Interim Report to AEATechnology

Dry deposition of ammonia on rain collectors

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SUMMARY

- Collectors from standard secondary network bulk rainfall samplers have been exposed under a roof to investigate the rate of accumulation of gaseous ammonia and particulate ammonium (together referred to as NH_x) over varying times up to one week, in conjunction with real-time measurement of ambient ammonia concentrations in air
- Deposition over one week was of the order of 10 μg per collector. Typical deposition in rain was several hundred μg per collector, meaning that the error caused by dry deposition of NH_x to bulk collectors was only a few percent of the wet deposition
- These results applied where air concentrations were small, typically 1-2 μg m^{-3}

- A second set of experiments was conducted in open-top chambers supplied with known measured large concentrations of ammonia gas, at concentrations between 15 and 70 μg m^{-3}
- There was no detectable difference in overall deposition rates over 24 h at the different air concentrations under these conditions, with ca. 1.2 μg NH_3 deposited per collector
- The deposition over 24 h is of the same order as that observed at ambient concentrations, despite the very large concentration difference
- Deposition to old collectors (after several years exposure in the field) was initially (over the first 8 h) faster than to new collectors, but the differences were not detectable after 24 h.

- The initial conclusion is that dry deposition to bulk rain collectors, as used in the UK secondary network, represents a negligible bias in estimating the wet deposition of ammonium ions in precipitation over the whole of the UK

- Future work will make measurements in order to model in more detail the relationship between dry deposition of NH_3, the dependence on SO_2 concentrations, and cycles of repeated wetting and drying of the funnel surface.

BACKGROUND

Concentrations of ammonium in precipitation across the UK are determined using 'bulk' rain collectors. These collectors are open all the time, so that during dry periods both gases and particles will deposit on the collector funnel, and will subsequently be washed into the collection bottle. This dry deposition on collectors represents a positive bias in estimating the true precipitation composition. Where air concentrations of gases and particles vary widely across a region, or across the country, any significant bias may produce patterns in precipitation composition that are (partly) an artefact derived from the contamination of the collectors by dry deposition. This study is designed to determine the magnitude of the bias for ammonia gas on the UK Secondary Network bulk collectors.

This report presents the initial findings from two sets of experimental measurements conducted at Bush, near Edinburgh, in 2000.

STUDY 1

Methods

Nine replicate funnel sections from the secondary network collector were exposed under a roof (which protected them from precipitation but allowed free air flow) for periods of up to one week. Funnels were rinsed with deionised water at pre-defined intervals to determine the amount of NH_4^+ deposited on the funnel surface as a function of time, and of ambient NH_3 concentration. The ambient air concentration of NH_3 was measured continuously using a rotating wet annular denuder (AMANDA) throughout the experiments. Actual rainfall was also recorded, using up to 3 standard UK Secondary Network bulk rainfall collectors, to determine the amount of NH_4^+ deposited in rain over the same period, for comparison.

Five different experiments were conducted – dates are given in Table 1, with average air concentrations and rainfall deposition over the period.

Table 1. 'Roof' experiments to measure dry deposition to collector funnels

Experiment	Date	Average (NH_3) µg m^{-3}	Total rainfall (mm)	Total NH_4^+ deposition to collector (µg)
1	10-17/4/00	1.03	25.4	670 ± 20
2	20-27/4/00	1.17	124	550 ± 10
3	1-8/5/00	1.53	-	40 ± 20
4	5-12/6/00	1.20	16.5	170 ± 10
5	31/7-7/8/00	1.80	5.5	50

Results

Deposition to the funnel surface was approximately constant over time (see for example, Figure 1), although there were small variations that were presumably related to changes in air concentrations and/or wind speed and turbulence. The average deposition rates (μg NH_4^+ d^{-1} per collector) in each of the experiments are shown in Table 2.

