Dear MetNH3 stakeholder,

EMRP JRP MetNH3 "Metrology for Ammonia in Ambient Air" officially ended on May 31st 2017. The project partners would like to thank you very much for your interest and your collaboration over the past 3 years.

More information on MetNH3 can be found, also in the future, on the project webpage http://www.metnh3.eu.

Over the course of summer 2017 three "Good Practice Guides" on the following subjects will be made available:

- **Good Practice Guide for accurate sampling and preparation of dynamic ammonia gas mixtures**
- **Good Practice Guide on the measurement system applicable as optical transfer standard for ammonia in ambient air**
- **Good Practice Guide for measurement of ambient ammonia concentrations in the field and application to policy evidence**

The final highlight of the project has been the 2nd MetNH3 workshop on ammonia measurement methodology taking place on May 09-10th at METAS in Switzerland which was attended by 40 stakeholders. The book of abstracts is available on the project website.

As one of the main objectives for the participating partners is to develop new capabilities and improved procedures the final newsletter aims at introducing their individual possibilities, particularly those transferable to stakeholders and end–users.

Improved gas mixture standards

The main objective of **WP1** was the **development of improved gas mixture standards for ammonia (NH_3) by static gravimetric and dynamic methods**. The highly adsorbing/desorbing behaviour of ammonia molecules and the purity of the balance gas challenge the **preparation of ammonia primary reference standards**. The findings of partners NPL, VSL, METAS and BAM will be transferred in the **Good Practice Guide for accurate sampling and preparation of dynamic NH_3 gas mixtures.**

NPL and VSL have tested **different cylinder types** by performing a series of **decant tests at the 100 and 10 µmol mol^{-1} levels and performed stability tests on those mixtures over a period of up to 24 months.**

VSL performed decanting and stability tests on 3 commercial types of gas cylinders: **Spectra Seal (BOC), Aculife 4 (Air Liquide)** and cylinders provided by **Takachiho. All cylinders showed individual**

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behaviour in adsorption on the interior surfaces. However, for all tested types of cylinders the **stability over long term stability is good**. **The stability tests performed at VSL show that (Fig. 1):**

- The ammonia mixtures of **100 µmol mol^{-1}are stable for 24 months** in both Aculife 4 and Spectra Seal cylinders **within a 1 % relative uncertainty (k = 2)**
- The ammonia mixtures of **10 µmol mol^{-1} are stable for a period of 12 months within a 3 % uncertainty**; cylinders under test were **Aculife 4 (AC4), Spectra Seal (SS)** and cylinders provided by **Takachiho (T)**

