Directional Ammonia Final Report

C.F. Braban, I.D. Leith, S. Leeson, Y.S. Tang, N. Van Dijk, L.J. Sheppard, M.A. Solera Garcia. & M.A. Sutton

NERC Centre for Ecology and Hydrology

Bush Estate, Penicuik, Midlothian, EH26 0QB

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Main authors: C.F. Braban, I.D. Leith, L.J. Sheppard, S. Leeson, Y.S. Tang, N. Van Dijk, M.A. Solera Garcia. & M.A. Sutton	
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Contents

Directional Ammonia

Summary

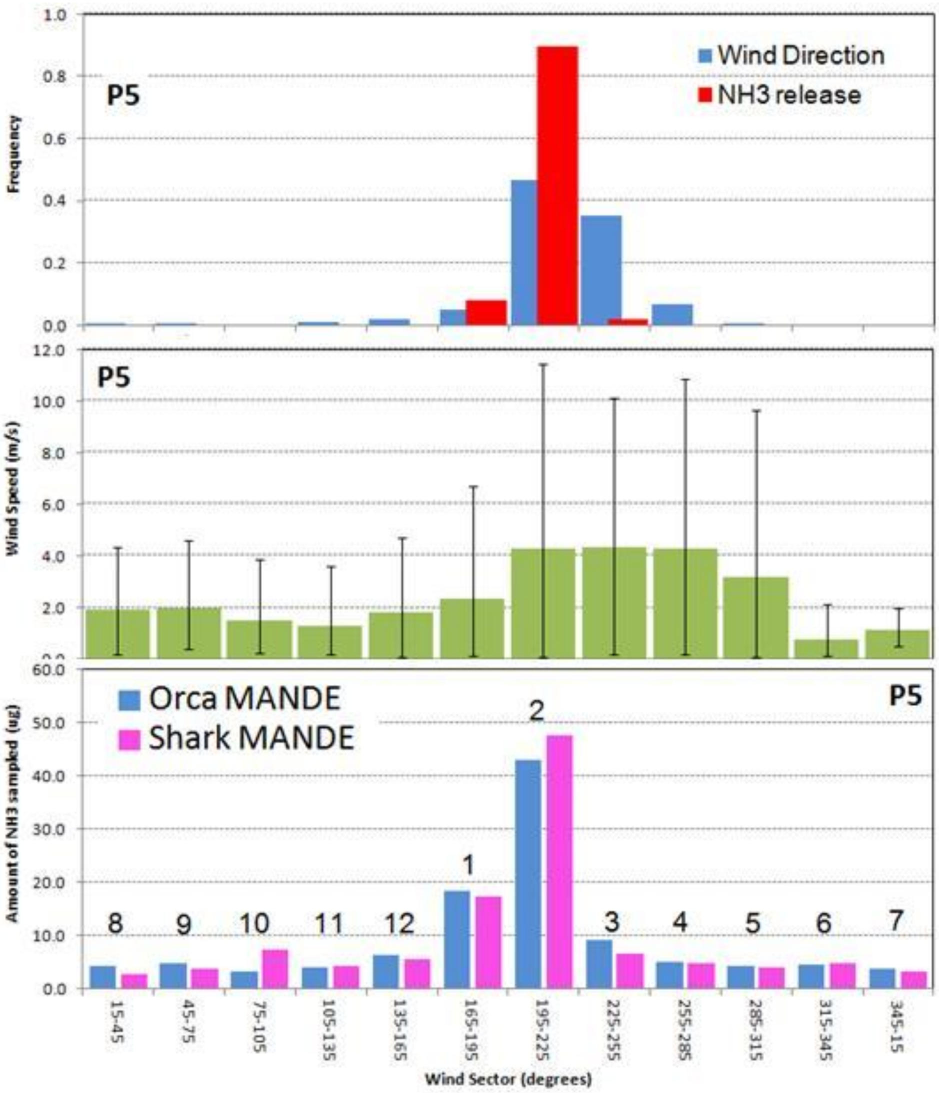
Directional passive samplers have been developed by EA/LEC (Lin et al, 2010a; Lin et al, 2010b, Lin et al, 2011; Ferranti 2012) and one application they could be potentially used for is ammonia source monitoring. The Whim ammonia release experiment site was used to test the EA/Lancaster directional passive ammonia samplers (DPAS) downwind of a line source of ammonia gas.

The aim of the experiments was to assess the performance of the DPAS systems for monitoring the directional distribution of ammonia at this site. Two types of ammonia samplers were tested in the DPAS systems, both of which have been developed by CEH Edinburgh: the CEH Adapted Low-cost Passive High Absorption (ALPHA) sampler (Tang *et al.*, 2001) and the CEH Mini Annular Denuder (MANDE) flux sampler. Testing was carried out over a period of six months with 5 exposure periods. This report summarises the results from these experiments and presents some discussion and interpretation.

ALPHA samplers proved not well suited for use in DPAS systems for two reasons: Firstly ALPHAs are designed to monitor concentration, whereas the DPAS system is designed to monitor fluxes. Effectively, ALPHAs use diffusive membranes to control the collection of gaseous species so that collection is by diffusion rather than by interception of fluxes. The second, related drawback was that the continuous diffusional sampling by the ALPHA samplers: ammonia as it disperses throughout the internal DPAS chamber becomes well mixed and hence each DPAS direction sampled slowly but continuously leading to a high "background" contribution to the measured ammonia mass in addition to the ammonia brought in with the specific wind direction.

MANDE samplers were much more successfully used in the DPAS. Though they also have a level of ammonia diffusion within the DPAS housing samplers leading to an above background ammonia measurement in all directions, this is an order of magnitude smaller effect than with the ALPHA. The direction in which the ammonia is coming from is clearly identifiable: in this case the line source release directions. Using the frequency of wind direction and the sampling rate of the MANDE as a function of wind speed, a wind run concept developed by EA/LEC has been applied to the data to calculate a "weighted ammonia wind run" which clearly shows a good reflection of the directions from which the ammonia was emitted.

Overall the DPAS-MANDE combination shows significant potential for studying the directional variation of ammonia in the environment when deployed in conjunctional with meteorological measurements. One caveat to be highlighted is that further work is required to assess sampling rate – wind-speed variation in order to move from a weighted ammonia wind run measurement to interpretation in terms of atmospheric ammonia concentrations.



Results from sampling Period 5 with MANDEs in 2 DPAS (named ORCA and SHARK): Frequency distribution of wind sectors (30 degree bins) corresponding to 12 sampling positions (Top panel); Mean wind speed (m/s) corresponding to 12 sampling positions. The error bars represents the min and max wind speeds (Middle Panel); Amount of NH_3 sampled (µg, Bottom Panel)

Full report

1. Introduction

Directional passive samplers have been developed for environmental applications over the past four years. (Lin *et al.*, 2010a; Lin *et al.*, 2010b; Lin *et al.*, 2011a; Lin *et al.*, 2011b; Ferranti *et al.*, 2014) One application they could be potentially used for is ammonia source monitoring. The Whim ammonia release experiment site is situated south of Edinburgh and is an ombrotrophic bog site which is used to compare the effects of dry and wet nitrogen deposition on the vegetation (Leith *et al.*, 2004; Sheppard *et al.*, 2011). The part of the site which is being used to test the EA/Lancaster University directional passive ammonia samplers (DPASs) is downwind (NE) of a line source of ammonia gas (Figure 1, lower LHS). Release of ammonia is coupled to wind direction and logged. Ammonia is released when the wind in the preceding minute has been in the correct wind sector and has exceeded 2.5 m/s. Otherwise the site is in an area of relatively low ambient ammonia concentration ($<1\ \mu g.m^{-3}$).

The aim of the experiments was to assess the performance of the DPAS systems for monitoring the directional distribution of ammonia at a site. Two types of ammonia samplers were tested, both of which have been developed by CEH Edinburgh: the CEH Adapted Low-cost Passive High Absorption (ALPHA) sampler (Tang *et al.*, 2001) and the CEH Mini Annular Denuder (MANDE) flux samplers. Testing was carried out over a period of six months with 5 exposure periods. This report summarises the results from these experiments and presents some discussion and interpretation.

