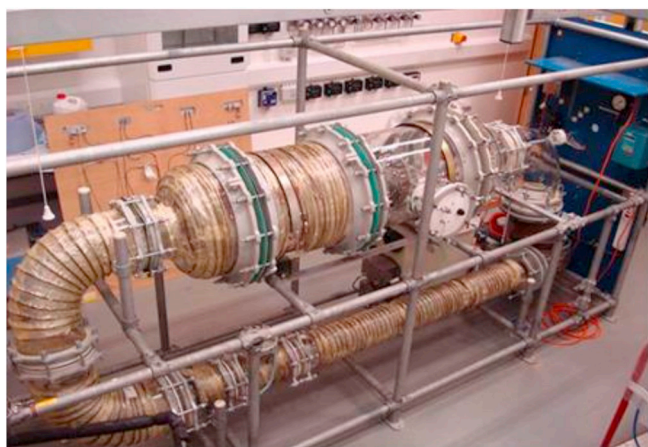


Fig. 1. Controlled Atmosphere Test Facility without insulation.

constant concentrations in the test chamber before being exhausted safely to atmosphere, thus minimising total gas consumption and the cost of its operation.

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

Continuous on-line monitoring of the test atmosphere concentration was achieved by extractive sampling through PFA pipework into a modified cavity ring-down spectrometer (CRDS) (Model G2103, Picarro Inc), which could detect both ammonia and water vapour. Initially, the spectrometer was found to be affected by direct and indirect cross-interference from H_2O . The spectrometer reported concentration based on peak absorption, which was correct for dry NH_3 atmospheres, but for humidified atmospheres of this molecule there was an under reporting due to the broadening of the NH_3 spectral feature, resulting in a reduction in peak height. In collaboration with the manufacturer a correction mechanism (Martin et al., 2016) was developed for the CRDS, which required new measurements of the collisional broadening due to water vapour of two NH_3 spectral lines in the near infrared (6548.6 and 6548.8 cm^{-1}). Traceability of the NH_3 spectrometer measurements was achieved through the use of NPL's stable PSMs of NH_3 to generate dry and humidified atmospheres at low concentrations. The correction has been incorporated by the manufacturer in all new CRDS ammonia sensors.

2.2. Primary standard gas mixtures: preparation, validation and statistical analysis of stability measurements

Stable PSMs were specifically developed for the exposure tests in the CATFAC in order to improve the current state-of-the-art metrological traceability and validation of ambient ammonia measurements by providing new diffusive sampling rate measurements for some of the devices tested. The PSMs used in this work were prepared gravimetrically using the method outlined in guide ISO 6142 (2001) from pure ammonia (Air Products, VLSI, 99.9999% purity) and nitrogen (Air Products, BIP+, 99.99995% purity). A more detailed account on the

development of the PSMs has been given previously (Martin et al., 2016; Pogány et al., 2015; Pogány et al., 2016). Mixtures of $100\text{ }\mu\text{mol mol}^{-1}$ NH_3 in nitrogen were prepared in Spectra-Seal™ (BOC plc) and Aculife IV™ (Air Liquide/Scott)-treated 10 L cylinders, whilst mixtures at $10\text{ }\mu\text{mol mol}^{-1}$ were prepared in 10 L Spectra-Seal™ cylinders and in 3.785 L stainless-steel cylinders (Swagelok) coated with the SilcoNert™2000 treatment (SilcoTek, Inc).

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

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

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

2.3. Samplers tested

There are numerous passive samplers on the market including tube-, badge- and radial-types, with designs having advantages and disadvantages depending on the ammonia concentration range being measured and deployment exposure time (Tang et al., 2001). A recent review was available to assist in the selection of devices to test in this study where the prior knowledge was without commercial restrictions and for which well-defined performance characteristics were published and publically accessible (Braban et al., 2018). 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 (#RAD1201)), Passam AG (Passam ammonia sampler), and FUB AG (Radiello radial sampler from the ICS Maugeri, but with white outer cylinder turbulence barrier (#RAD120)). There is no difference in porosity between the white (#RAD120) and blue diffusive bodies (#RAD1201). The blue type was developed by ICS Maugeri with the aim of protecting photosensitive reagents and/or products from sunlight before, during and/or after sampling (ICS Maugeri, 2018). The devices were randomly distributed inside the section of the exposure chamber perpendicular to the direction of gas flow. The diffusive samplers were exposed to each relevant atmosphere for 28 days, with the exception of Radiello samplers: these were dosed for periods of 14 days as recommended by the manufacturer. The denuders actively sampled through separate

perfluoroalkoxy (PFA) ports in the CATFAC for either 14 or 28 days. The DELTA denuder is less prone to cross-interference by particulate capture due to the laminar air flow conditions (Sutton et al., 2001).