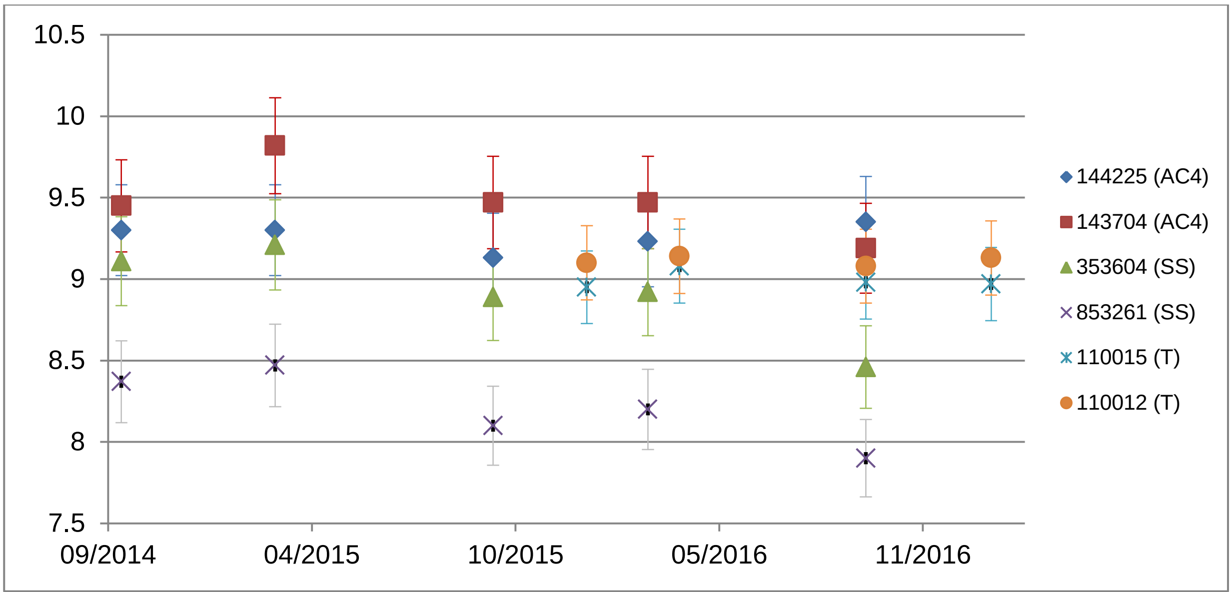

Figure 1: Results for the stability of 6 VSL mixtures at 10 µmol mol^{-1}of NH_3 in nitrogen. The uncertainty bars represent an expanded uncertainty (with *k* = 2 for a coverage probability of approximately 95 %).

The stability measurements carried out at NPL show that (Fig. 2):

- the **ammonia standard mixtures are completely stable in the BOC cylinders at 100 µmol mol^{-1} level** and, after an **initial small decay, are stable at 10 µmol mol^{-1}, over the time period studied**;
- **the SilcoNert2000® treatment applied to stainless steel cylinders is the most suitable for ammonia mixtures at the lowest level of the NH_3 amount fraction investigated i.e. 10 µmol mol^{-1}. No adsorption loss can be observed.**

NPL is experienced in both dynamic and gravimetric preparation of many reference gas mixtures relevant to the atmospheric measurement community. Among the several **Calibration and Measurement Capabilities (CMCs)** that NPL has, it is worth to mention the **CMC for NH_3 in nitrogen NPL Primary Reference Materials (NPL PRMs) and NPL Calibrated Gas Mixtures (NPL CGMs) in the 10 – 100 µmol mol^{-1} range, with an expanded uncertainty (k = 2) of 10 – 5 % respectively**. During

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the MetNH3 project, 8 NH_3/N_2 NPL PRMs, in the 10 - 2000 µmol mol^{-1} range, and one 140 µmol mol^{-1} NH_3/N_2 NPL CGM have been sold.