Figure 1: Site photos of Whim experimental site, showing deployment of the two DPASs.

2. Methodology

2.1 Set-up

The DPAS consists of the directional sampler body mounted on a post, approximately 1 m above ground. At the Whim site, the DPAS samplers had to be stabilised using a flat slab base and, due to the exposed nature of Whim, weighed down with several concrete blocks (as seen in Figure 1 upper LHS and RHS). The DPAS were set up at 32 m downwind of the ammonia line source. During set-up and sample change-over, the DPAS was taken into either the shed at Whim or back into the laboratory to allow careful changing of samplers. When installing (and re-installing), alignment of the north for the sampler was confirmed, and the free rotation of the DPAS sampler on its axis checked.

One ammonia sampler, either ALPHA or MANDE, was placed into each of the DPAS's 12 directional holders. There is also space in the middle which can accommodate an additional ALPHA sampler but not the MANDE, (Figure 2). When the wind is blowing in the direction that exposes that direction's single sampler, ammonia will be trapped in that sampler, enabling the total ammonia emitted from a particular direction to be estimated for the exposure period. ALPHA samplers are used in the Defra funded UK National Ammonia Monitoring Network (NAMN) since 2000 (see http://pollutantdeposition.defra.gov.uk/ukeap). The MANDEs have been developed in-house at CEH by Sim Tang. Each MANDE consists of a short 5 cm long annular denuder (1 cm outer diameter) coated on the inside with citric acid, connected in series to a 2.3 cm glass tube with a thin stainless steel disc having a 1mm orifice in the centre. The orifice serves to decrease air flow speed inside the MANDE, thereby achieving low friction velocity and providing high NH_3 collection efficiency.

The MANDEs are placed horizontally and aligned with the orifice facing the air flow through the DPAS. Air flow through the MANDE deployed in the current passive flux mode is in theory at a rate linearly proportional to the external wind speed multiplied with the cosine of the angle between the wind direction and the sampler axis, which would allow an estimation of NH_3 concentration and flux (Schjoerring 1995).

It is noted that in ALPHA sampler deployments all 13 sample positions were filled, but for the MANDEs only the 12 directional positions were used, the central holder was left empty, because the DPAS does not have room to house a central MANDE.

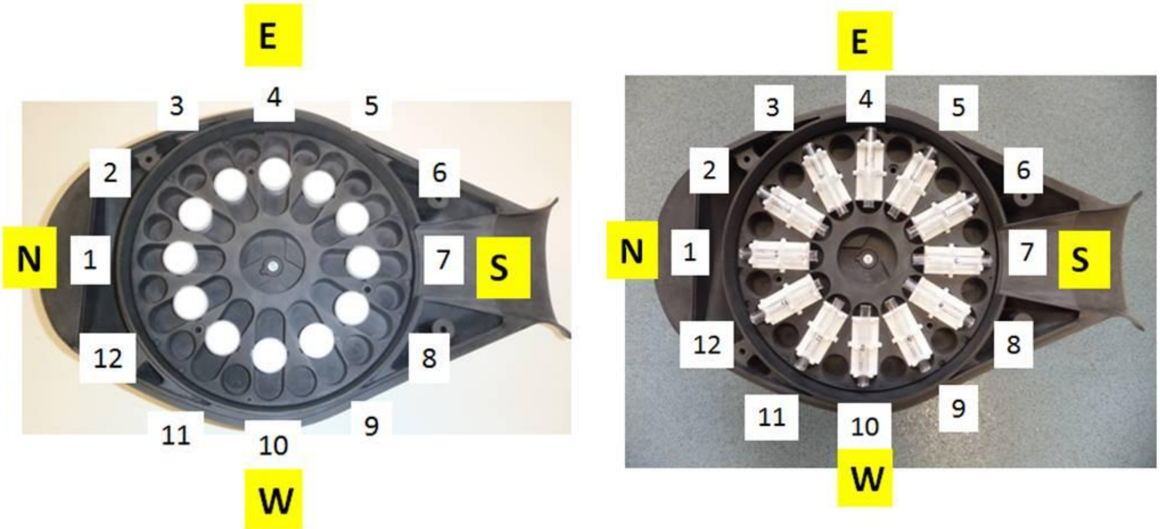


Figure 2 Orientation and corresponding numbering of sampling position within the DPAS LHS: ALPHA; RHS: MANDEs

In order to compare the concentrations being measured by the DPAS systems with the ambient average concentration, an additional ALPHA sampler was deployed at 32m using a standard passive sampling post (as has been deployed in NAMN and used at Whim). This has three replicate ALPHA samplers, attached with Velcro to an aerodynamically shaped support (upturned frisbee or plant saucer) on a post, ~1.0 m above ground. Anti-bird spikes are mounted on top to deter birds from perching.

MANDEs and ALPHAs are stored in air-tight containers at 4^{o}C until analysis in the CEH laboratories. Protocols developed for the UK NAMN (Tang et al. 2003) and working instructions are in place to cover ALPHA sampler deployment covering: sample preparation, sample dispatch, sample handling at monitoring locations, sample receipt, sample analysis at CEH Edinburgh and data quality control. Samples are extracted with deionised water and analysed for NH_4^+ with an Ammonium Flow Injection Analysis system with conductivity detection (AMFIA; ECN, NL) (Wyers *et al.*, 1993). The LOD calculation of this method is determined as three times the standard deviations of the laboratory blanks. Typical LOD for the measurement method is 0.02 µg NH_3 m^{-3} for monthly sampling.

2.2 Measurement periods

The five exposure periods and the corresponding exposure to ammonia release information are summarised in Table 1. The parallel ALPHA sampler deployments are summarised in Table 2. For the first two periods, a single DPAS was deployed containing ALPHA samplers in the 12 directional positions plus a 13th sampler in the centre. In periods 3 and 4, a second DPAS was made available and two parallel DPASs were deployed' one containing ALPHA samplers and the other containing MANDEs. During Period 4, the roof of the DPAS was painted with a citric acid solution in order to attempt to minimise the diffusional signal from ammonia by scavenging it with a large acidic surface area. For the final Period 5 both DPASs were deployed with MANDEs to test method reproducibility. Exposure periods and local activity at Whim are noted in the site electronic lab book. The timing, duration, wind speed and direction and release of ammonia from the line source are also recorded automatically. QA/QC processes are used to check raw concentration data from analysed samples for analytical quality. Subsequently calculation of air concentrations and further QAQC are carried out. It is noted that for the calculations an assumption is made that the DPAS sampling rate is wind speed independent. This has not been verified and may not be appropriate as the air flow over the sampler is determined by the external wind speed and the internal air turbulence within the DPAS.

Table 1 DPAS Deployment periods and ammonia release details

	ID	Sampler	Date Out	Time Out	Date in	Time in	Exposure (hrs)	NH3 release (hrs)	Comments
P1	Shark	ALPHA	02/11/12	13:10	15/11/12	10:25	309.25	50.80	None
P2	Shark	ALPHA	15/11/12	11:50	26/11/12	10:12	262.37	82.08	None
P3	Shark	MANDE	11/12/12	11:12	07/01/13	13:45	650.55	0.00	Small amount of rain inside sampler mouth & inner chamber. No NH_3 release
	Orca	ALPHA	11/12/12	11:20	07/01/13	13:45	650.42		
P4	Shark	MANDE	04/03/13	11:08	25/03/13	11:00	503.87	19.28	Top half of DPAS coated with citric acid solution. Snow inside sampler mouth & inner chamber.
	Orca	ALPHA	04/03/13	11:08	25/03/13	11:00	503.87		
P5	Shark	MANDE	21/04/13	14:23	07/05/13	14:03	191.67	43.05	None
	Orca	MANDE	21/04/13	14:29	07/05/13	14:05	191.60		None

Table 2 Sampling information for parallel monitoring of ambient NH3 concentrations with either ALPHA and/or MANDEs at 32m. One DPAS was deployed in periods 1 & 2 and two DPASs in periods 3-5.

