



**Centre for
Ecology & Hydrology**

NATURAL ENVIRONMENT RESEARCH COUNCIL

MetNH₃ Whim Bog Intercomparison

Off-line ammonia metrology

intercomparison

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MetNH3 Whim Bog Intercomparison Off-line ammonia metrology intercomparison

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1. Aim and overview

There is no regular quality assurance programme for ammonia passive samplers despite widespread use of these samplers across Europe and the rest of the world. In order to improve standards and begin to embed quality assurance in the measurement of ambient ammonia using passive samplers, within the EMRP MetNH₃ project a passive sampler intercomparison was planned to enable side-by-side exposure of the samplers to varying levels of ammonia in the field. From this experiment and in parallel the NPL CATFAC experiment (also within MetNH₃), sufficient information and protocols could be developed. The method and infrastructure developed will then be available for future studies.

The aim of the intercomparison exercise was to:

- 1) develop the equipment to intercompare different passive samplers
- 2) deploy the equipment to the Whim Bog ammonia line source site
- 3) expose ammonia passive samplers simultaneously at different points on the Whim Bog transect with the aim of sampling a wide range of ammonia concentrations
- 4) At one point measure NH₃ using a well-calibrated continuous automatic instrument in parallel to passive samplers.

An open invitation to the ammonia measurement community was made to maximise participation and it was offered provide intercomparison and feedback to sampler providers. Sampler providers were also invited to take part in a laboratory quality assurance exercise.

Seven organisations participated in the intercomparison with 11 sets of samplers exposed for two four week (or four two week) periods. The results from the experiment were sent to the individual sampler providers and also used within the MetNH₃ project as part of the development of the CEN standard for ammonia passive sampler measurement protocols.

2. Methodology and experiment details

Participation and schedule

The intercomparison schedule is summarised in Table 1. The participants are summarised in Table 2, with details of the participant instructions shown in Appendix 1.

Table 1 Intercomparison schedule

Activity	Start Date	End Date
Intercomparison period 1	16 August 2016	13 September 2016
Intercomparison period 2	13 September 2016	11 October 2016
Chemical analysis	October 2016	December 2016
Collation	November 2016	January 2017

Table 2 Summary of participating organisations and samplers for 2016 Intercomparison

Participant Organisation	Samplers
CEH Edinburgh (UK)	➤ ALPHA samplers (2*4-week exposures) x 2
CEH Lancaster (UK)	➤ ALPHA samplers (2*4-week exposures)
IVL (Sweden)	➤ IVL samplers (4*2-week exposures)
FUB (Switzerland):	➤ Radiello samplers ➤ IVL samplers
Fondazione Salvatore Maugeri, FSM (Italy)	➤ Radiello (4*2-week exposures)
Gradko (UK)	➤ diffusion tubes ➤ DIFRAM
RIVM (NL)	➤ diffusion tubes
Passam (Switzerland)	➤ Passam samplers

Field Set up

The Whim Bog field site is situated ~20 km to the south of Edinburgh. It is an ombrotrophic bog which is used to assess the effects of dry and wet nitrogen deposition on vegetation (Leith *et al.*, 2004; Sheppard *et al.*, 2011). There is a permanent synthetic line release system to simulate ammonia emissions from intensive animal housing at ground level (Figure 1). Automated conditional release of ammonia from the line source occurs when the wind direction in the preceding minute is from the northeast (wind sector 180-215°) and wind speed is >5 ms⁻¹.

Atmospheric gaseous NH₃ concentrations have been measured continuously with CEH ALPHA samplers on a monthly timescale along a transect downwind of the line source since 2002. The downwind transect is established along the SW-NE axis along the prevailing wind direction at distances of 1, 2, 4, 8, 12, 16, 32, 60 and 81 m northeast of line source. An example ammonia concentration profile is shown in Figure 2; concentrations can vary by several orders of magnitude, directly correlated to the frequency of ammonia release in a particular month.

The 81 m location represents the background site. Background ambient concentrations of ammonia at the site is relatively low, with annual mean concentration of <1 µg m⁻³. In addition, there are also two upwind monitoring locations at 4 and 9 m southwest of line source. Positions at 12 m, 32 m and 60 m (Figure 3) were chosen to provide a range of NH₃ concentrations for the passive sampler field intercomparison exercise. A fourth point a background position was also selected.

In addition to the exposed samplers, transport and laboratory blanks were included: Transport blank samplers are not removed from their packaging. They are stored refrigerated and then sent back to the respective labs with exposed samplers. The instructions provided to participants are shown in Appendix 1. The assembly of the different types of samplers is shown in Figure 4.

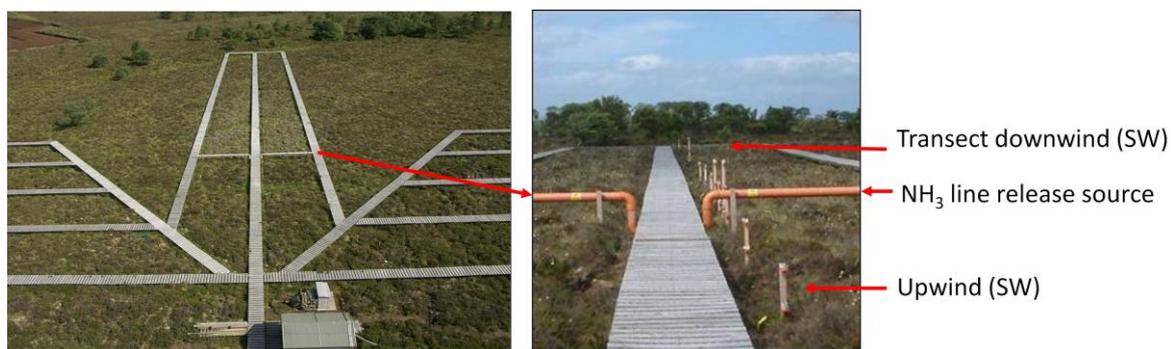


Figure 1 (Left) Photo showing layout of Whim Bog field site. (Right) transect downwind and upwind of synthetic line release source for NH₃.