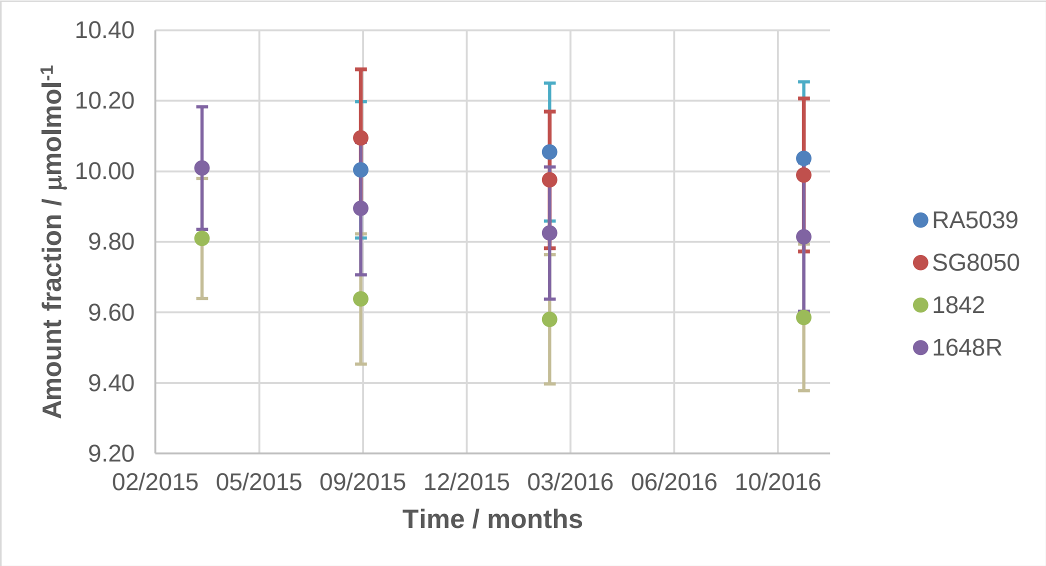

Figure 2: Results for the stability of 4 NPL mixtures at 10 µmol/mol of NH_3 in nitrogen of which RA5039 and SG8050 are SilcoNert2000 coated cylinders and 1842 and 1648R are BOC cylinders treated with Spectraseal. The uncertainty bars represent an expanded uncertainty (with k = 2 for a coverage probability of approximately 95%).

Over the course of MetNH3 **VSL adapted its preparation procedure** to reduce adsorption by minimising the surface exposed to NH_3 during decanting and by applying only coated materials. Moreover, the **analysis and verification procedure for NH_3 mixtures were optimised**, **thus reducing the analytical uncertainty from 3 % relative to 1 % relative on the 30 µmol mol^{-1} amount fraction**. Currently, VSL has CMCs for ammonia in the range from 30 - 300 **µmol mol^{-1}** with an expanded uncertainty of 3 – 2 % relative (k=2) and provides calibration services and reference materials world-wide.

VSL is responsible for **organising the next key comparison between national metrology institutes (CCQM-K117) for NH_3 in N_2 gas mixtures** in collaboration with NIST (USA). **The knowledge gained within MetNH3 should enable VSL and other participating institutes (e.g. NPL and METAS) to expand their NH_3 CMCs to a range of 10 – 300 µmol mol^{-1} with an expanded uncertainty of 3 – 1 % relative (k = 2).**

New dynamic calibration capabilities

METAS has considerable experience in the dynamic-gravimetric generation of reference gas mixtures combining the permeation method (ISO6145-10) with the dynamic dilution using thermal mass flow controllers (ISO6145-7). The level of uncertainty in the dynamic generation is unaffected

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by loss of NH_3 molecules through adsorption yet, adsorption increases stabilisation times. Thus, **tests of the effects of adsorption and desorption** were carried out on different surfaces of materials widely used for the preparation of reference gas mixtures (e.g. PFA, PTFE, stainless steel). In addition the **influence of humidity on the adsorption of NH_3** in the preparation of reference gas mixtures was assessed. It was concluded that adsorption on stainless steel surfaces in contact with NH_3 can be minimised by up to 90 % when a silica-based coating (SilcoNert2000®, SilcoTek Inc.) is applied on gas-wetted surfaces. Thus, for the **construction of a mobile reference gas generator (ReGaS1) combining permeation and dynamic dilution** SilcoNert2000® has been applied to all surfaces in contact with NH_3. **ReGaS1 is a development beyond the state of the art** as it allows for the on-site permeation and dynamic dilution over two dilution steps and thus for the **dynamic generation of NH_3 at ambient amount fractions (0.5 – 500 nmol mol^{-1}) with U_{NH3} ≤ 3 % (Fig. 3)**. **ReGaS1 is available for rent for applications in the field and in laboratories** (applied in the three MetNH3 intercomparisons). In addition, **METAS offers calibration services** for extractive optical NH_3 instrumentation as well as for gas mixtures in pressurised cylinders (< 300 µmol mol^{-1}), the latter at very low gas consumption from the cylinder to be tested. **The next NH_3 calibration campaign at METAS will be carried out in autumn 2017.**