Period	Date Out	Time Out	Date in	Time in	Sampler	Comments
P1	02/11/2012	13:12	15/11/2012	10:25	3 x ALPHA	
P2	15/11/2012	11:45	26/11/2012	10:12	3 x ALPHA	
P3	11/12/2013	11:12	07/01/2013	13:45	3 x ALPHA	
	11/12/2013	11:12	07/01/2013	13:45	3 x MANDE	Attached horizontally to the underside of ALPHA shelter ; orifice pointing into prevailing wind direction – not ideal
P4	04/03/2013	11:15	25/03/2013	11:06	3 x MANDE	Attached to diffusion tube holder, with orifice pointing to the ground. Note: holder shifted during exposure, changing angle.
	04/03/2013	11:15	25/03/2013	11:06	3 x ALPHA	
P5	21/04/2013	14:33	07/05/2013	14:07	3 x ALPHA	
	21/04/2013	14:33	07/05/2013	14:07	3 x MANDE	Attached to an improvised shelter to allow free air flow through MANDE; orifice pointing into prevailing wind.

3. Results

The results from the five exposure periods are summarised in Figures 3-5, with the detailed results presented in graphs and tables in Appendices 1-5. Overall three types of experiment were carried out. In Periods 1 and 2 (Figure 3) one DPAS system was tested with ALPHA samplers in all sample positions. Period 3 and 4 ALPHA sampler in 1 DPAS results and MANDEs in the other and in Period 5 both DPAS held MANDE flux samplers. Details of the results are discussed below.

3.1 Periods 1 and 2: ALPHA samplers only

In both Periods 1 and 2 there was a significant release of ammonia therefore the exposure period was relatively short due to making sure that the ammonia samplers did not saturate. The concentration measured at 32 m during Periods 1 and 2 was 41.2 and 77.1 µg m^{-3} respectively, compared with an annual average at this distance of ~13-20 µg m^{-3} (Gyarmati-Szabo *et al.*, 2011). This is not unexpected given that the periods were selected to cover ~80-100 hours of ammonia release and on both occasions this happened in a relatively short time period. It is clear from the results (Figure 3) that samplers which are sampling the air flow directly from the line source (primarily positions 1 and 2) have significantly higher concentrations than those seen from adjacent samplers. However all the samplers see a much higher concentration than the concentrations of the local background (~0.7 µg m^{-3} (Leith *et al.*, 2004). The results from Period 1 and 2 indicate that there is significant diffusion or “cross-talk” between the samplers within the DPAS body: in particular the decrease in ammonia concentrations measured by ALPHA samplers on either side of the “target” sampler is consistent with the decay in ammonia concentrations due to dispersion away from the target sampler and the measurement of significant levels of ammonia in all directions rather than mostly the release directions show that diffusion sampling of ammonia within the body of the DPAS is occurring. There are slightly elevated concentrations also to the NNE/NE which may be attributable to the winds coming from the farm about 1.5 km distant in that direction.

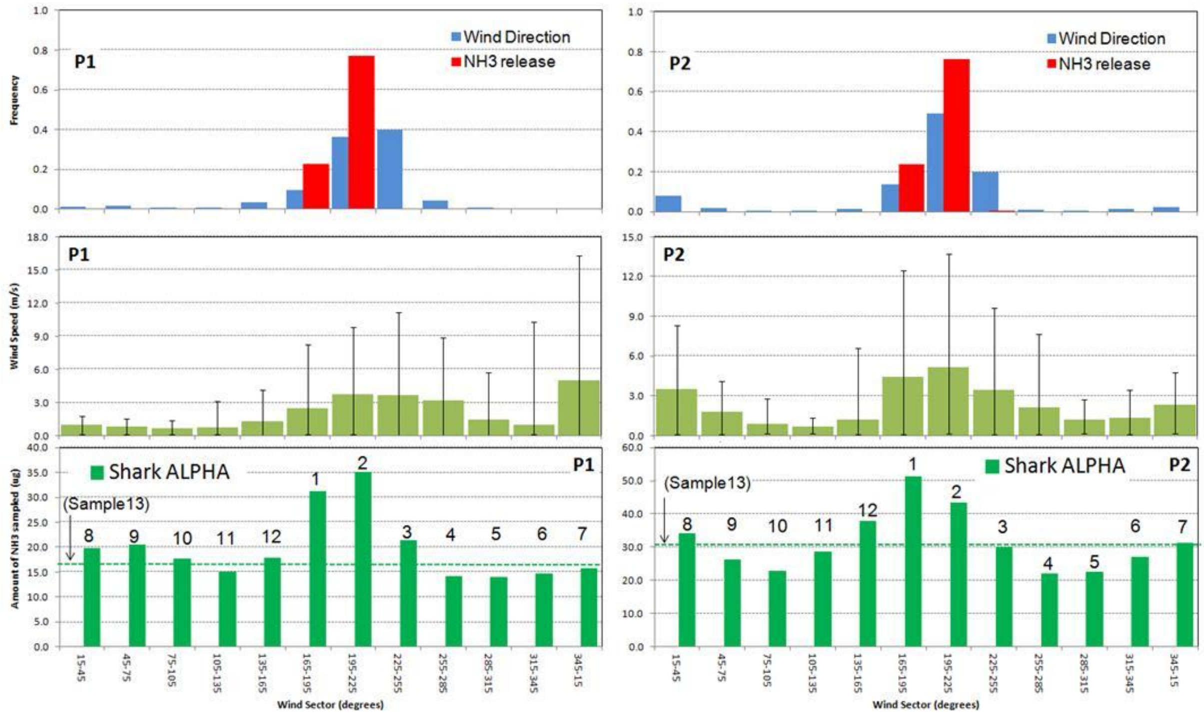


Figure 3 Results from Period 1 and 2: ALPHA samplers in one DPAS: (Top) Frequency distribution of wind sectors (30 degree bins) corresponding to 12 sampling positions. (Middle) Mean wind speed (m/s) corresponding to 12 sampling positions. The error bars represents the min and max wind speeds. (Bottom) Amount of NH_3 sampled by ALPHA samplers in each of 12 sampling positions in the Shark DPAS. Note sample 13 is the central sampling point in the DPAS

3.2 Periods 3 and 4: ALPHA and MANDE sampler side-by-side comparison

Period 3 and 4 tested two DPAS side by side (one at 31 m and one at 32m downwind from the ammonia line source). In Period 3, the monitors sampled background concentrations with the ammonia line source turned off (due to winter conditions at site). Low concentrations were observed from all directions during this period. The ALPHA monitoring post measured 0.7 µg m^{-3} which is within the range of the site background (Cape *et al.*, 2008). It is noted that the MANDE signal is significantly larger for a couple of directions (positions 10, 11, 12) which may be due to farm sources about 1 – 1.5 km distance. Note that these would not be the same as the 'possible' farm source in periods 1-2, which was in a different direction (position 8,9) however this has not been investigated in detail. For the DPAS ALPHA sampler there were no significant differences in concentration as a function of direction. Average concentrations were 0.56 ± 0.04 µg m^{-3} (assumed sample volume) or ~1µg NH_3 sampled. However this is significantly lower than the external ambient concentration (0.7 µg m^{-3}), implying that there are losses of ammonia either in the inlet or to sampling uncertainties within the DPAS. The ALPHA sampler in position 13 was similar to all the other ALPHA samplers.

For period 4 (Figure 4 RHS) the ammonia release system was switched on as indicated by the red bar in the top graph. During Period 4, unfortunately there were severe adverse weather conditions, including driving snow and rain. These weather conditions were seen to significantly affect the operation of the DPAS sampling system in two ways: firstly the mouth of the DPAS clogged with snow reducing the sampling air flow and putting a “reactive” surface onto which the ammonia would readily absorb, as shown in Figure 5. Secondly, as illustrated in Figure 6, condensation or impaction of snow (or rain) inside the DPAS led to citric acid painted on the DPAS roof surface (as described in Section 2.2) being dissolved. It is possible that the snow (or rain) also affected the individual ALPHAs and MANDEs during this period. Bearing these issues and caveats with Period 4 data, a few clear observations can be made from these results: As with the Period 3 results, there is clearly a much higher mass of ammonia sampled onto the Period 4 MANDEs in the direction from which the ammonia is released (primarily positions 12, 1 and 2). As with the previous periods, the ALPHAs do capture some directional variation that trends smoothly from a maximum of ~12µg at position 9 (N/ENE) to a minimum of 2.5 µg at position 3 (SW/WSW). However the ALPHAs do not capture the particular directional signal associated with the ammonia line source at positions 1-2 (S/SW which should dominate the signals) and there is a consistently higher measured ammonia in all directions compared to the MANDE DPAS. It is possible the issues with condensation of the precipitation (snow, ice, rain) caused the lower ammonia masses to be sampled in direction of the ammonia line source.