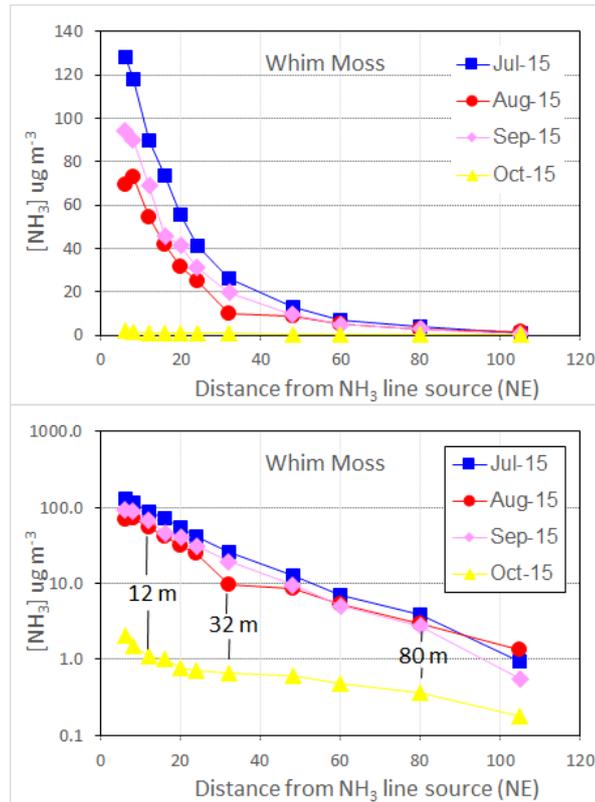


Figure 2 Example NH_3 concentration profile along transect for the months of July to October 2015 (July to September = release, October = non release). The months with ammonia release shows the classic exponential decay in concentrations due to dilution and dispersion

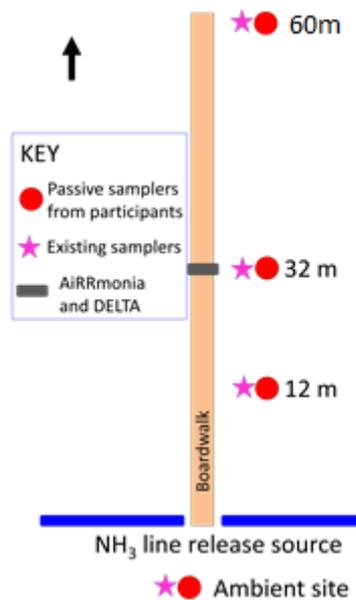


Figure 3 Sampler locations along transect (16m, 32 m and 60 m) for passive sampler intercomparison

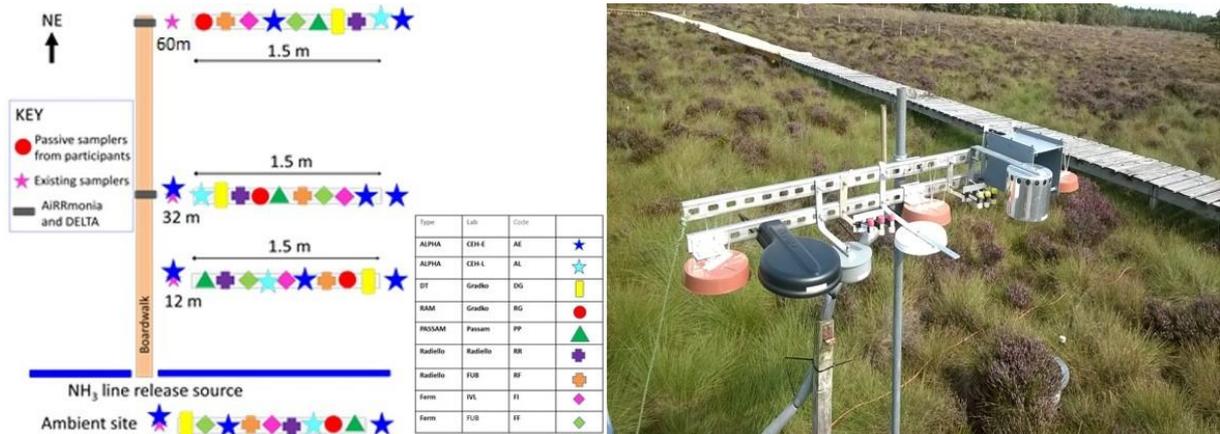


Figure 4 Left: Schematic mounting arrangement; Right: Picture of sampler assembly

3. Intercomparison overview:

Field Intercomparison of passive samplers:

Most samplers were exposed for 2 periods of 4 weeks over the 56 days (8 weeks) duration. Some samplers were replaced every two weeks, producing four x two-weekly averages, on the instructions of the supplier. The passive samplers were exposed along a metal frame on a post erected at 1.5 m above ground. Bases of shelters were set at an equal height to minimise the impact of any disruption to air flow by other shelters. All samplers were exposed in triplicate. The samplers at 32m were approximately within 1m of, and at the same height as, the inlet to the AiRRmonia automatic instrument. Prior to exposure all samplers were stored in sealed containers as directed by suppliers in a cold room at 4°C.

Ammonium analysis: Laboratory Intercomparison

In a laboratory intercomparison exercise for the analysis of ammonium test solutions (2 solutions from low (0.5 – 2 mg / L NH_4^+) to high (5 – 10 mg / L NH_4^+) [NH_4^+]) were provided by CEH and diluted and measured to observe any dilution errors in laboratory. Recovery tests were also conducted by adding diluted test solutions to samplers and measuring NH_4^+ to observe impact of different samplers and individual laboratory recovery procedures.

Table 3 Participating Passive Samplers and Corresponding Shelters

Laboratory and Sampler Type	Shelter Design
CEH Edinburgh – ALPHA	
Gradko - Diffusion tubes	
Gradko – RAM	
Passam – Passam	
Radiello – Radiello	
FUB – FUB	
IVL – IVL	
FUB – FERM	

Continuous NH₃ measurement – AiRRmonia

An automated ammonia analyser, AiRRmonia (Mechatronics, NL: Figure 5) was deployed to provide continuous ammonia measurements in the field. The analyser comprises a membrane sampler for quantitative sampling of gas-phase ammonia, followed by online measurement of NH₃ concentrations. Diffusion of NH₃ from the air stream occurs across a 0.22 µm pore size teflon membrane into a counter flow of deionised water. At pH 7 the NH₃ converts back to NH₄⁺ and is then transported to the detector block below. In the detector block, aqueous sample from sampling block is mixed with a carrier flow of deionised water to which an alkali (NaOH) is added. This converts all NH₄⁺ to NH₃ in solution around pH 12. At this pH, NH₃ is the only small molecule in solution that will readily diffuse across a 0.22 µm pore size teflon membrane. The sample is passed one side of a membrane with NH₃ passing over into a counter flow of deionised water. At pH 7 the NH₃ converts back to NH₄⁺ and the ion concentration is then analysed by conductivity. The air sampling rate is 1 L min⁻¹ with measurements recorded every minute. The AiRRmonia has a limit of detection of ~0.1 µg.m⁻³. Calibration was carried every 2 weeks using 50 and 500 ppb NH₄⁺ standard solutions.



Figure 5: AiRRmonia automated ammonia analyser (Mechatronics, NL)

Meteorological measurements

There is a meteorological station on site. Core parameters are wind speed, direction, temperature, relative humidity and rainfall, which are used to help interpret the measurements. The instrumentation for these measurement are summarised below.