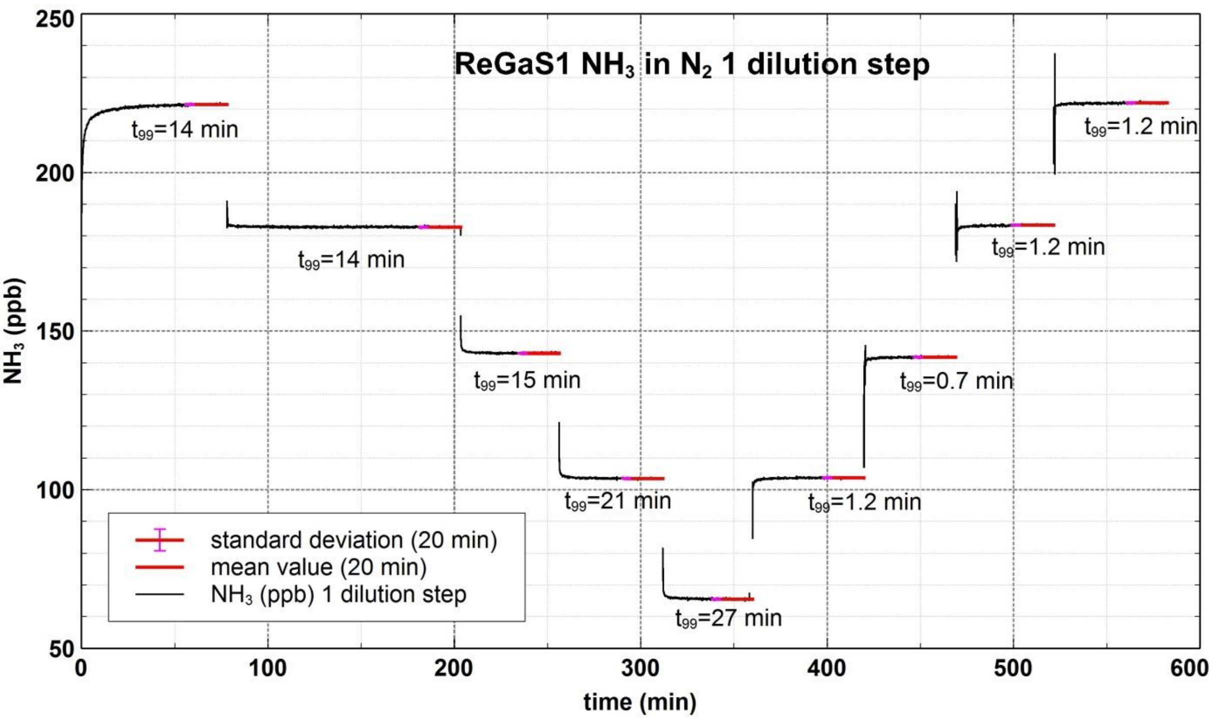

Figure 3: Different NH_3 in N_2 amount fractions generated with ReGaS1 using one dilution step, recorded with a CRDS. The response to a new concentration setting is imminent and the stabilisation time at a new concentration level very fast and with variability ≤ 0.5 %. The uncertainty in the generated NH_3 amount fractions is ≤ 1.5 % for NH_3 > 10 nmol mol-1 and ≤ 3.0 % for NH_3 > 10 nmol mol^{-1} (with k = 2 for a coverage probability of 95%).

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A similar **mobile gas standard generator (GASI2) has been developed at BAM** also combining the permeation method with dynamic dilution to the relevant amount fraction range (0.5 – 500 nmol mol^{-1}), yet with slightly higher uncertainty $U_{NH3} \leq 3.7$ %. It can be applied for the calibration of extractive optical methods and sensor measuring devices.

Improved optical transfer standards

The goal of WP2 was the realisation of optical transfer standards (OTS) for NH_3, i.e. IR spectrometric analysers performing absolute NH_3 amount fraction measurements. Such instrumental standards do not rely on a calibration with NH_3 gas standards but use stable molecular parameters (so-called spectral line parameters) to describe the light absorption properties of ammonia and to deduce the amount fraction in air samples. This **opens a complementary route to traceability and instrument calibration** and circumvents difficulties in the temporal stability of NH_3 reference gas standards normally used for instrument calibration.