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

Using their own in-house validated/accredited procedures, the participants employed de-ionised water to extract the ammonia chemically captured by their samplers which, in the aqueous phase, is in the form of ammonium (NH_4^+). As an example of the procedure, the NH_3 captured on the acidified filter paper of the ALPHA diffusive sampler and on the acid coated DELTA denuders (20 cm long borosilicate glass tubes) was extracted into 3 mL and 5 mL deionised water, respectively. The extracts were analysed for ammonium using an AMFIA (ammonia flow injection) system, which is based on the selective dialysis of ammonium across a membrane, at high pH, with subsequent analysis by conductivity (Wyers et al., 1993). The results from all participants were reported to NPL as a concentration in the conventional units of $\mu\text{g m}^{-3}$.

For the redetermination of the diffusive sampling rates, ϑ , 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, as described in Section 2.4. Lack of fit plots were generated using XLGENLINE, which is a generalised least-squares (GLS) Microsoft Excel-based software package for low-degree polynomial fitting developed at NPL (Smith, 2010).

XLGENLINE employed a user-defined input file: this required values of x and $u(x)$ (respectively the known NH_3 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.

2.4. Diffusive sampling rate and pumped denuder sampler calculations

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

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

where m is the measured mass of NH_3 (after correction for the laboratory blank value), ϑ is the diffusive sampling rate and t is the exposure time.

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

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

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

The value of the diffusion constant of NH_3 in air is stated as $0.1978 \text{ cm}^2 \text{s}^{-1}$ at 273 K, 101.3 kPa (Massman, 1998), obtained from an earlier study (Wintergerst, 1930), while its temperature dependence is given by (ISO: 16339:2013):

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

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

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

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

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

where V is the calibrated volume of air sampled.

2.5. Treatment of uncertainties

The combined standard uncertainty, u_ϑ , for each determination of the diffusive sampling rate is given by Equation (6):

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

where u_{Cfinal} 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, and u_t is the standard uncertainty for the relevant sampler exposure time.

For the orthogonal regression analysis described in Section 3.2 the combined uncertainties for the first two components in Equation (6) 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_{Cfinal} , for each exposure has been described previously (Martin et al., 2016), and follows a standard international method (ISO 6145-7:2010). 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. 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 NO_2 diffusive samplers in EN 16339:2013-11. It is noted that systematic method or extraction errors by a laboratory would not be captured in this study as there was no agreed central analytical laboratory. All laboratories participating are either accredited or participate in analytical comparisons.

2.6. Field procedures

A field study was carried out in Scotland (Stephens et al., 2017) where there is a facility in place for controlled releases of NH_3 on a