Table 4: Meteorological Measurements

Parameter	Equipment used for measurement
Wind speed and direction	Gill Windsonic
Temperature and Relative humidity	Vaisala HMP60
Rainfall	R.M.Young Tipping bucket

4. Summary of fumigation and high resolution ammonia measurement during intercomparison

Figure 6 shows all the data from the fumigation operation and the on-line NH₃ results at 32m. The NH₃ values observed ranged from 0 to nearly 800 µg.m⁻³ over the 8 week period with an average value of 50 µg.m⁻³ in the first 4 weeks and 41 µg.m⁻³ in the second. The higher levels of fumigation in weeks 2-6 can be clearly observed by the high peaks in this time. The high release rate, and hence high concentrations in this period resulted in some of the samplers at the 12m intercomparison point showing indications of being saturated. It is a learning point for future quality assurance experiments that the risk of saturation should be explored prior to the experiment, though the amount of release was relatively uncommon for the time of year in the experience of the 13 years of operation at the site. NH₃ data capture by the Airrmonia was 98.7%. Instrument downtime was due to periods where the instrument was in calibration mode due to the fortnightly calibration required.

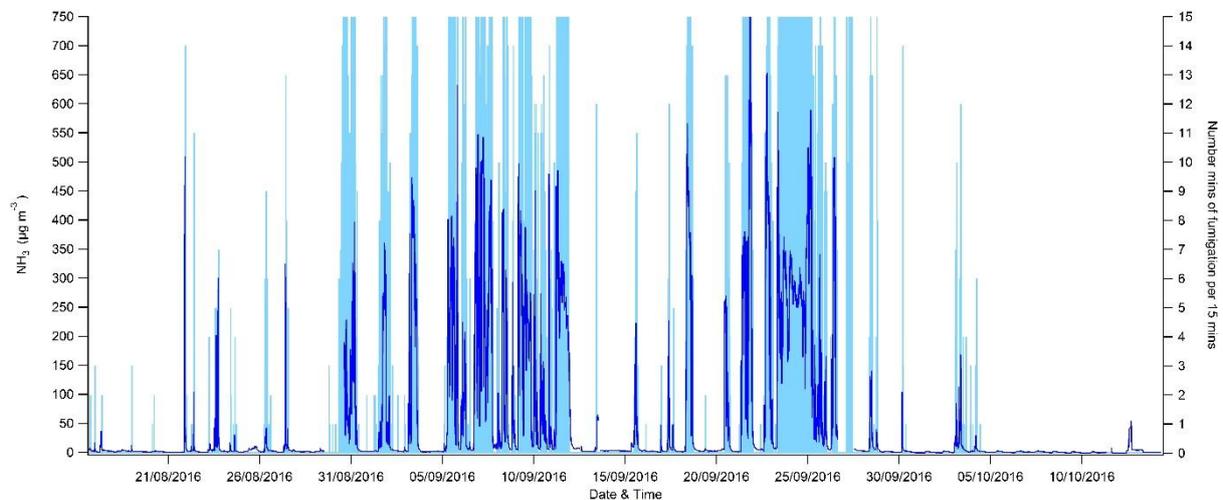


Figure 6 Ammonia concentrations and fumigation amount (# minutes in 15 minute period) time series for intercomparison periods. Date and time is displayed on the x-axis, NH₃ (µg.m⁻³) on the left y-axis and fumigation level (as number of minutes fumigation per 15 min period) on the right y-axis. The dark blue line corresponds to the Airrmonia result and the light blue line indicates the fumigation.

5. Passive sampler results

The passive samplers were deployed over the 8-week campaign period. From a practical “sampler user assessment” all the passive samplers taking part in the study were simple and easy to use. Clear and easy to understand instructions were provided by all suppliers. Shelter design was for most a similar principle (see Table 3 for images). Feedback from the field deployment and staff suggestions for improvements can be found below (Table 5).

Table 5 Sampler deployment feedback for participants

Laboratory	Comments and Suggestions for Improvements
CEH Edinburgh – ALPHA	<ul style="list-style-type: none"> Shelters are labour intensive to produce and are not a good shape for easy shipment compared to other designs. Shelter brackets hold shelter steady even in high winds however the user must ensure screws from brackets onto shelter are screwed tightly or alternatively use locking nuts to secure. Shelter is naturally coloured to blend in with environment.
Gradko - Diffusion tubes	<ul style="list-style-type: none"> Clips attached by sticky pads did not cope well in wet weather but the additional cable tie provided held the clips in place for duration of study. In future for wet weather areas may be worth looking into putting holes into the clips base so they may be attached by screws which will not be impacted by weather.
Gradko - RAM	<ul style="list-style-type: none"> Samples were lost in high winds. Suggested improvement is to way of fixing shelter. The current method of a single cable tie allows for movement in high winds which perhaps encouraged the samples to fall off shelter. The addition of a second cable tie may provide a more stable anchor point and remove this movement. Samples also quite heavy so might need more heavy duty fixer than Velcro spots.
Passam – Passam	<ul style="list-style-type: none"> Shelters had a small base which makes them convenient for shipping but causes difficulties in accessing the clips for sample changes. Suggested improvement is to use a wider base to allow better access Shelter was fixed by 2 cable ties which was easy to set up and provided a stable anchor point for the shelter.
Radiello – Radiello	<ul style="list-style-type: none"> Shelter was shipped in parts with instructions for construction. Parts were tight fitting and required strength and patience to put together. Shelter was attached by fixing to an open back plate at 4 points by cable ties which gave shelter a solid fixing point whilst allowing for good air flow around samples. Samples were attached via clips which rusted over the short test duration, may be worth looking into changing the material the clips are made from for longer study durations or changing clips regularly. Clips held samples securely.
FUB – Radiello	<ul style="list-style-type: none"> Shelters was very sturdy and could easily be reused. Base was wide enough to allow sufficient access for sample changes. Sample clips were easy to change but held samples securely.
IVL – IVL	<ul style="list-style-type: none"> Samples lost in high winds – entire shelter came off arm. For the study a shorter length of arm was used to bring shelter in line with others. Even with this shorter arm a large amount of movement was observed in high winds. This up and down movement succeeded in undoing the bolt affixing the shelter to the arm and causing it to fall to the ground. All samplers remained attached to the shelter which was retrieved. Clips held samples in place well but are very tight. This makes sample exchange difficult. May be worth looking at alternative clips.
FUB – FERM	<ul style="list-style-type: none"> Magnetic fitting on shelter enabled easy removal of sample attachment making sample exchange easy. Magnetic fitting held samples even throughout high winds and bad weather. Shelter was very sturdy and could easily be reused.

Figure 7 displays the results for all samplers over the two exposure periods. Period one on the left hand side and period 2 on the right hand side. All samplers show a higher level of NH₃ closer to the source and ambient levels were low (< 2 µg.m⁻³). The detailed results from all samplers are tabulated in Appendix 3. This is both to ascertain precision in the sampling and have contingency against loss of samplers. All outlier or contaminated sampler results were excluded from the analysis – for example if it had been recorded that the sampler had fallen to ground. Six of the participating samplers (Passam, CEH Ed, CEH L, Gradko tubes, FUB FERM and FUB Radiello) had 100% data capture for the 2 exposure periods. RIVM had 100% data capture for the two exposure periods but chose not to expose samplers at the 12m point as given previous levels they would become saturated (leading to 75% data capture overall). FSM had a data capture of 98% due to the loss of a sample during handling in the laboratory. Gradko diffram had a data capture of 96% due to the loss of a few samplers in high winds. IVL had a data capture of 75% due to the high levels causing saturation in samplers and the loss of two shelters and their samplers due to high winds and bad weather. It was assessed that all samplers achieved. Taking into consideration the number of samples exposed, the high levels of fumigation and a period of particularly bad weather all laboratories achieved a satisfactory percentage data collection.