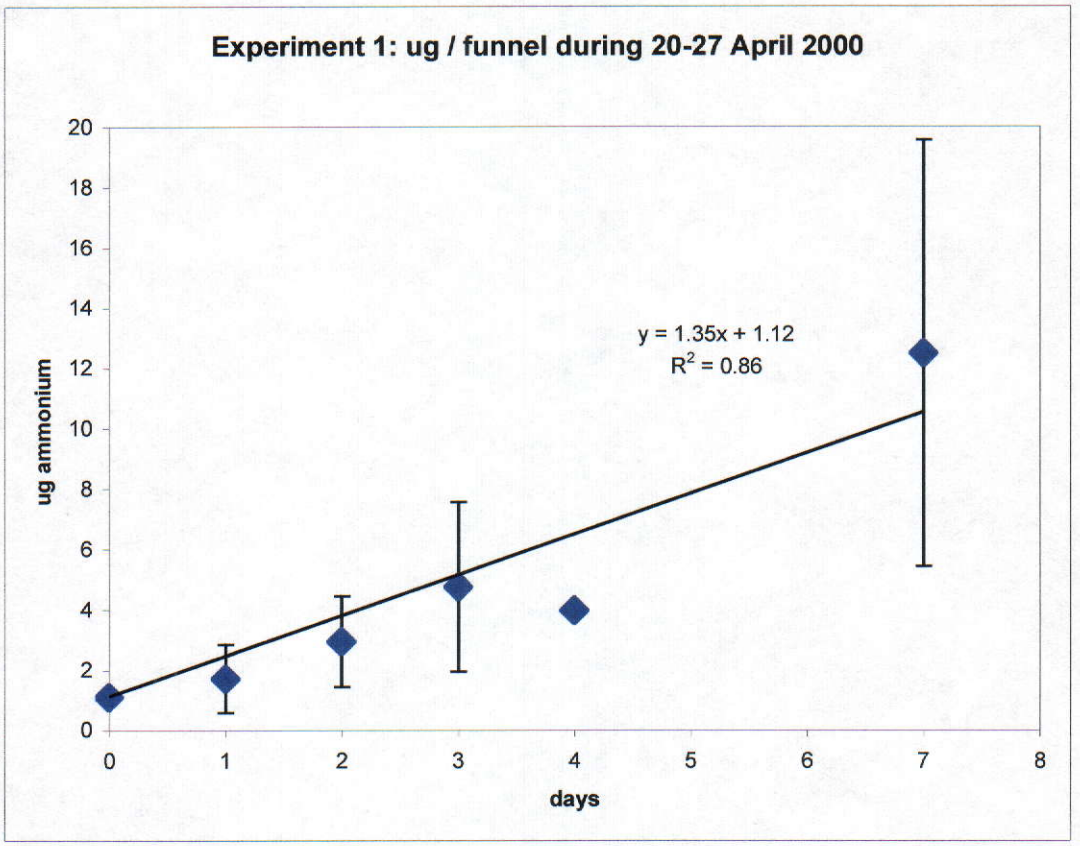

Figure 1: Dry deposition of NH_3 to funnels during Experiment 1. The intercept at t=0 is constrained by the value of the 'blank' washing from an unexposed funnel.

Table 2. Rate of NH_x deposition to protected funnels (μg NH_4^+ d^{-1})

Experiment	NH_x deposition rate (μg d^{-1})	R^2
1	1.4	0.86
2	0.9	0.47
3	2.8	0.55
4	0.2	0.36
5	0.0	0.06

Note: in Experiment 5 the amounts washed from funnels after 1 week were less than the amounts washed from funnels after shorter exposure times

STUDY 2

Methods

Controlled air concentrations of NH_3 were generated in an open-top chamber at CEH Edinburgh by the evaporation of an aqueous solution of ammonia at a known rate into the chamber air stream. Air concentrations were monitored using an AMANDA analyser, and an internal roof was fitted to the chamber to exclude rainfall. Collector funnels were exposed for pre-determined times, then washed with deionised water to determine the amount of NH_3 deposited. Both new (made in 2000) funnels and older funnels of the same design, which had been exposed for several years in collectors, were used in these experiments. Details of the experiments are shown in Table 3.

Table 3. Details of open-top chamber exposure experiments

Experiment	Dates	Average (NH_3) µg m^{-3}	Average deposition rate (µg d^{-1})
A	21-22/8/00	70	0.8
B	23-24/8/00	32	1.3
C	28/9-2/10/00	12	1.1
D	7-9/10/00	47	0.3

Results

The data for each of the funnels exposed in Experiment A are shown in Figure 2. Periods of short exposure started at different times within the overall 24 h measurement period, so that changes in temperature and relative humidity may have led to some of the variability observed. Deposition to the old funnels appeared to be much greater, in general, than to the new funnels, for equivalent exposure times. The 'odd' value at 16 hours is the mean of 3 replicates, and cannot be excluded arbitrarily from the data set. However, even after up to 24 h exposure at 70 µg m^{-3} the deposition is no more than 1.4 µg, even to the older funnels. The average deposition rate (for new funnels), given by the slope of the line in Figure 2, was 0.8 µg d^{-1}.