An extractive, commercial cavity ring-down (CRDS) instrument by Picarro Inc. with a detection limit < 1 nmol mol^{-1} was used by PTB as a starting point to realise an OTS. **PTB developed an OTS in collaboration with DFM by accomplishing the following steps:**

1. **Writing a new validated spectral data evaluation routine** enabling absolute measurements including uncertainty contributions from all relevant parameters in compliance with the GUM
2. **Re-measuring and refining required infrared spectral parameters of ammonia** (line strengths) with unprecedented measurement uncertainty (see publication list)
3. **Metrological characterisation of the instrument**
4. **Performing validation measurements** of reference gas mixtures
5. **Implementing the approach** in a field comparison of NH_3 analysers

This approach will be described in more detail in the **Good Practice Guide on the measurement system applicable as optical transfer standard for ammonia in ambient air**. From the field trial, the expanded uncertainty was found to be approximately $U(x_{NH3}) \approx 2.4\ \%\ x_{NH3} + 0.8$ nmol mol^{-1} ($k = 2$). Under laboratory conditions with dry gas samples, the performance is better, approximately $U(x_{NH3}) \approx 2.0\ \%\ x_{NH3} + 0.2$ nmol mol^{-1}. The OTS developed in MetNH3 extends PTB's portfolio of absolute spectroscopic methods to trace ammonia in air.

State of the art test facility commissioned

As part of the **planned NH_3 sensor validation programme in WP3**, NPL's **Controlled Atmosphere Test Facility (CATFAC)** was commissioned in the early stages in $MetNH_3$ and employed for the first systematic exposure testing of ambient ammonia passive samplers. **Seven 28-day exposure tests at different concentrations with ALPHA, Gradko, PASSAM and Radiello diffusive samplers (14 days),**

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and DELTA denuders. The exposed samplers were returned to the different manufacturers for analysis. **Fig.4 shows the percentage deviation reported by each participant from the known traceable concentrations of NH_3.** Some measurements were in good agreement with the known traceable reference concentrations while other devices exhibited over-reading and under-reading thereby clearly demonstrating the need for this validation work to be carried out.

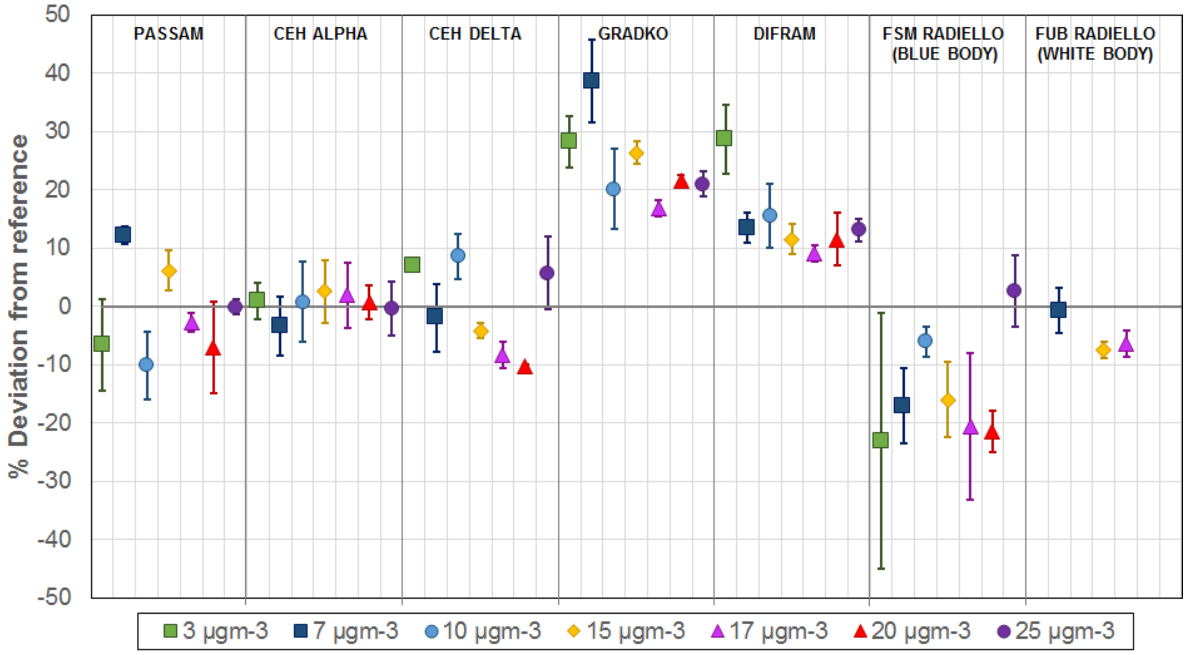

Figure 4: Summary of the mean of the reported NH_3 concentrations for diffusive and pumped samplers tested in the CATFAC, expressed as a percentage deviation from the reference values.