Several laboratories reported single outliers in the reported datasets:

- 1) Gradko tubes- single low value thought to be due to experimental error during prep or analysis.
- 2) Gradko Diffram – several single high values.
- 3) FSM – consistent issues at low concentrations suggesting issue with analysis method.
- 4) FUB FERM - single low value thought to be due to experimental error during prep or analysis.

The majority of laboratories returned data from the triplicate samplers with a precision of better than 15% (as defined as the relative standard deviation (SD) of the three measurements. Where issues were observed it was at either high NH₃ (12m point) or very low NH₃ concentrations (ambient). These issues can potentially understood from sampler saturation at the high levels, analysis method limit of detection at low levels and occasionally dilution errors. Data from all the samplers are tabulated in Appendix 3.

MetNH3 Whim Bog Intercomparison Off-line ammonia metrology intercomparison

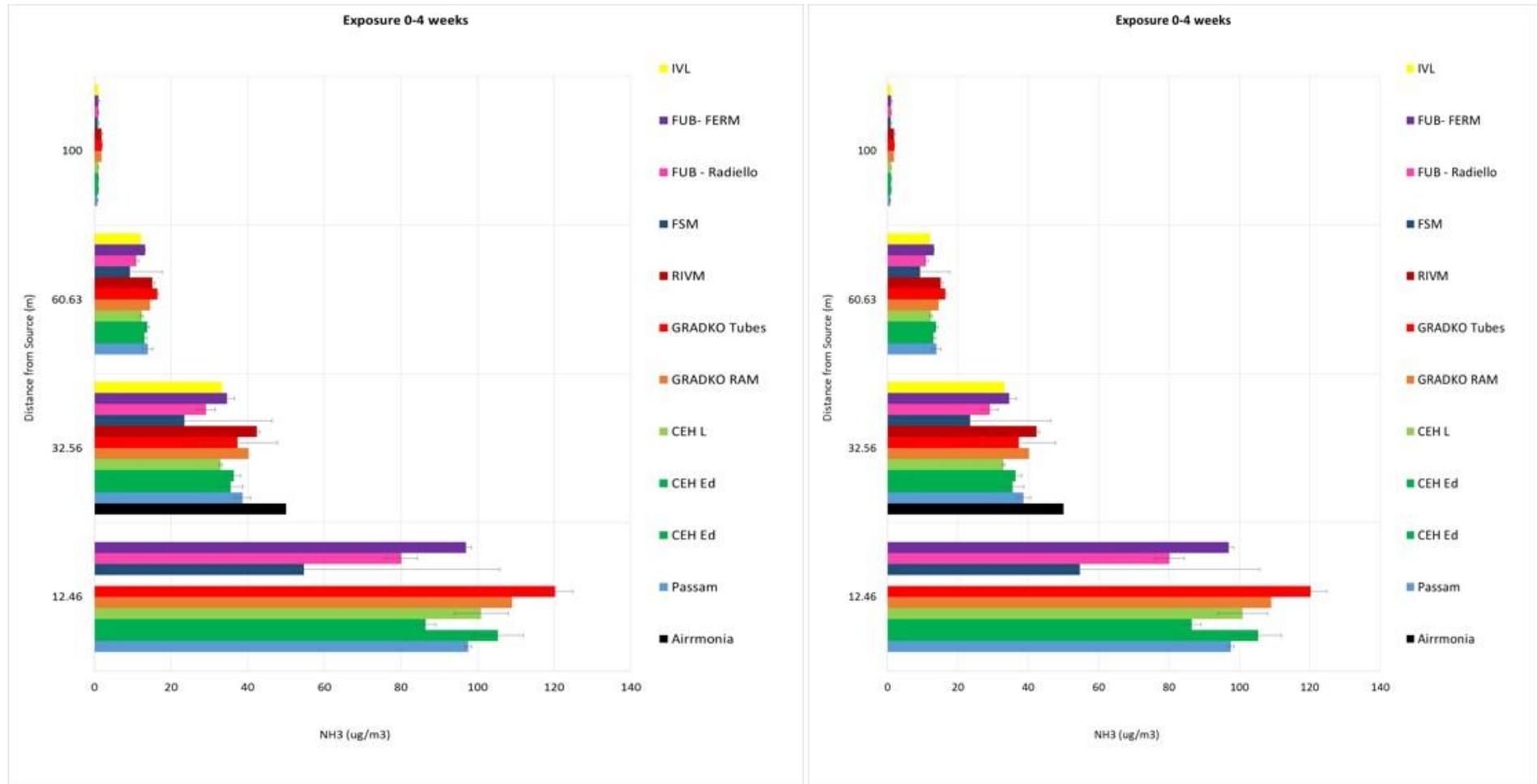


Figure 7 Results from passive sampler intercomparison, LHS: Week 0-4; RHS: Week 4-8

For QA, laboratory and transport blanks were included in the intercomparison. Laboratory blanks are blanks retained by the analysis laboratory under conditions that they would normally store samplers. They provide a background reading of NH₄⁺ which is present on all samplers. Passam, Gradko and IVL all reported low lab blank values, generally [NH₃] < 0.5 µg.m⁻³. CEH lab blank values were higher than normally observed, this has been investigated and has been determined as due to a contaminated batch of capture membranes. FSM reported very high blank values >2 µg/m³ NH₃ however after discussion with FSM, these are believed to be actually transport blanks.

Transport blanks are unexposed samplers sent with and stored alongside samplers for the duration of their exposure. They show any contamination occurring during storage or transport. As all samplers were stored in the same environment for the same duration any differences can be assumed to be due to their supplied packaging or contamination in transport. CEH, RIVM, Passam, IVL FUB- FERM and Gradko transport blanks displayed minimal differences as compared to laboratory blanks. Overall little contamination was observed from transport and or storage. A summary of blank results can be seen in Figure 8 below. The majority of laboratories achieved good blank values of <1 µg NH₄ in extract. With little difference observed between transport and laboratory blanks.