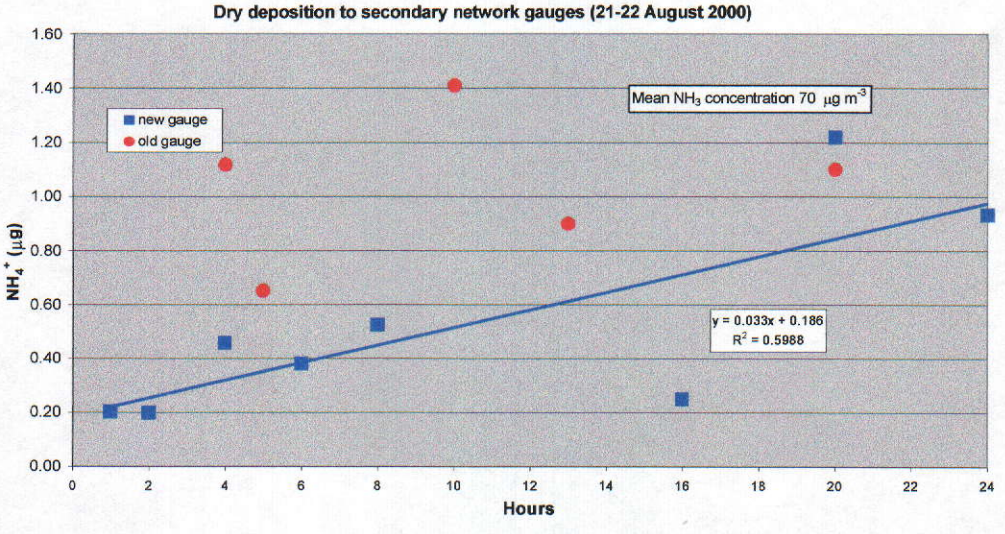

Figure 2: Dry deposition of NH_3 to funnels in open-top chamber – Experiment A

In Experiment B (Figure 3) there was less scatter to the data, and it appeared that an initially rapid rate of deposition decreased after 8 h exposure. Despite a halving of the exposure concentration compared to Experiment A, the deposited NH_3 after 24 h was very similar, at 1.4 µg per funnel. The initial deposition rate over the first 8 h was 2.9 µg d^{-1}, but over the whole experiment the average deposition rate was 1.3 µg d^{-1}.

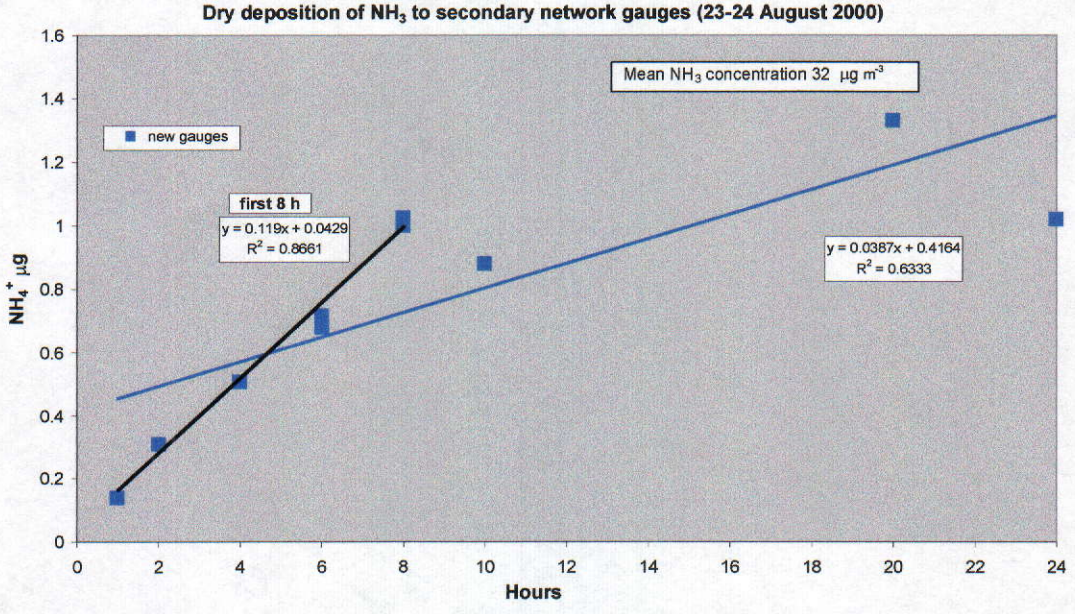

Figure 3: Dry deposition of NH_3 to funnels in open-top chamber - Experiment B

In Experiment C (Figure 4) the concentration was approximately halved again, to an average of 12 µg m^{-3}. There was more scatter than in the previous experiment, but the amount deposited after 1 day was approximately the same, at between 1 and 1.5 µg per funnel. Extending the period of exposure for a further day led to an approximate