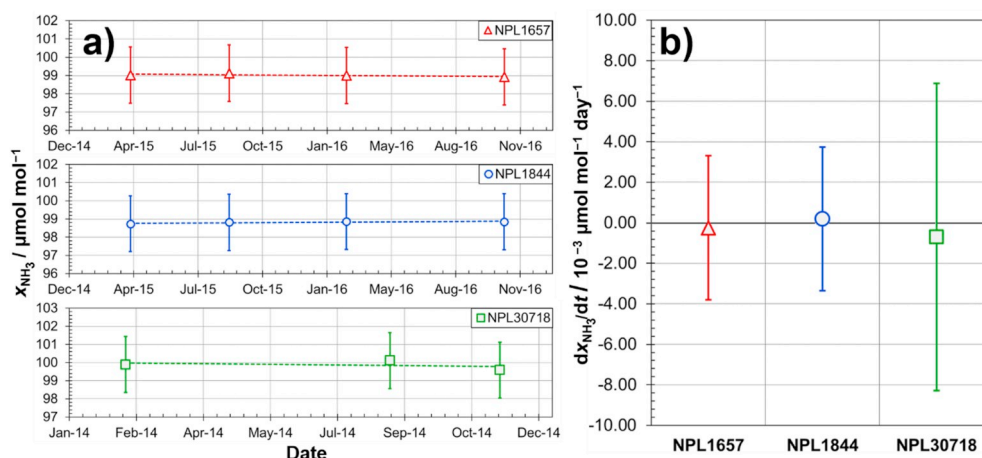


Fig. 2. Plots showing results of the long-term stability tests of three PSMs of $100 \mu\text{mol mol}^{-1}$ NH_3 in N_2 . Panel a) shows the periodic measurements of the ammonia amount fraction, x_{NH_3} , of the PSMs: two prepared in Spectra-Seal™ (BOC plc) cylinders (NPL1657 and NPL1844) and one in 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_{NH_3} with time.

peatland site (Leith et al., 2004; Whim Bog, 2016). Ammonia was released at a known rate of 0.2 kg h^{-1} , when the wind in the preceding minute was in a particular 30° wind sector. Over two consecutive 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.

3. Results and discussion

3.1. Stability of NH_3 primary standard gas mixtures

The stability of the PSMs was monitored over a period ranging from approximately 10 months (Aculife IV™) to 19 months (Spectra-Seal™ and SilcoNert™2000); the certified ammonia content of each mixture as a function of time is shown in Fig. 2a for the $100 \mu\text{mol mol}^{-1}$ mixtures and Fig. 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 instability within the given analytical uncertainty ($< 2\%$) for any of the mixtures under test. This was also the case for the $10 \mu\text{mol mol}^{-1}$ mixtures in SilcoNert™2000-treated cylinders, whereas the $10 \mu\text{mol mol}^{-1}$ mixtures in Spectra-Seal™ cylinders exhibited a decrease in ammonia content.

The outcome of the significance analysis is shown in Figs. 2b and 3b for the 100 and $10 \mu\text{mol mol}^{-1}$ mixtures respectively. In both diagrams all the gradients of the stability plots overlap with zero within the given uncertainty at the $k = 2$ level (corresponding to a 95% confidence level), indicating no statistically significant sign of instability within the ammonia PSMs. However the downward trend in ammonia amount fraction observed in the $10 \mu\text{mol mol}^{-1}$ mixtures in Spectra-Seal™ is statistically significant at the $k = 1$ level. This, along with the elevated gas consumption rate associated with using PSMs at low amount fractions, led to the use of the $100 \mu\text{mol mol}^{-1}$ mixtures for the exposure tests described here.

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

The results of the stability measurements provided confidence to the use of the $100 \mu\text{mol mol}^{-1}$ PSMs in the exposure tests as they demonstrated that the samplers were exposed to ammonia atmospheres that

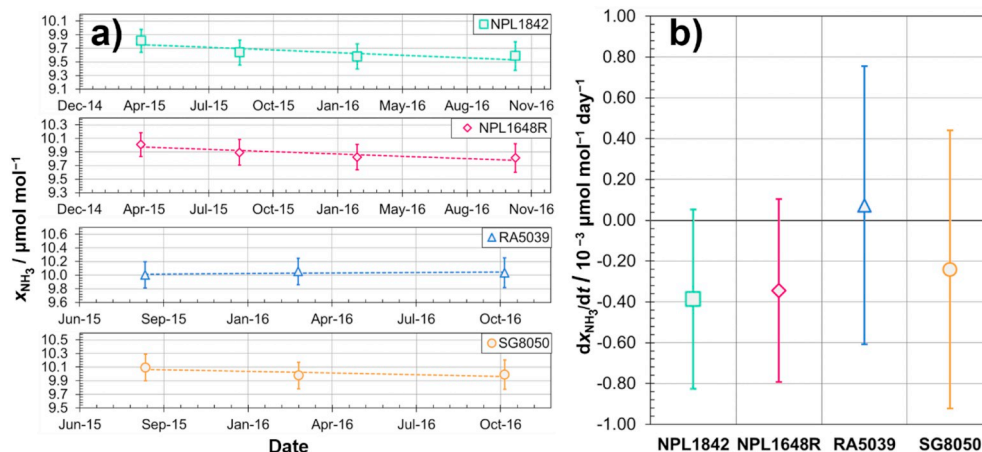


Fig. 3. Plots showing results of the long-term stability tests of four PSMs of $10 \mu\text{mol mol}^{-1}$ NH_3 in N_2 . Panel a) shows the periodic measurements of the ammonia amount fraction, x_{NH_3} , of the PSMs: two prepared in Spectra-Seal™ (BOC plc) cylinders (NPL1842 and NPL1648R) and two in 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_{NH_3} with time.