Manufacturer	Diffusive sampler	Sampling rate U/ m^3 h^{-1} (Measured, this work)	Reference T °C (Measured, this work)	Sampling rate U/ m^3 h^{-1} (Manufacturer provided)	Reference T (°C) (Manufacturer provided)
CEH	ALPHA sampler	3.49 x 10^{-3}	20 ± 1	3.45 x 10^{-3} 3.24 x 10^{-3}	20 10
Gradko	3.5 cm diffusion tube	2.00 x 10^{-4}	20 ± 1	1.62 x 10^{-4}	20
Gradko	DIFRAM-400	3.15 x 10^{-3}	20 ± 1	2.82 x 10^{-3}	20
PASSAM	Passam ammonia sampler	1.88 x 10^{-3}	20 ± 1	1.89 x 10^{-3}	20
Fondazione Salvatore Maugeri (FSM)	Radiello sampler (blue body)	1.14 x 10^{-2}	20 ± 1	1.37 x 10^{-2} 1.41 x 10^{-2}	20 25
FUB	Radiello sampler (white body)	1.28 x 10^{-2}	20 ± 1	Not Applicable	Not Applicable

Table 1: Summary of NPL CATFAC measured and manufacturer diffusive sampling rates of NH3 passive samplers.

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The results were employed to **determine new provisional values of the diffusive sampling rates for the devices tested**. Table 1 summarises the provisional data obtained. This work has provided the tools to improve the chain of traceability for low concentration ambient measurements of ammonia.

Two international field measurement intercomparisons hosted

CEH has more than 20 years' experience in the field application of NH_3 measurements and supported the application of new standards and processes by designing and hosting two intercomparison studies as part of the MetNH3 project: **one for intercomparing commercial passive samplers and the second for high resolution active ammonia measurement**. Both took place in the summer of 2016 and were open application events. The passive sampler intercomparison was linked to the CATFAC facility experiment (see above). All participants took part in both, with additional participants in the field experiment. The contacts for all the sampler providers including CEH are listed below.