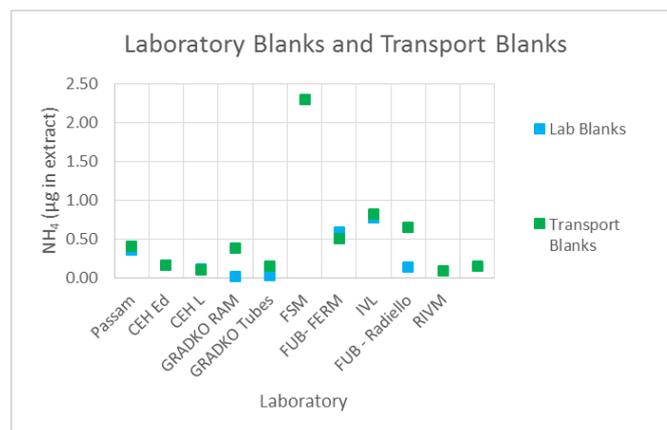


Figure 8: Laboratory and transport blanks

The final part of the intercomparison was the distribution of standard solutions, four laboratories took part in the laboratory intercomparison; Gradko, IVL, CEH Edinburgh, CEH Lancaster and FUB. The concentrations measured for prepared solutions X and Y are summarised in Figure 9 and Figure 10. Good accuracy in dilution was observed for all labs solution X which had an analytical concentration of 1 mg.l⁻¹ preparation and measurement

with values from 0.97 to 1.05 mg.l⁻¹. All samples were within 0.1mg.l⁻¹ of each other and the expected value of 1mg l⁻¹. Test solution Y (5 mg l⁻¹) results had slightly more variability with laboratories giving results from 4.85-5.25 mg l⁻¹. Where duplicate measurements were reported, precision reported was good. Recovery test results are shown in Figures 11. Figure 11 shows results of recovery tests using DI water and a blank sampler. Figures 12 and 13 show the results of recovery tests using the prepared solutions X and Y to conduct the extraction of blank samplers.

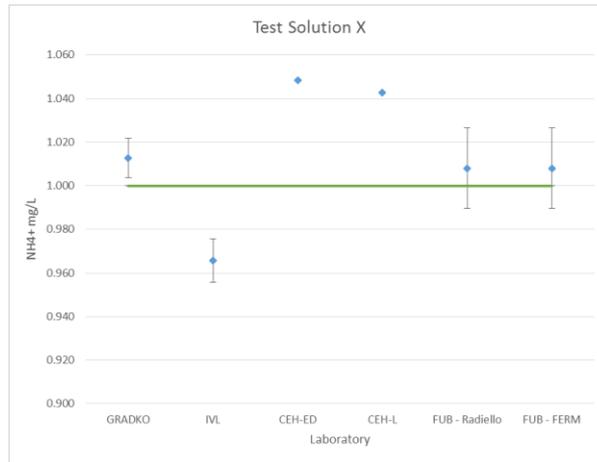


Figure 9 NH4+ measured for prepared solutions X, The x-axis shows the corresponding laboratory and the y-axis the measured NH4+ in mg/L. The green line designates the actual value expected for the prepared solution

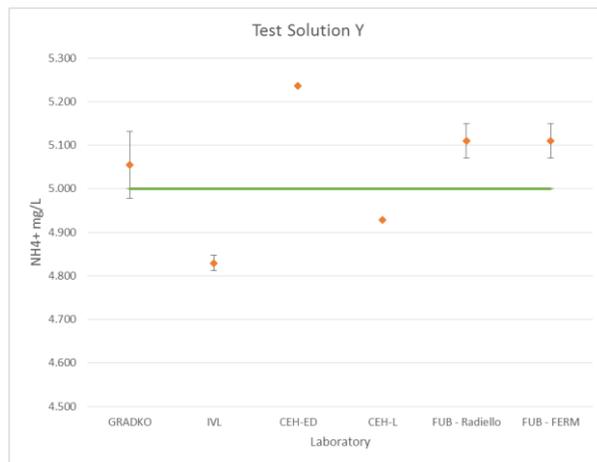


Figure 10 NH4+ measured for prepared solutions Y, The x-axis shows the corresponding laboratory and the y-axis the measured NH4+ in mg/L. The green line designates the actual value expected for the prepared solution

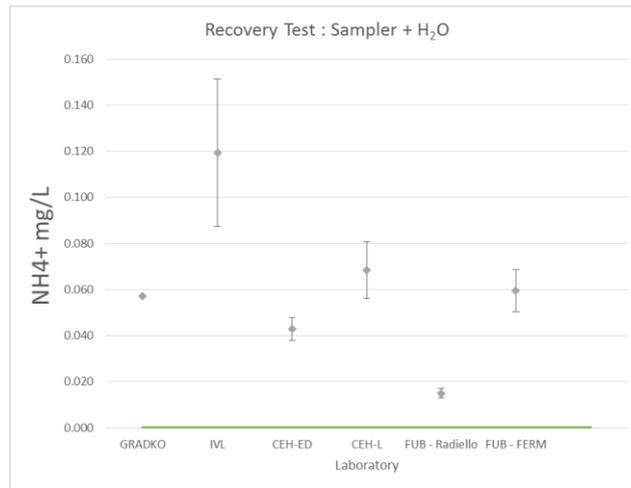


Figure 11 Results of laboratory intercomparison recovery tests: sampler + water

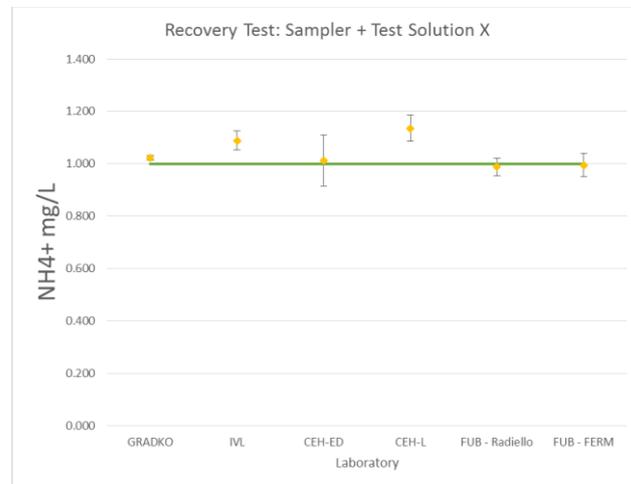


Figure 12 Results of laboratory intercomparison recovery tests: sampler + solution X (X = 1.00 mg/l)

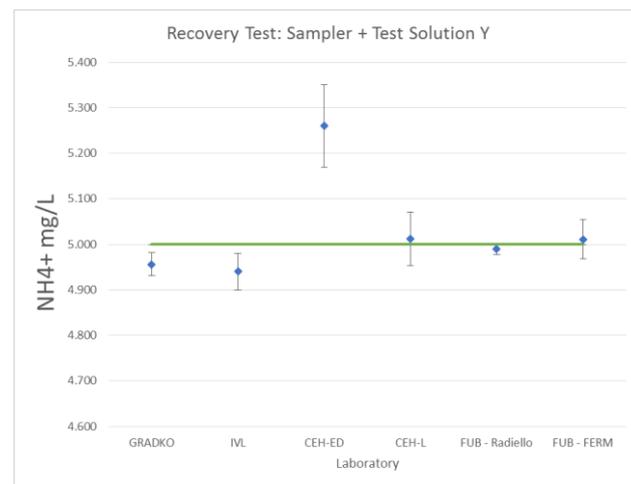


Figure 13 Results of laboratory intercomparison recovery tests: sampler + solution Y (Y = 5.00 mg/l)

The high resolution NH₃ instrument (AiRRmonia) was deployed at the 32.5m point to give the hourly concentration of NH₃ for comparison. Average concentrations at this point are higher than all passive sampler measurements. Reasons for this potentially include ammonium from PM contribution to the on-line gas sampling and or under-measurement due to a physical reason by the passive samplers. Further analysis is required to fully understand, however it is noted in one previous experiment good agreement was obtained between CEH ALPHA samplers and the Airmonia measurement on a farm study.