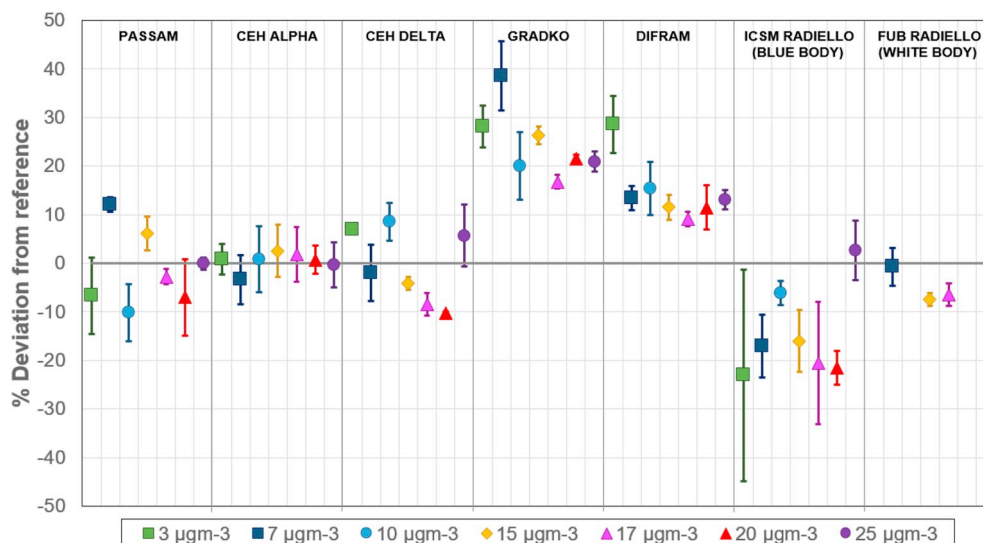


Fig. 4. Summary of the mean of the reported NH_3 concentrations for diffusive and pumped samplers tested in the CATFAC, expressed as a percentage deviation from the reference values.

were stable throughout the duration of the entire test programme. The development of new PSMs of ammonia will be further exploited in a forthcoming international key comparison for ammonia (CCQM-K117), scheduled to be carried out 2018, to establish whether progress by all NMIs has been achieved since CCQM-K46.

3.2. Experimental determination of the NH_3 diffusive sampling rates

Fig. 4 shows the initial assessment of the CATFAC exposure study data for both diffusive and pumped samplers. The results are based on the application of the relevant manufacturers' historical diffusive sampling rates, analysis procedure, and calibrations, which in many cases may not have been extensively validated prior to this study. The ordinate axis shows the results reported by each participant, expressed as the mean percentage deviation from the known ammonia reference concentrations introduced into the CATFAC. The nominal values of the seven traceable NH_3 reference concentrations are detailed in the legend.

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

Fig. 5 shows the lack of fit plots for each sampler type tested while Table 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 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 are included, together with the reference temperature (in $^{\circ}\text{C}$). In the cases where the sampling rates were originally reported at either 25°C or 10°C then Equation (4) was employed to adjust the manufacturers' values to a reference temperature of 20°C . We kept the results from ICS

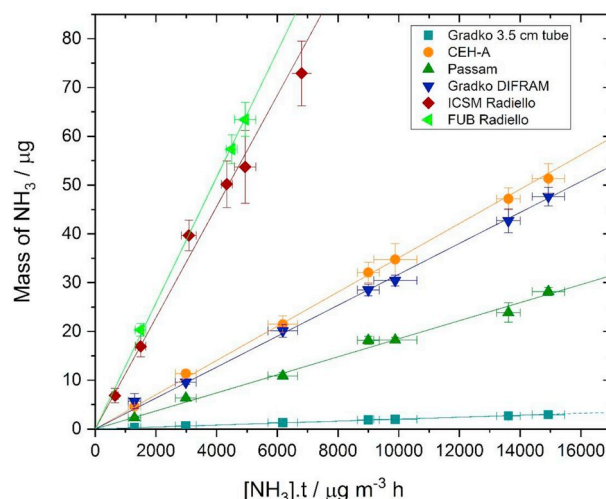


Fig. 5. Lack of fit plots for the diffusive samplers tested in the CATFAC laboratory study.