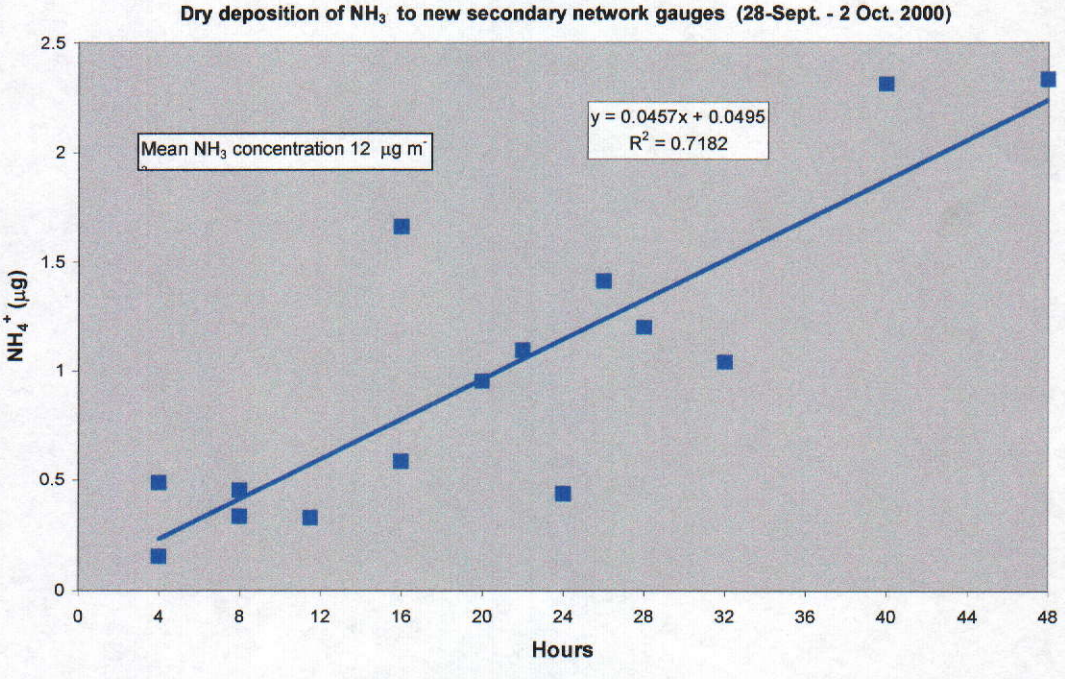

Figure 4: Dry deposition of NH3 to funnels in open-top chamber - Experiment C

doubling in deposition. As in the long-term (week) exposures at low ambient concentrations in Study 1, deposition to the funnel continued at the same rate. The average deposition rate for all samples was 1.1 μg d^{-1}. Deposition to old funnels was significantly greater than to new funnels exposed over the same period for times up to 8 hours, but thereafter no significant differences related to the age and previous history of the funnels could be detected (Table 4).

Table 4. Comparison of deposited NH_3 to old and new funnels (triplicate) after exposure to 12 μg NH_3 m^{-3} in an open-top chamber

	old		new		
Exposure time (h)	**Mean deposited NH_3 (μg)**	**Standard deviation**	**Mean deposited NH_3 (μg)**	**Standard deviation**	**Probability that old and new were same (Student's t-test)**
4	0.93	0.17	0.53	0.33	0.1
8	0.56	0.10	0.37	0.04	0.04*
16	2.05	1.25	1.71	1.09	0.7
20	1.00	0.25	0.99	0.32	1.0
24	0.58	0.263	0.48	0.08	0.5
32	0.87	0.21	1.09	0.38	0.4
48	0.84	0.39	0.58	0.11	0.2

Note that samples at 16 h may have been contaminated.
Samples at 48 h were from Experiment D, exposed to 47 μg m^{-3}.

Experiment D was designed to test for differences between new and old funnels. Three old and 5 new funnels were exposed for 48 h to an average NH_3 concentration of 47 μg m^{-3} before washing. There was no significant difference over this time period (Table 4), but the overall rate of deposition was smaller than in the earlier experiments of shorter duration, despite the larger NH_3 concentrations than in Experiment C.