Figure 14 shows the percentage different of each lab sampler from the values. Grey points are from weeks 0 to 4 and green points are from weeks 4 to 8. CEH, Gradko Ram, FUB FERM all display consistent percentage differences to the AiRRmonia values over the two time periods. Percentage difference values for all the samplers range from -15 to -53%. It should be noted that during the middle four weeks of the experiment there was a period of dry weather which resulted in dust plumes. The dust particles from these plumes may have impact the ability of some samplers to capture ammonia effectively. Radiello samplers have previously been evaluated to find quantitative sampling in the presence of dust (from poultry house experiments) challenging. Samplers showing greatest percentage differences from AiRRmonia were in a position where the membrane surface would be greatly exposed to the dust plumes, however that is merely a hypothesis and samplers in theory should be able to sample in the presence of particulate matter.

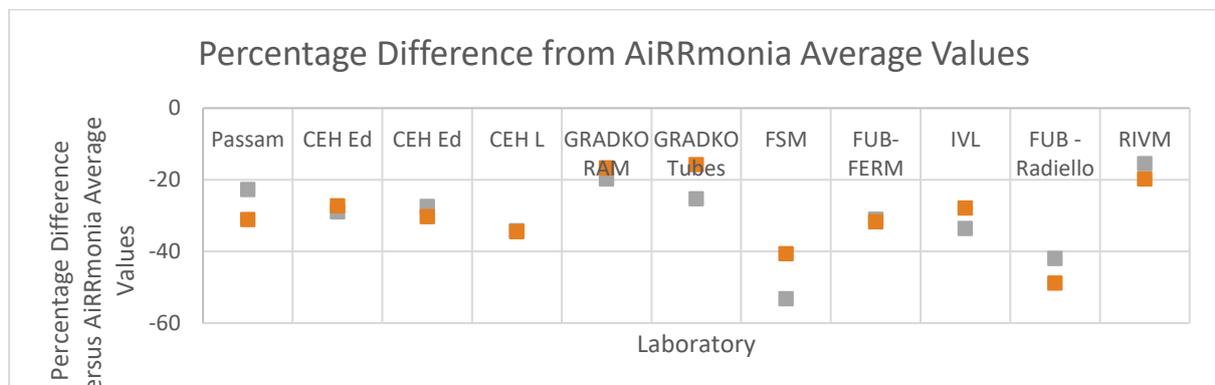


Figure 14 Relative difference of passive samplers to averaged high resolution ammonia measurement

Due to the systematically higher value of the Airrmonia it is useful to compare the relative differences of the samplers to the mean of the ensemble (e.g. Figure 15 for the second two weeks absolute concentration). Figure 16 shows the percentage relative deviation from the ensemble mean for all measurements. Considering each distance separately: At the closest point (12m) the range of concentrations are $>50 \mu\text{g}/\text{m}^3$, with all participants within the $\pm 40\%$ RSD. It is likely at this high concentration, there is some saturation of some samplers, and it is not clear that the “true concentration” is measured either quantitatively or qualitatively.

At the two intermediate distances (32 and 60 m) the range of concentrations measured is much smaller (20 and $7 \mu\text{g}/\text{m}^3$ respectively) with $>90\%$ data points falling within the $\pm 20\%$ RSD of the mean. There is a clear systematic graduation of the types across the range rather than a more random distribution, implying the samplers have systematic differences causing different concentration to be measured.

For the “background”, 83 m point, it is a similar situation where most points are within 1SD of the ensemble mean. However it can be clearly seen in Figure 16 that the diffusion tube samplers and the passive badge type samplers form separate populations in the distributions. Hence the agreement seen in Figure 15 is partly an artefact, and is likely skewed high due to the diffusion tube measurements which have a higher detection limit than the badge type samplers. This is consistent with the finding of Martin et al. (2017, in prep) in the controlled atmosphere test facility (CATFAC).

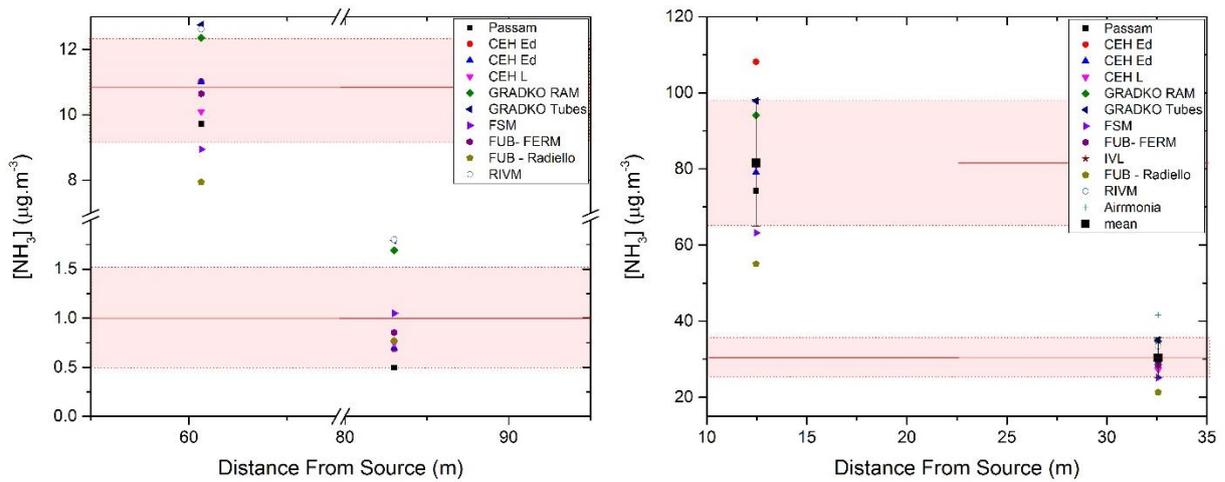


Figure 15 Summary of measurements at each point on the transect. Red line = ensemble mean; shaded area 1SD from mean. LHS: 62 and 83 m results; RHS: 12 and 32 m