Overall the results from Periods 3 and 4 indicated that the performance of the MANDE samplers was much more successful for directionally sampling the ammonia, compared to the ALPHA sampler. However due to the confounding factor of the snow and rain during Period 4 the experiment was extended to a final period to test the DPAS with the MANDE samplers further.

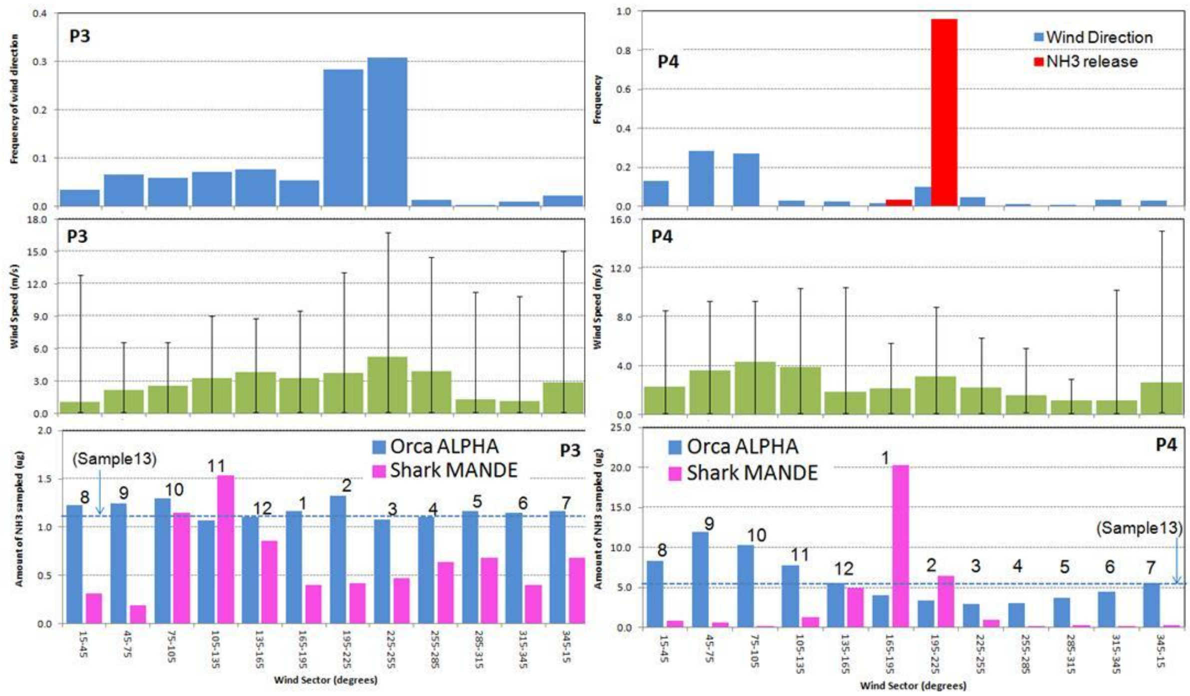


Figure 4 Period 3 and 4 ALPHA sampler in 1 DPAS results and MANDEs in the other: (Top) Frequency distribution of wind sectors (30 degree bins) corresponding to 12 sampling positions. (Middle) Mean wind speed (m/s) corresponding to 12 sampling positions. The error bars represents the min and max wind speeds. (Bottom) Amount of NH_3 sampled in each of 12 sampling positions. *Note differences in y-axis scales between periods.*

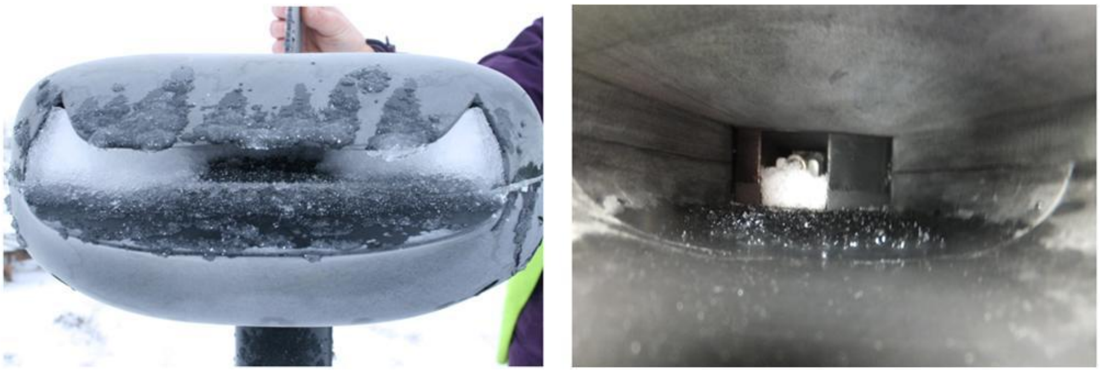


Figure 5 Heavy snowfall during period 3. LHS: Mouth of DPAS is pictured here filled with snow ; RHS: Air channel inside DPAS is pictured here blocked up with snow

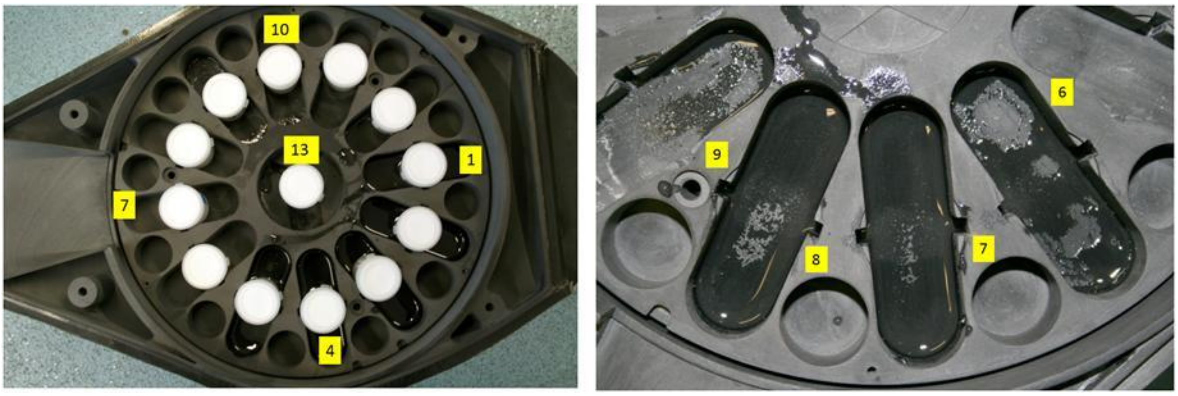


Figure 6 Rain water inside interior of DPAS. Citric acid that had leached from the coated surface of the DPAS interface and subsequently recrystallised is also visible

3.3 Period 5: MANDE samplers in DPAS side-by-side comparison

In the final Period 5, MANDE samplers were placed in both DPAS at 31m and 32 m respectively. The results are summarised in Figure 7. During this period there were no significantly severe adverse meteorological conditions and there was a reasonably high level of ammonia release. The ammonia measured on the MANDEs was clearly higher in the direction from the line source, primarily positions 1 and 2. Generally ammonia masses not from the direction of the line source were of an order of magnitude lower than in the direction of release. In addition, there was relatively good agreement between the two parallel DPAS in all sampler positions, proving that the method was reproducible in two parallel samplers.