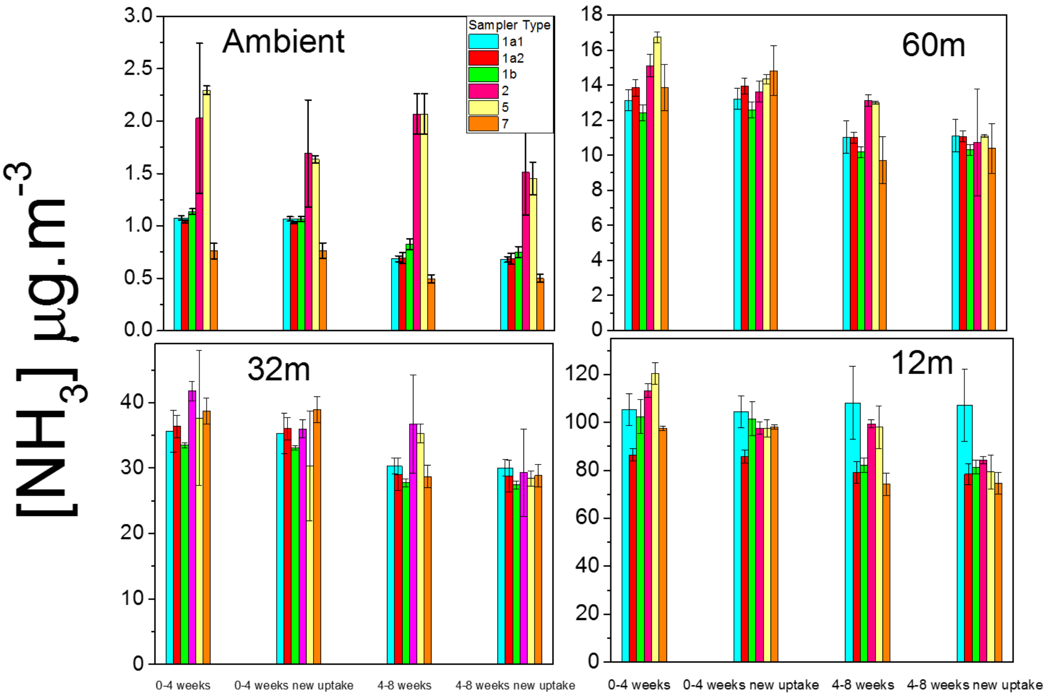

Figure 5 Diffusion samplers exposed over 4 week periods, with both the manufacturer uptake rate and the new uptake rate that was derived by the CATFAC study in WP3. 1a1 ALPHA CEH Edinburgh 1, 1a2 ALPHA CEH Edinburgh 2, 1 b ALPHA CEH Lancaster, 2 Gradko DIFRAM, 5 Gradko tubes, 7 Passam.

The **NH_3 passive sampler field application intercomparison study** as part of WP3, was undertaken at an **artificial NH_3 release on a peatland site that simulates NH_3 emissions from a medium range**

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poultry farm. Samplers were placed at 12m, 32m and 60m from the emission source, as well as at a background site (ambient concentrations). In total there were 8 participants in the intercomparison with 12 different sets of samplers being tested. **Samplers were exposed for a period of 2 or 4 weeks** dependent on the recommendations by the supplier, over the period from the 16th August 2016 to 11th October 2016. The results are summarised in Fig. 5. **All samplers and laboratories had good data capture and excellent quality assurance results**. Fig. 5 shows the reported concentrations for two periods for samplers/laboratories which had taken part in the CATFAC study and the impact of the new uptake rates had on the agreement between samplers. **Following this study a peer reviewed publication are currently being written and an annual quality assurance activity based on the intercomparison has been integrated into the UK's National Ammonia Monitoring Network in 2017 and 2018.**