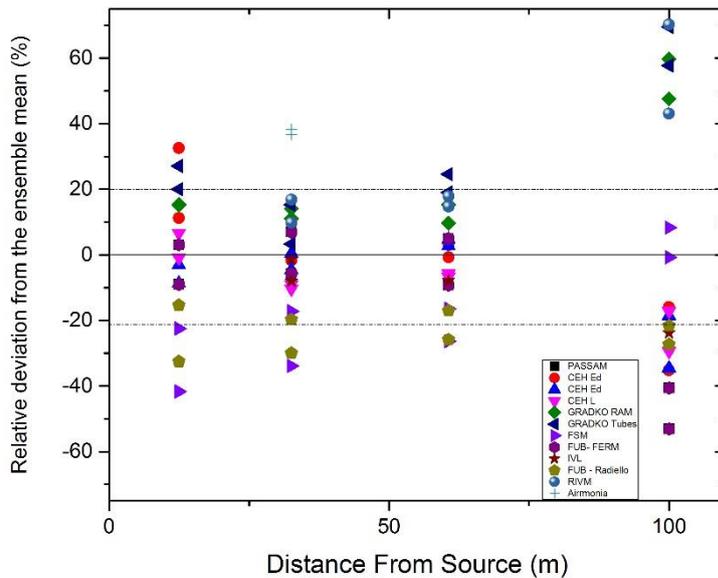


Figure 16 Relative deviation from ensemble mean for all measurements at each distance down the transect. Sampler types in legend inset box

Data from this intercomparison was used by Martin et al to investigate the application of revised diffusional uptake parameters used by the manufacturers and analysis laboratories. Though an improvement in the variability of the measurements was observed, it does not explain the sizeable differences in concentrations measured.

Conclusions and future work

The passive sampler intercomparison was undertaken successfully and the practical equipment was fabricated to host the intercomparison. Samplers were exposed to 4 concentrations of NH₃ covering the range 1 – 100 µg m⁻³. All passive samplers sampled ammonia effectively. Variability between samplers were observed at all concentrations. A more detailed analysis will be provided in the research paper derived from this experiment

The laboratory solution and extraction quality assurance demonstrated high levels of performance by the laboratories. Future work includes agreeing a standard report format to provide feedback to participants and write up the work for peer review. The format of the intercomparison is available to perform regular quality assurance exercises and help with improvement of measurement of ammonia in the future. There is still considerable work to be done in order to fully understand the variability observed and to enhance performance of passive samplers in environmental applications.

Acknowledgements

We gratefully acknowledge the funding received from NERC National Capability projects which fund the Whim Bog facility and the European Metrology Programme (EMRP) of the European Union. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union. This experiment was supported by the CEH Edinburgh field team.

References

- Leith, I., Sheppard, L., Fowler, D., Cape, J.N., Jones, M., Crossley, A., Hargreaves, K., Tang, Y.S., Theobald, M., Sutton, M., 2004. Quantifying Dry NH₃ Deposition to an Ombrotrophic Bog from an Automated NH₃ Field Release System. *Water Air Soil Pollut: Focus* 4, 207-218.
- Sheppard, L.J., Leith, I.D., Mizunuma, T., Cape, J.N., Crossley, A., Leeson, S., Sutton, M.A., van Dijk, N., Fowler, D., 2011. Dry deposition of ammonia gas drives species change faster than wet deposition of ammonium ions: evidence from a long-term field manipulation. *Global Change Biology* 17, 3589-3607.
- Martin, N.A. Ferracci V., Cassidy N., Hook J., Battersby RM., Amico di Meane, E., Tang YS, Stevens, ACM. Jones, M.R., Braban C.F., Gates L., Hangartner, M. Stoll, J.M., Sacco P., Pagani D., Hoffnagle, J., Seitler, E. Validation of ammonia diffusive and active samplers in a controlled atmosphere test facility using traceable Primary Standard Gas Mixtures (in prep. *Atmos Environ.*)

Appendix 1 Intercomparison Instruction Details for participants



*MetNH₃ project
Field inter-comparison of NH₃ passive samplers
at Whim Bog
Aug – Oct 2016*



Instruction Sheet

NPL and CEH are coordinating a field inter-comparison of NH₃ passive samplers for the MetNH₃ project.

Test site: Whim Bog

Whim Bog is an experimental Nitrogen manipulation site with automated conditional release of NH₃ from a synthetic NH₃ line source. Diffusive samplers will be placed at 3 locations downwind of the line source and also at a background site.

- 12 m along an NH₃ transect (55 - 90 µg m⁻³ NH₃ measured in Jul-Sep 2015)
- 32 m along an NH₃ transect (9.8 - 36 µg m⁻³ NH₃ measured in Jul-Sep 2015). AiRRmonia and DELTA will run in parallel at this location.
- 80 m along an NH₃ transect (2.8 – 3.8 µg m⁻³ NH₃ measured in Jul-Sep 2015)
- Background (0.7 – 1 µg m⁻³ NH₃ measured in Jul-Sep 2015)

Timetable:

Work Item	Milestone
Inter-comparison period	15/08/2016 – 10/10/2016 (2 x 4-week or 4 x 2-week, as instructed)
Delivery of shelters* (if normally used) or mounting device (e.g. clips for diffusion tubes) + instructions to CEH by laboratories	To arrive at CEH by 04/07/2016 * Samplers expected to use shelters: ALPHA, Radiello, Passam, Ferm.
Delivery of samples + instructions to CEH by laboratories.	To arrive at CEH by 01/08/2016 : <ul style="list-style-type: none"> • For 2 x 4-week exposures = 24 test samplers + 3 transport blanks (total = 27) • For 4 x 2-week exposures = 48 test samplers + 3 transport blanks (total = 51)
Return of exposed samplers to laboratories	At end of last inter-comparison period
Analysis and data submission by laboratories	Results to be submitted to CEH by 07/11/2016
Evaluation by NPL/CEH	Inter-comparison results to be analysed and made available by 12/12/2016

Further notes and instructions:

- Exposure height will be ~ 1.5 m above ground.
- Samples and sample record cards should be clearly labelled with the name of the participating laboratory and type of diffusive sampler (e.g. CEH, ALPHA).
- Transport blanks should be clearly labelled to distinguish them from field samples.
- Transport blanks will remain in the transport box and stored refrigerated at CEH.
- At the end of the last inter-comparison period, all exposed field samples and transport blanks will be sent back to the laboratories by courier post, together with completed record cards, noting the date/time of exposure, including any relevant comments.
- The coordinator will document records of receipt and dispatch of samples to laboratories.
- The laboratories shall analyse the samplers according to that laboratory's normal operating procedure and report the results on the report template to the coordinator.
- The laboratory shall document full traceability of the method systems including:
 - level of QA/QC, e.g. accreditation
 - details of the analytical methods, including limits of detection

Coordinator contact details:

Contact name: Ms Amy Stephens

Address: CEH, Bush Estate, Penicuik, Midlothian EH26 0QB, UK

Tel: +44(0)131 445 8448

Email: amstep@ceh.ac.uk

Appendix 2 Participating laboratories for MetNH₃ field and lab intercomparison:

- **CEH Edinburgh (UK): ALPHA samplers (2*4-week exposures)**

Contact name/s: Ms Amy Steph and Ms Sim Tang
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Tel: +44(0)131 445 8448 (Amy), +44(0)131 445 8562 (Sim)
Email: amstep@ceh.ac.uk (Amy), yst@ceh.ac.uk (Sim).