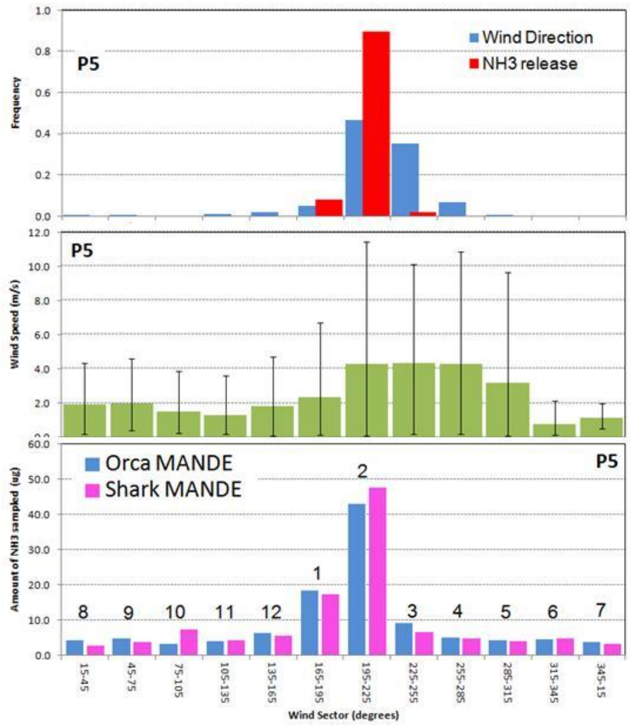


Figure 7 Period 5 results with MANDEs in both DPASs (Top) Frequency distribution of wind sectors (30 degree bins) corresponding to 12 sampling positions. (Middle) Mean wind speed (m/s) corresponding to 12 sampling positions. The error bars represents the min and max wind speeds. (Bottom) Amount of NH_3 sampled

4. Theoretical Discussion (R. Timmis and M.A. Solera Garcia)

4.1 Process framework

There are 2 main sources of ammonia at Whim: an artificial line source ($_S$) coupled to wind, and the existing landscape ($_L$) ammonia. Ammonia makes its way into the MANDEs by either ventilation (V), variable according to wind direction and speed, or diffusion (D):

$$\text{MANDE ammonia} = V_S + V_L + D_S + D_L$$

4.2 Aim of analysis

To estimate an average directional concentration of ammonia equivalent to the average from an automatic monitor, based on MANDE total ammonia collected. We start by extracting/estimating individual components.

4.2.1 Quantify or estimate diffusion ($D_S + D_L$)

The diffusion component ($D_S + D_L$) could have been estimated directly if we had any sectors without ventilation. However the wind data shows that none of the MANDEs were subject to a diffusion-only component. Sector 7 had the lowest ventilation of all, with 0.22 % of total ventilated hours (0.43 h out of 194 h). The average mass of ammonia collected in that sector for both samplers is 3.5 µg. Assuming some of that mass may be due to ventilation, we estimate 3 µg of diffusion-derived ammonia ($D_S + D_L$) per MANDE (applies to all sectors).

4.2.2 Estimate ventilated components ($V_S + V_L$) by removing diffusion (3 µg)

The ammonia release at Whim is triggered by wind speed (>2.5 m/s) and direction (180-215°), see Figure 8, orange shading. The release in one minute is determined by the wind status in the previous minute and the wind that reaches the DPAS is determined by the 'current' wind data, rather than the 'previous minute' wind data. The one-minute time difference between the current DPAS direction and the previous source direction means that ammonia can be effectively released over a wider arc of wind directions than 180-215°. Specifically, the wind data for period 5 shows ammonia effectively released between 154-241° (yellow shading in Figure 8), which corresponds to DPAS sectors 12-3. There are occasions when the alignment of the sampler to the prevailing wind will mean that 2 sectors are ventilated at the same time, in varying proportions. To take this into account, the wind run per sector is estimated proportionately using a 'weighted approach' rather than an 'all or nothing' approach.

Table 3 shows the estimates of ammonia for all sectors, averaged from both samplers, and after removing the diffusion estimate of 3 µg. It also shows the total weighted wind run per sector (length of wind that went through that particular sector). Sectors 12-3 were subject to both the artificial ammonia source and the landscape ammonia ($V_S + V_L$). The 8 sectors (4-11) were only subject to the landscape ammonia (V_L) and received an average of 1.5 µg per sector; sectors 4 and 11 adjoin the set of four sectors that received line source ammonia, and their average landscape ammonia is also 1.5 µg. On this basis, it was estimated that the landscape ammonia (V_L) contribution to the four sectors 12-3 was 1.5 µg.

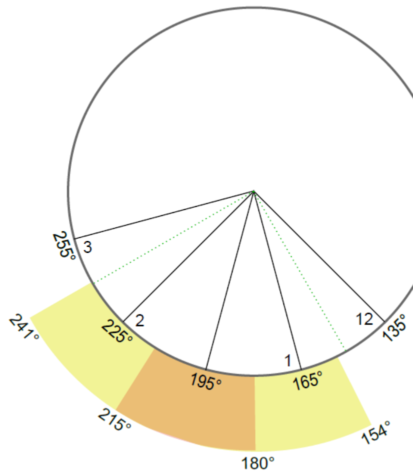


Figure 8 Conceptual diagram of ammonia release in relation to DPAS sectors. The ammonia release at Whim is triggered by wind speed (>2.5 m/s) and direction (180-215°), see orange shading. The wind data during period 5 shows ammonia release between 154-241° (yellow shading). The dotted green lines show how two sectors could be ventilated at the same time due to wind direction falling between sectors.

Table 3 Estimates of ventilated ammonia per sector (in µg) after removing the diffusion component from all sectors (3 µg).

Sector	12	1	2	3	4	5	6	7	8	9	10	11
[Mass – D] (µg)	4	16	42	5	2	1	2	1	0	2	3	1
Weighted wind run (km)	34	203	1363	1009	217	26	2	2	8	8	4	10

4.2.3 Estimating the uptake efficiency of ammonia for sectors 12-3

The sectors subject to the artificial ammonia source can then be used to estimate the uptake efficiency. For this calculation, the weighted NH_3 wind run is used; this is the proportionately-weighted wind run occurring at those times during Period 5 when the line source was releasing ammonia.

The results are summarised in Table 4. It can be seen that for sectors 1-3 the uptake efficiency is fairly consistent, suggesting a similar ammonia uptake process is at work. Sector 12 has a very low wind run, which suggests that it is important to maximise the amount of wind exposure, i.e. the location of the samplers in the field needs to take into account the predominant wind direction. Figure 9 shows the relationship between the wind speed profile and the ammonia captured for sectors 12-3. Sectors 1 and 3 have similar wind profile distributions. Sector 2 has a higher proportion of the higher wind speeds and it is the sector with the longest exposure to the artificial ammonia source and with the largest amount of ammonia collected (42 µg).

Table 4 Estimates of uptake efficiency of ammonia for sectors 12-3

Sector	Weighted NH3 wind run (km)	V_S (µg)*	E (µg NH_3/ km)
12	2	2.5	1.25
1	153	14.5	0.09
2	602	40.5	0.07
3	41	3.5	0.09

*Evaluated by subtracting the total diffusive contribution (D) and the ventilated landscape contribution (V_L) from the total mass sampled