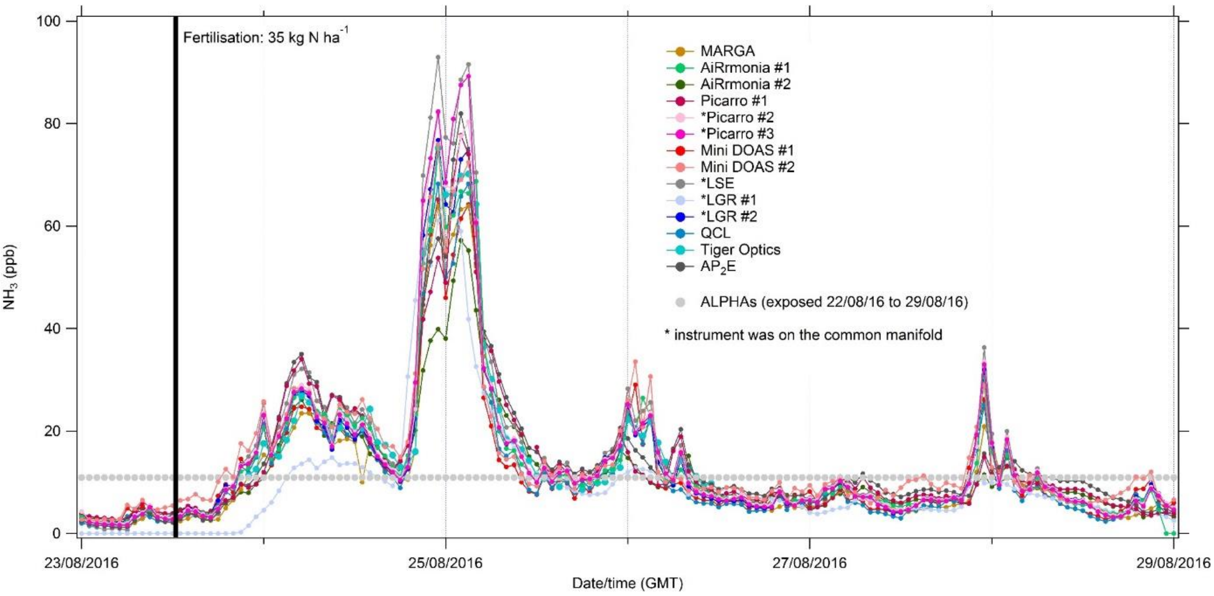

Figure 6: Provisional results of the NH3 intercomparison study held in South East Scotland.

The **NH_3 on-line ambient ammonia measurement field intercomparison study** was held at an intensively managed grassland in south east Scotland from the 21 August 2016 to the 1st September 2016. In total **15 participants, including SMEs, regional and national institutions and MetNH3 project partners took part in the intercomparison and 10 different measurement technologies were applied**. Several techniques were replicated but with different field set-ups, which has allowed an assessment of the effect of set-up on ammonia measurement to be undertaken. Fig. 6 is a provisional summary of the ammonia concentration measurement made over the full intercomparion period by all instruments. It is expected that a peer-review publication will be submitted and the observations from the exercise incorporated into the **Good Practice Guide for measurement of ambient ammonia concentrations in the field and application to policy evidence.**

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Ammonia passive sampler providers and institutes which participated in the field passive sampler intercomparison:

CEH Edinburgh (UK): ALPHA samplers Contact name/s: Amy Stephens and Sim Tang	**CEH Lancaster (UK): ALPHA samplers** Contact name/s: Jan Poskitt
IVL (Sweden): IVL samplers Contact name/s: Martin Ferm	**FUB (Switzerland): Radiello and IVL samplers** Contact name/s: Eva Seitler and fub@fub-ag.ch
Fondazione Salvatore Maugeri, FSM (Italy): Radiello Contact name/s: Paolo Sacco	**Gradko (UK): diffusion tubes and DIFRAM samplers** Contact name/s: Linda Gates
RIVM (NL): diffusion tubes Contact name/s: Ariën Stolk	**Passam (Switzerland): Passam samplers** Contact name/s: Jean-Marc Stoll

Peer-reviewed publications

The following **peer-reviewed publications** have to date been published in the framework of MetNH3:

- Andrea Pogány et al.: A metrological approach to improve accuracy and reliability of ammonia measurements in ambient air. Meas. Sci. Technol. (2016) **27** 115012
- Nicholas A. Martin et al.: The application of a cavity ring-down spectrometer to measurements of ambient ammonia using traceable primary standard gas mixtures. Appl. Phys. B (2016) 122: 219.
- A. Pogány et al.: High-Accuracy Ammonia Line Intensity Measurements at 1.5 µm. Imaging and Applied Optics 2016, paper JT3A.15.

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Contact and further information

You are very welcome to forward our **newsletter** to your contacts interested in metrology for ammonia in ambient air. **Contact any JRP partner for further information**.

METAS (Federal Institute of Metrology), Switzerland. Bernhard Niederhauser (Coordinator)

BAM (Federal Institute for Materials Research and Testing), Germany. Dr. Carlo Tiebe

DFM (National Metrology Institute), Denmark. Dr. David Balslev-Harder

MIKES Metrology (VTT Technical Research Centre), Finland. Dr. Timo Rajamäki

NPL (National Physical Laboratory), United Kingdom. Dr. Nicholas Martin

PTB (National Metrology Institute), Germany. Dr. Nils Lüttschwager

UBA (Federal Environment Agency), Germany. Dr. Klaus Wirtz

VSL (National Metrology Institute), The Netherlands. Janneke van Wijk

Researcher Excellence Grants

REG1: CEH Centre for Ecology and Hydrology, United Kingdom. Dr. Christine Braban

REG2: UH University of Helsinki, Finland. Dr. Olavi Vaittinen

The JRP partners have been regularly consulted by an external board of advisors

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