DISCUSSION and CONCLUSIONS

The dry deposition of NH_3 gas on bulk rain collectors increases linearly with time, at a rate of around 1 μg N per day, and does not appear to depend on the ambient NH_3 concentration. The results were occasionally rather variable, perhaps reflecting the small overall quantities of NH_4^+ ions (often less than 1 μg) deposited on the funnels, and the possibility of contamination. In practice, this means that the bias caused by ignoring the contribution of dry deposition to the NH_4^+ deposition in bulk precipitation is negligible.

However, this result is counter-intuitive and needs further study to elucidate the cause. The most likely hypothesis is that NH_3 gas is not strongly retained (if at all) by the materials of the collector funnel, but the presence of acidic gases may lead to the formation of involatile salts on the funnel surface. The lack of SO_2 in the filtered air of the open-top chamber would therefore mean very little retention of gaseous NH_3 on the funnel surface. If this were true, then one would expect a strong correlation between the concentrations of NH_4^+ and SO_4^{2-} ions in the funnel washings, and a weak correlation with NO_3^- ions, given that NH_4NO_3 is volatile. The washings after 24 h exposure under the roof (Study 1) support this hypothesis (Figure 5). There is a correlation between NH_4^+ and SO_4^{2-} ions, but none between NH_4^+ and NO_3^- ions However, this result could also have been caused by dry deposition of $(NH_4)_2SO_4$ particles on the funnel surfaces. Further controlled experiments in the open-top chambers, where both NH_3 and SO_2 concentrations can be manipulated, will be required to test the hypothesis and to develop models applicable for use across the United Kingdom.

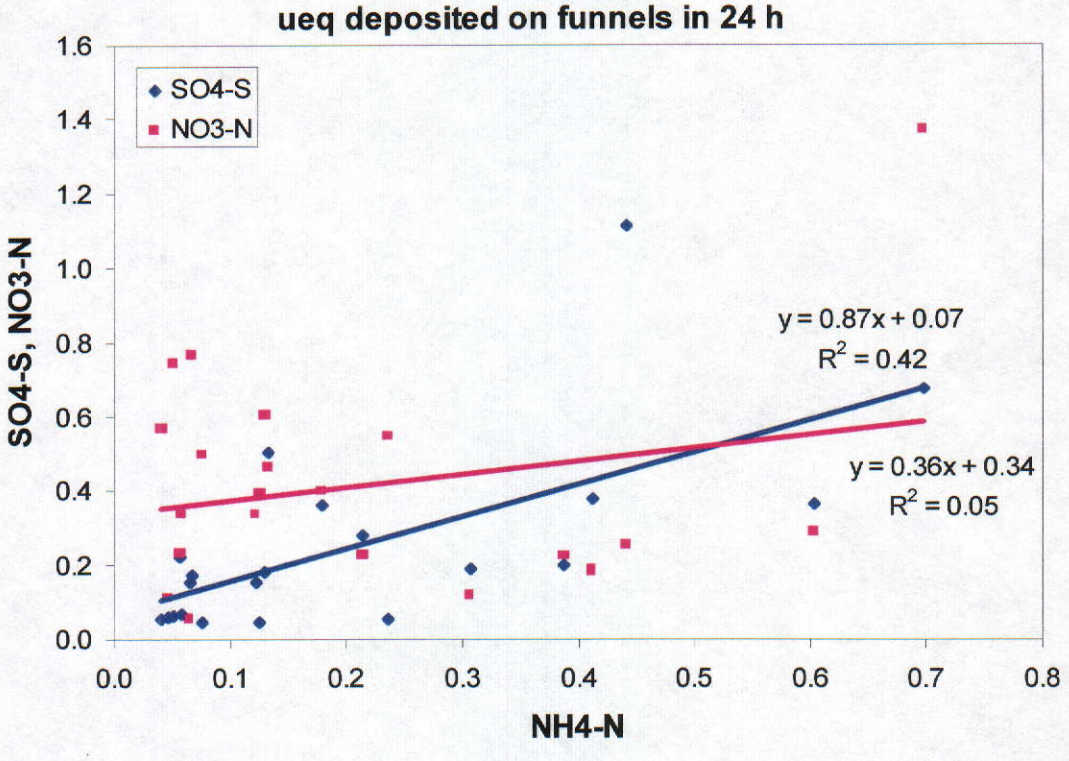

Figure 5: Deposition of sulphate and nitrate ions to funnel surface over 24 h, as function of deposited ammonium ions (Study 1)