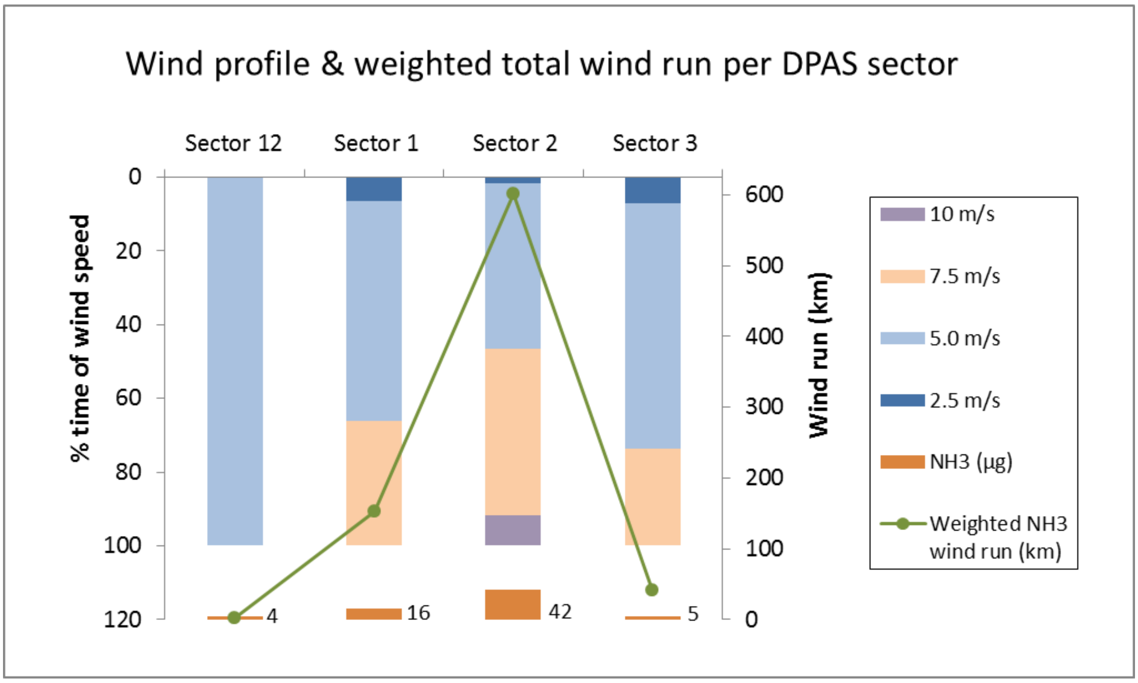


Figure 9. Summary of DPAS deployment results, showing the 4 sectors subject to the artificial ammonia source in relation to the ammonia mass measured (µg)

5. Conclusions and recommendations

The DPAS sampling system was successfully tested at the Whim Bog site in 2012-2013. During 5 exposure periods both the operation of the DPAS with ALPHA passive samplers and MANDE flux samplers were assessed. It is noted that the DPAS are compromised in snowy conditions, as illustrated in Figure 5

ALPHA samplers have a relatively low specificity with respect to the line source directions due to the high background observed in all sample directions. This is due to the continuous nature of the diffusion sampling method and the mixing of ammonia within the body of the DPAS. Directional identification was possible in Periods 1 and 2, no directional resolution was observed during background conditions in Period 3 and due to the additional problems with snow in Period 4, proved inaccurate in identifying the direction of the line source. Overall the ALPHA samplers are not appropriate for use in DPAS systems as they do not respond quantitatively to ammonia fluxes.

MANDE samplers in each measurement period they were deployed clearly identified the direction in which the ammonia was coming: in Period 3 from background sources and in Periods 4 and 5 from the four wind sectors from which the line source released. The MANDEs do have a level of ammonia diffusion within the housing samplers leading to an above background ammonia measurement in all directions; however this is an order of magnitude smaller effect than with the ALPHA samplers. It is noted that without quantification of wind characteristics - in particular the frequency of wind direction and the sampling rate of the MANDE as a function of wind speed – the mass of ammonia collected on the sampler cannot be converted into an air concentration. The wind run concept developed by EA/LEC has been applied to the data to calculate a “weighted ammonia wind run” which clearly shows a good reflection of the directions from which the ammonia was emitted.

The DPAS-MANDE combination shows great potential for studying the directional variation of ammonia in the environment, with the caveats about sampling rate characterisation taken into account. Subsequent to this work the DPAS were deployed to a farm experiment where co-located meteorology and high resolution measurements of ammonia concentrations were made. This study in combination with the farm data could be used to more fully understand the sampling characteristics of the DPAS with MANDEs.

6. References

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Appendix 1: Summary of ambient ammonia concentration measurements

Estimated[1] = calculation of air concentration using theoretically derived air sampling rate for ALPHA sampler; Calibrated[2] = calibration factor applied to estimated air concentration, based on calibration of ALPHA samplers against a reference method (CEH DELTA method).

Table 5: Period 1: Monitored ambient NH_3 concentrations with triplicate ALPHA samplers at 32m.

Period 1: 3 x ALPHA samplers							Sample	BLANK	Amount	Estimated[1]	Calibrated[2]
	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	ppm NH_4^+	ppm NH_4^+	ug NH3	NH_3 (ug m^{-3})	NH_3 (ug m^{-3})
1	02/11/12	13:10	15/11/12	10:25	309.3	1.34	14.667	0.029	41.47	30.88	41.38
2	02/11/12	13:10	15/11/12	10:25	309.3	1.34	14.503	0.029	41.01	30.53	40.91
3	02/11/12	13:10	15/11/12	10:25	309.3	1.34	15.222	0.029	43.05	32.05	42.94
										Mean	41.7
										SD	1.1
										CV (%)	2.6

Table 6: Monitored ambient NH_3 concentrations with triplicate ALPHA samplers at 32m.

Period 2: 3 x ALPHA samplers							Sample	BLANK	Amount	Estimated[1]	Calibrated[2]
	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	ppm NH_4^+	ppm NH_4^+	ug NH3	NH_3 (ug m^{-3})	NH_3 (ug m^{-3})
1	15/11/12	11:50	26/11/12	10:12	262.4	1.14	23.525	0.025	66.58	58.4	78.3
2	15/11/12	11:50	26/11/12	10:12	262.4	1.14	22.815	0.025	64.57	56.7	75.9
3	15/11/12	11:50	26/11/12	10:12	262.4	1.14	23.405	0.025	66.24	58.1	77.9
										Mean	77.4
										SD	1.3
										CV (%)	1.6

Table 7: Monitored ambient NH_3 concentrations with triplicate ALPHA samplers at 32m.

Period 3: 3 x ALPHA samplers							Sample	BLANK	Amount	Estimated[1]	Calibrated[2]
	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	ppm NH_4^+	ppm NH_4^+	ug NH3	NH_3 (ug m^{-3})	NH_3 (ug m^{-3})
1	11/12/12	11:20	07/01/13	13:45	650.4	2.82	0.610	0.039	1.62	0.57	0.77
2	11/12/12	11:20	07/01/13	13:45	650.4	2.82	0.595	0.039	1.58	0.56	0.75
3	11/12/12	11:20	07/01/13	13:45	650.4	2.82	0.605	0.039	1.60	0.57	0.76
										Mean	0.76
										SD	0.01
										CV (%)	1.4

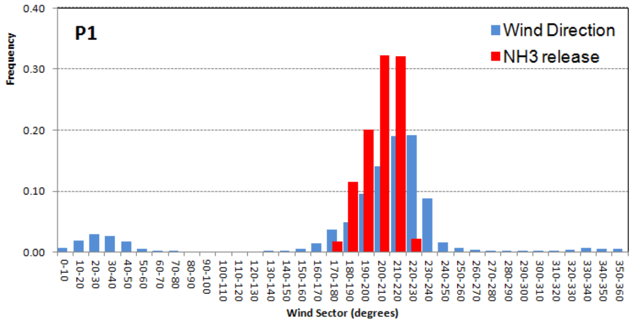
Table 8: Period 4 Monitored ambient NH_3 concentrations with triplicate ALPHA samplers at 32m.

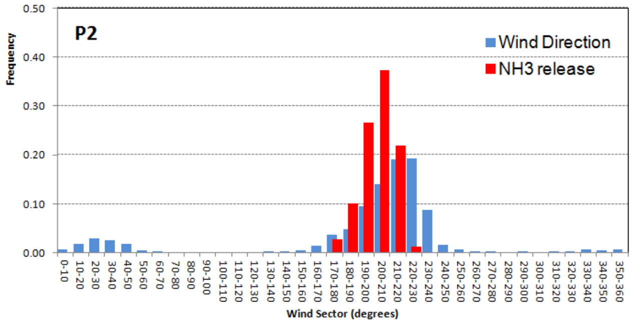
Period 4: 3 x ALPHA samplers							Sample	BLANK	Amount	Estimated[1]	Calibrated[2]
	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	ppm NH_4^+	ppm NH_4^+	ug NH3	NH_3 (ug m^{-3})	NH_3 (ug m^{-3})
1	04/03/13	11:05	25/03/13	14:00	506.9	2.20	5.339	0.010	15.10	6.86	9.19
2	04/03/13	11:05	25/03/13	14:00	506.9	2.20	5.345	0.010	15.12	6.87	9.20
3	04/03/13	11:05	25/03/13	14:00	506.9	2.20	5.794	0.010	16.39	7.44	9.97
										Mean	9.5
										SD	0.5
										CV (%)	4.8

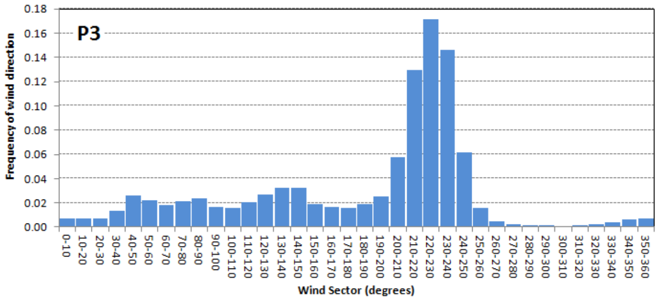
Table 9: Monitored ambient NH_3 concentrations with triplicate ALPHA samplers at 32m.