Maugeri separate from FUB since the two diffusive sampling rates did not overlap within their measurement uncertainties. We cannot decouple the effects of the body types and the potential analysis differences from the two different laboratories. The strong linear behaviour over the concentration range tested shown in Fig. 5 indicates that all the samplers design work well and that biases (where found in the original diffusive sampling rates) can be corrected.

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). These data are shown in Fig. 6 (with one outlier removed), together with the linear equation and the value of R^2 , which is effectively equal to 0.99. 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 comparison 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 $\pm 11\%$.

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

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

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

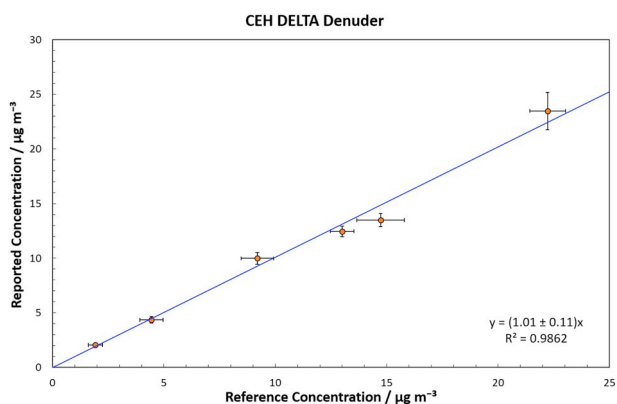


Fig. 6. Lack of fit plot for CEH DELTA denuder.

A worked example calculation of the relative expanded uncertainty estimation for ammonia measurements ($k = 2$) is provided in Table 2 for an annual critical level of $1 \mu\text{g m}^{-3}$. The results shown are for the

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

Reference concentration	1	$\mu\text{g m}^{-3}$				
Mole mass NH_3	17.03	g mol^{-1}				
Mole mass NH_4^+	18.03	g mol^{-1}				
Volume of air sampled						
<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	3.51×10^{-3}	$\text{m}^3 \text{h}^{-1}$	1	3.28×10^{-2}	1.07×10^{-3}
sampling time	t	672	h	1	1.49×10^{-3}	2.21×10^{-6}
air pressure	P	101	kPa	1	2.0×10^{-2}	4.0×10^{-4}
air temperature	T	293	K	1	2.0×10^{-2}	4.0×10^{-4}
Sampled volume at STP	V_{stp}	2.37	m^3		4.3×10^{-2}	1.9×10^{-3}
Mass of ammonium determined			Sample			
<i>Uncertainty component</i>	<i>Symbol</i>	<i>Value</i>	<i>Unit</i>			
concentration in calibration standards	m_{cs}	2	%	1		4.0×10^{-3}
lack-of-fit of calibration function	l	0.2	% max	3		1.33×10^{-6}
response drift between calibrations	D	0.9	% max	3		2.7×10^{-5}
analytical precision	R	3	%	1		9.0×10^{-4}
Mass of ammonium in sample	m_s	2.61	μg			1.3×10^{-3}
Uncertainty	$u(m_s)$	0.095	μg			3.6×10^{-2}
Mass of ammonium determined			Blank			
Mass of ammonium in blank	m_b	0.10	μg			
Uncertainty	$u(m_b)$	0.003	μg			
Net mass of ammonium		2.51	μg			
Uncertainty		0.095	μg			
Relative uncertainty		0.038				
Mass of ammonia		2.37	μg			
Concentration of ammonia		1.0	$\mu\text{g m}^{-3}$			
Relative uncertainty		0.058				
Expanded relative uncertainty		11.5	%			

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 3 contains a summary of the data for all the diffusive sampler designs 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 measurement uncertainties are different for the various sampler designs tested with the radial type being the poorest. Nevertheless, the expanded relative uncertainty values for the 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 (Directive, 2008/50/EC).

3.3. Field tests

The CATFAC study delivered new values of the diffusive sampling rates; these were applied to the field comparison results to determine whether there was improved agreement between the different types of

Table 3
Summary of expanded uncertainties of diffusive samplers.