- **CEH Lancaster (UK): ALPHA samplers (2*4-week exposures)**

Contact name/s: Jan Poskitt
Address: Lancaster Environment Centre, Library venue, Bailrigg, Lancaster LA1 4AP, UK
Tel: +44 (0)1524595897
Email: jposkitt@ceh.ac.uk

- **IVL (Sweden): IVL samplers (4*2-week exposures)**

Contact name/s: Martin Ferm
Address: Swedish Environmental Research Institute, Aschebergsgatan 44, SE-411 33, Gothenburg, SWEDEN
Email: martin.ferm@ivl.se

- **FUB (Switzerland): Radiello and IVL samplers**

Contact name/s: Eva Seitler / Lotti
Address: FUB (Forschungsstelle für Umweltbeobachtung), Alte Jonastrasse 83, CH-8640 Rapperswil, SWITZERLAND
Tel: +41 55 211 05 55
Email: fub@fub-ag.ch

- **Fondazione Salvatore Maugeri, FSM (Italy): Radiello (4*2-week exposures)**

Contact name/s: Paolo Sacco
Address: Fondazione Salvatore Maugeri (FSM), Centro di Ricerche Ambientali
Via Svizzera 16, 35127 PADOVA, ITALY
phone +39 049 8064511
fax +39 049 8064555
Email: paolo.sacco@fsm.it

- **Gradko (UK): diffusion tubes and DIFRAM samplers**

Contact name/s: Linda Gates (Laboratory Manager)
Address: Gradko International Ltd, St Martins House, 77 Wales Street, Winchester SO23 0RH
Tel: 01962 860331
Email: Linda@gradkolab.com

- **RIVM (NL): diffusion tubes**

Contact name/s: Ariën Stolk
Address: RIVM
Tel: +31 30 274 2412
Email: arien.stolk@rivm.nl

- **Passam (Switzerland): Passam samplers**

Contact name/s: Prof. Jean-Marc Stoll
Address: Abwasser, Wasser und Geruch, Hochschule für Technik Rapperswil HSR
Institut für Umwelt- und Verfahrenstechnik UMTEC, Oberseestrasse 10, CH 8640 Rapperswil
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Appendix 3 Intercomparison Results

Exposure Period	Distance From Source (m)		0-4 weeks NH3 (ug/m3)										High Res NH ₃		
			Passam	CEH Ed	CEH Ed	CEH L	GRADKO RAM	GRADKO Tubes	FSM	FUB-FERM	IVL	FUB - Radiello		RIVM	
0-4weeks	12.46	Av.	97.57	105.35	86.49	100.97	109.02	120.32	54.73	96.97	SAT	80.15			
		St Dev	0.94	6.61	2.62	7.03	104.17	4.55	51.05	1.39		4.20			
	32.56	Av.	38.72	35.60	36.35	32.95	40.20	37.41	23.46	34.56	33.29	29.06	42.31	50.06	
		St Dev	1.99	3.17	1.72	0.34	38.16	10.34	22.92	2.06	31.51	2.40	0.84		
	60.63	Av.	13.88	13.12	13.85	12.34	14.50	16.47	9.27	13.20	12.18	10.97	15.17		
		St Dev	1.32	0.60	0.47	0.45	12.85	0.31	8.39	0.06	11.01	0.57	0.55		
	100 (Ambient)	Av.	0.76	1.08	1.04	1.06	1.89	2.02	0.91	1.04	0.98	1.00	1.83		
		St Dev	0.07	0.02	0.01	0.03	0.57	0.04	0.26	0.22	0.35	0.09	0.35		
	0-4weeks	12.46	Av.	74.20	108.16	79.10	80.91	94.11	97.89	62.75	81.52	SAT	55.05		
			St Dev	4.63	15.24	4.41	2.89	88.00	8.88	49.40071	1.65		1.41		
		32.56	Av.	28.69	30.30	29.05	27.28	34.72	35.09	24.72	28.43	30.02	21.33	33.42	41.63
			St Dev	1.71	1.24	2.46	0.58	30.42	1.43	23.28303	0.31	28.03	2.98	1.57	
60.63		Av.	9.72	11.03	11.00	10.10	12.35	12.75	8.48	10.65		7.95	12.62		
		St Dev	1.32	0.92	0.29	0.31	10.34	0.08	8.353138	0.33		0.25	0.61		
100 (Ambient)		Av.	0.50	0.69	0.69	0.75	1.69	1.79	0.58	0.85		0.77	1.80		
		St Dev	0.04	0.03	0.05	0.05	0.46	0.19	0.162208	0.11		0.07	0.14		

Exposure Period	Distance From Source (m)		4-8 weeks NH3 (ug/m3)										High Res NH ₃		
			Passam	CEH Ed	CEH Ed	CEH L	GRADKO RAM	GRADKO Tubes	FSM	FUB-FERM	IVL	FUB - Radiello		RIVM	
0-4weeks	12.46	Av.	97.57	105.35	86.49	100.97	109.02	120.32	54.73	96.97	SAT	80.15			
		St Dev	0.94	6.61	2.62	7.03	104.17	4.55	51.05	1.39		4.20			
	32.56	Av.	38.72	35.60	36.35	32.95	40.20	37.41	23.46	34.56	33.29	29.06	42.31	50.06	
		St Dev	1.99	3.17	1.72	0.34	38.16	10.34	22.92	2.06	31.51	2.40	0.84		
	60.63	Av.	13.88	13.12	13.85	12.34	14.50	16.47	9.27	13.20	12.18	10.97	15.17		
		St Dev	1.32	0.60	0.47	0.45	12.85	0.31	8.39	0.06	11.01	0.57	0.55		
	100 (Ambient)	Av.	0.76	1.08	1.04	1.06	1.89	2.02	0.91	1.04	0.98	1.00	1.83		
		St Dev	0.07	0.02	0.01	0.03	0.57	0.04	0.26	0.22	0.35	0.09	0.35		
	0-4weeks	12.46	Av.	74.20	108.16	79.10	80.91	94.11	97.89	62.75	81.52	SAT	55.05		
			St Dev	4.63	15.24	4.41	2.89	88.00	8.88	49.40071	1.65		1.41		
		32.56	Av.	28.69	30.30	29.05	27.28	34.72	35.09	24.72	28.43	30.02	21.33	33.42	41.63
			St Dev	1.71	1.24	2.46	0.58	30.42	1.43	23.28303	0.31	28.03	2.98	1.57	
60.63		Av.	9.72	11.03	11.00	10.10	12.35	12.75	8.48	10.65		7.95	12.62		
		St Dev	1.32	0.92	0.29	0.31	10.34	0.08	8.353138	0.33		0.25	0.61		
100 (Ambient)		Av.	0.50	0.69	0.69	0.75	1.69	1.79	0.58	0.85		0.77	1.80		
		St Dev	0.04	0.03	0.05	0.05	0.46	0.19	0.162208	0.11		0.07	0.14		

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