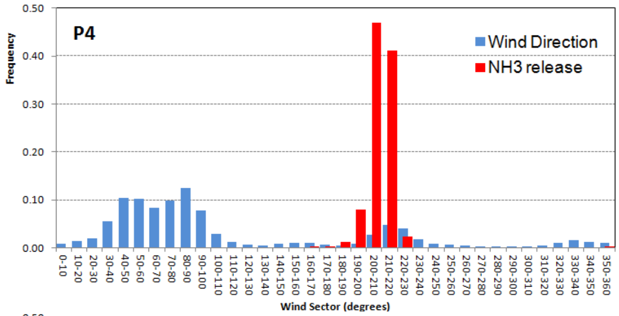
Period 5: 3 x ALPHA samplers							Sample	BLANK	Amount	Estimated[1]	Calibrated[2]
	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	ppm NH_4^+	ppm NH_4^+	ug NH3	NH_3 (ug m^{-3})	NH_3 (ug m^{-3})
1	21/04/13	14:29	07/05/13	14:05	383.6	1.67	11.395	0.033	32.19	19.32	25.89
2	21/04/13	14:29	07/05/13	14:05	383.6	1.67	10.035	0.033	28.34	17.01	22.79
3	21/04/13	14:29	07/05/13	14:05	383.6	1.67	10.615	0.033	29.98	18.00	24.11
										Mean	24.3
										SD	1.6
										CV (%)	6.4

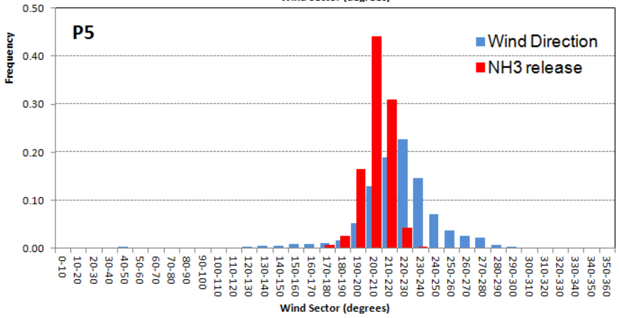
Appendix 2: Frequencies of winds and ammonia releases for 10° sectors











Appendix 3: Results for all 5 periods presented in wind rose format

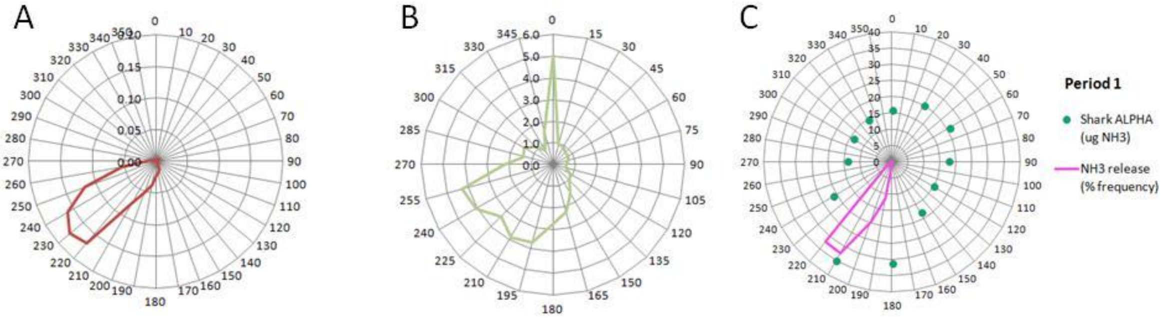


Figure 10 Period 1 Directionally resolved characteristics: A: Wind rose (radius axis: frequency); B: Mean wind speed ($m.s^{-1}$); C: mass of ammonia measured (green dots, $u.gm^{-3}$) and ammonia release (pink line, % occurance)

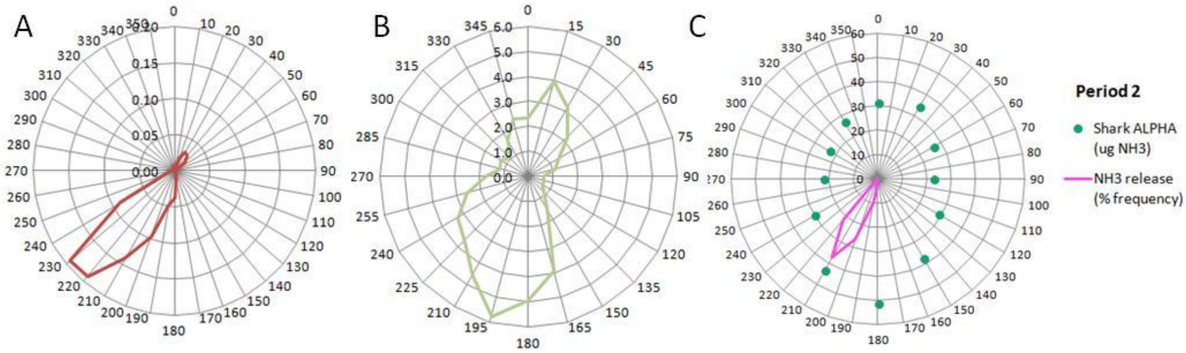


Figure 11 Period 2 Directionally resolved characteristics: A: Wind rose (radius axis: frequency); B: Mean wind speed (m.s-1); C: mass of ammonia measured (green dots, u.gm-3) and ammonia release (pink line, % occurance)

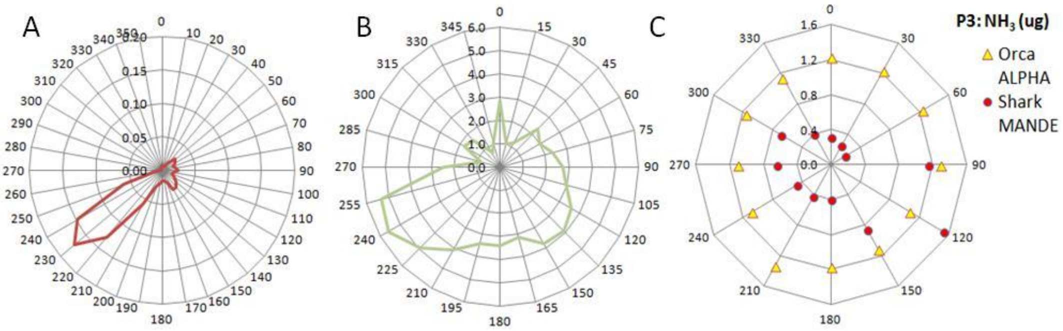


Figure 12 Period 3 Directionally resolved characteristics: A: Wind rose (radius axis: frequency); B: Mean wind speed (m.s-1); C: mass of ammonia measured (red dots Shark MANDEs; yellow triangles Orca ALPHAs). Note no ammonia release during this period.