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

samplers. Fig. 7 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 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. Three diffusive samplers of each type were deployed at each of the four locations from the release point.

The coefficients of variation (COVs) (i.e., ratio of one sigma standard deviation and the mean NH_3 concentration of samplers multiplied by 100%) have also been calculated for all results of all samplers using diffusive sampling rates provided by the manufacturers and those from the laboratory tests described; the COVs provide evidence (Table 4) that the agreement between the results improves when diffusive sampling rates from this study are used. This is particularly evident for the higher concentration locations, but less so at background levels.

Sampler types should be suitably matched to the measurement requirements. The low diffusive sampling rates of some tube-type samplers make them too uncertain to use at background concentrations $< 1 \mu\text{g m}^{-3}$ where it seems they can significantly overestimate

concentrations (Tang et al., 2001). Instead, badge- or radial-type samplers can be used to monitor low concentrations of NH_3 in background areas, but then they may be less suitable for monitoring in source regions for longer-term exposures due to potential saturation problems. Clearly there are also other factors which can affect the variability of the measurements including wind speed, temperature range, dust deposition on turbulence barrier, location in the plume of gas and the laboratory analysis.

4. Conclusions

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

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

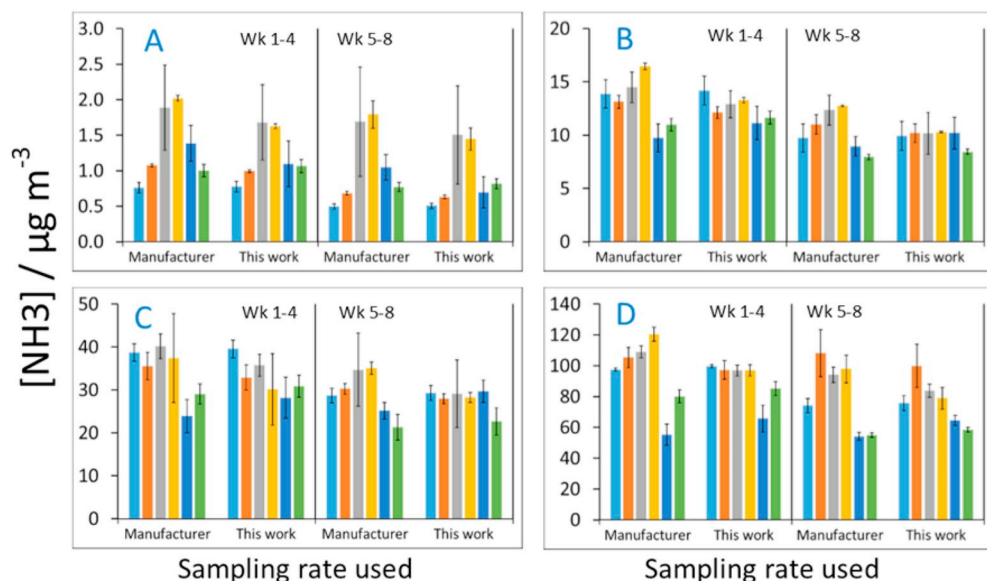


Fig. 7. Summary of NH_3 concentrations measured by passive samplers in field comparison for two four-week periods, using both the manufacturer provided uptake rate and the uptake rate derived in this work (see Table 1 for details). Ammonia concentrations measured away from line source at distances of A: 83 m (background); B: 60 m; C: 32 m; D: 12 m; Bars: Light Blue: Passam; Orange: ALPHA Samplers; Grey: Gradko DIFRAM; Yellow: Gradko diffusion tube; Dark Blue: ICSM Radiello; Green: FUB Radiello. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4

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	83 m		60 m		32 m		12 m	
	Weeks 1–4	Weeks 5–8	Weeks 1–4	Weeks 5–8	Weeks 1–4	Weeks 5–8	Weeks 1–4	Weeks 5–8
Exposure period								
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%

property.

We understand that Nicholas A. Martin is the sole contact for the Editorial process (including Editorial Manager and direct communications with the office). He is responsible for communicating with the other authors about progress, submissions of revisions and final approval of proofs. We confirm that we have provided a current, correct email address which is accessible by Nicholas A. Martin and which has been configured to accept email from Nick.Martin@npl.co.uk.

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