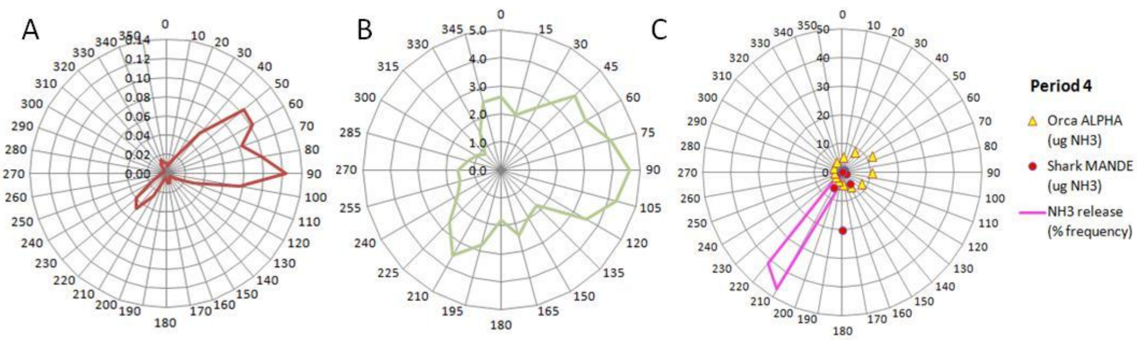


Figure 13 Period 3 Directionally resolved characteristics: A: Wind rose (radius axis: frequency); B: Mean wind speed (m.s-1); C: mass of ammonia measured (red dots Shark MANDEs; yellow triangles Orca ALPHAs; pink line ammonia release)

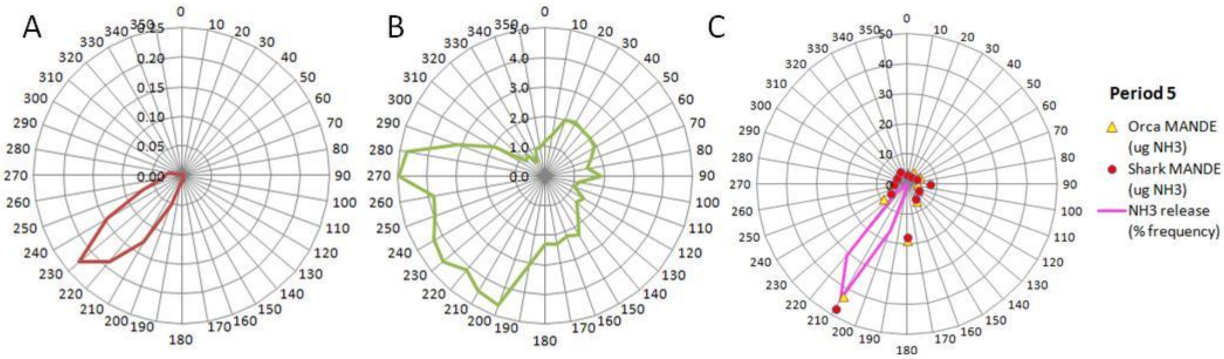


Figure 14 Directionally resolved characteristics: A: Wind rose (radius axis: frequency); B: Mean wind speed (m.s-1); C: mass of ammonia measured (red dots Shark MANDEs; yellow triangles Orca MANDEs; pink line ammonia release)

Appendix 4: Detailed results tables

Table 10: Period 1: Summary of meteorological data, NH_3 release and measured amount of NH_3 concentrations with ALPHA samplers in the DPAS Shark for corresponding 30 degree wind sectors.

PERIOD 1 Wind sector (degrees)	Wind Direction % Frequency	Mean Wind Speed (m/s)	Ammonia release % Frequency	Shark DPAS Amount of NH_3 sampled (ug)
15-45	1.50	0.96	0.00	19.85
45-75	1.58	0.79	0.00	20.47
75-105	0.71	0.66	0.00	17.69
105-135	0.92	0.76	0.00	15.00
135-165	3.48	1.31	0.00	17.94
165-195	9.59	2.49	22.57	31.31
195-225	36.31	3.78	77.01	35.10
225-255	39.80	3.688	0.39	21.32
255-285	4.32	3.233	0.00	14.19
285-315	0.74	1.440	0.00	14.03
315-345	0.47	0.977	0.00	14.77
345-15	0.58	5.047	0.03	15.73
Non-directional	n/a	n/a	100	41.8

Table 11: Summary of meteorological data, NH_3 release and measured amount of NH_3 concentrations with ALPHA samplers in the DPAS Shark for corresponding 30 degree wind sectors.

PERIOD 2 Wind sector (degrees)	Wind Direction % Frequency	Mean Wind Speed (m/s)	Ammonia release % Frequency	Shark DPAS Amount of NH_3 sampled (ug)
15-45	8.00	3.537	0.00	34.30
45-75	1.75	1.799	0.00	26.37
75-105	0.50	0.866	0.00	22.90
105-135	0.43	0.664	0.00	28.53
135-165	1.51	1.187	0.00	37.85
165-195	13.52	4.435	23.56	51.24
195-225	49.14	5.157	76.38	43.41
225-255	19.68	3.461	0.06	29.86
255-285	1.00	2.139	0.00	21.99
285-315	0.70	1.233	0.00	22.73
315-345	1.52	1.367	0.00	26.95
345-15	2.24	2.354	0.00	31.35

Table 12: Summary of meteorological data, NH_3 release and measured amount of NH_3 concentrations with ALPHA samplers in the DPAS Shark for corresponding 30 degree wind sectors.

PERIOD 3 Wind sector (degrees)	Wind Direction % Frequency	Mean Wind Speed (m/s)	Ammonia release % Frequency	Shark DPAS Amount of NH_3 sampled (ug) on MANDE	ORCA DPAS Amount of NH_3 sampled (ug) on ALPHA
15-45	3.55	1.088	0.00	0.31	1.22
45-75	6.54	2.142	0.00	0.19	1.25
75-105	5.84	2.533	0.00	1.15	1.30
105-135	7.09	3.259	0.00	1.53	1.07
135-165	7.62	3.857	0.00	0.86	1.11
165-195	5.40	3.249	0.00	0.40	1.17
195-225	28.27	3.757	0.00	0.42	1.33
225-255	30.89	5.244	0.00	0.47	1.08
255-285	1.33	3.912	0.00	0.64	1.10
285-315	0.37	1.340	0.00	0.68	1.17
315-345	0.95	1.153	0.00	0.40	1.15
345-15	2.15	2.846	0.00	0.68	1.17

Table 13: Summary of meteorological data, NH_3 release and measured amount of NH_3 concentrations with ALPHA samplers in the DPAS Shark for corresponding 30 degree wind sectors.

PERIOD 4 Wind sector (degrees)	Wind Direction % Frequency	Mean Wind Speed (m/s)	Ammonia release % Frequency	Shark DPAS Amount of NH_3 sampled (ug) on MANDE	ORCA DPAS Amount of NH_3 sampled (ug) on ALPHA
15-45	13.13	2.299	0.00	0.82	8.32
45-75	28.43	3.621	0.00	0.68	11.89
75-105	27.33	4.339	0.00	0.24	10.33
105-135	3.24	3.890	0.00	1.26	7.74
135-165	2.75	1.866	0.00	4.93	5.54
165-195	1.84	2.108	3.46	20.25	4.06
195-225	10.18	3.147	95.94	6.50	3.37
225-255	4.64	2.233	0.52	0.98	2.91
255-285	1.28	1.569	0.00	0.23	3.10
285-315	0.82	1.127	0.00	0.31	3.68
315-345	3.30	1.165	0.00	0.20	4.45
345-15	3.04	2.620	0.09	0.26	5.53

Table 14: Summary of meteorological data, NH_3 release and measured amount of NH_3 concentrations with MANDE samplers in the DPAS Shark and ORCA for corresponding 30 degree wind sectors.

PERIOD 5 Wind sector (degrees)	Wind Direction Frequency	Mean Wind Speed (m/s)	Ammonia release Frequency	Shark DPAS Amount of NH_3 sampled (ug) on MANDE	ORCA DPAS Amount of NH_3 sampled (ug) on MANDE
15-45	0.63	1.918	0.00	2.86	4.38
45-75	0.62	1.973	0.00	3.69	4.85
75-105	0.34	1.524	0.00	7.48	3.35
105-135	0.92	1.313	0.00	4.37	3.98
135-165	2.20	1.837	0.19	5.66	6.27
165-195	5.04	2.331	8.09	17.40	18.44
195-225	46.60	4.309	89.85	47.59	42.97
225-255	35.27	4.345	1.86	6.51	9.19
255-285	6.91	4.294	0.00	4.68	5.00
285-315	0.88	3.195	0.00	3.91	4.17
315-345	0.40	0.764	0.00	4.78	4.63
345-15	0.21	1.143	0.00	3.22	3.83