

# A new diffusion denuder system for long-term, regional monitoring of atmospheric ammonia and ammonium.

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**Abstract:** Estimating regional patterns in concentrations of atmospheric ammonia (NH<sub>3</sub>) gas and ammonium (NH<sub>4</sub><sup>+</sup>) in aerosol is essential to assess dry deposition, as well as to test the performance of long-range transport models. Until now, methods for monitoring NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> (collectively NH<sub>x</sub>) have focused on either passive sampling, which does not sample aerosol NH<sub>4</sub><sup>+</sup>, or active sampling techniques suitable for sampling over several minutes to 24 hours. The classical active sampling approach is the diffusion denuder, which typically involves either a complex annular denuder or a long (0.5 m) and fragile glass tube. A new denuder implementation is reported here that has been designed for long-term sampling of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>. By sampling at just 0.35 l min<sup>-1</sup>, the method is suitable for monthly measurements and uses 0.1 m long glass denuders, which may be sent safely by the normal postal service to monitoring sites. Two denuders are applied in series to test for adequate NH<sub>3</sub> capture efficiency in each sample, while a subsequent acidified paper filter collects NH<sub>4</sub><sup>+</sup>. The method has been implemented at over 50 sites across the UK as part of a new national monitoring network. The detection limit is <0.01 µg m<sup>-3</sup> and the sampling is sufficiently accurate to show the seasonal patterns at different sites. This low-cost method will be useful to address future trends in NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>, especially in relation to compliance with international agreements to reduce NH<sub>3</sub> emissions.

Keywords: ammonia, ammonium, monitoring, denuder, sampling methods.

## INTRODUCTION

The increase in anthropogenic activities leading to ammonia (NH<sub>3</sub>) emission has led to concerns over the impacts of ammonia on atmospheric chemistry and ecosystems. Reaction of

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NH<sub>3</sub> to form NH<sub>4</sub><sup>+</sup> containing aerosol affects the atmospheric transport distance of other regional pollutants, as well as the global radiative balance through light scattering effects (Sutton et al. 1994, ten Brink et al. 1996). Deposition of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> (collectively NH<sub>x</sub>) leads to acidification and eutrophication of sensitive habitats, with consequent changes in plant and animal communities (Sutton et al. 1993, Fangmeier et al. 1994). Assessment of these impacts requires that concentrations and fluxes of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> be quantified.

Monitoring of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations is important for several purposes and the monitoring approach selected may vary for each. In the first instance, it is of interest to observe trends between years, with some indication of seasonal variability. This might be accomplished by detailed time resolved monitors, which also provide data at an hourly level. However, while such measurements (e.g. Buijsman et al. 1998; Burkhardt et al. 1998) fulfil an important role in improving process understanding, they are too expensive to implement at more than a few sites. By contrast, a second interest of being able to map the spatial pattern of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations requires that sampling be made at a larger number of sites. This is particularly important for NH<sub>3</sub>, which is very locally variable (e.g. Asman et al. 1998). Although a monitoring network could never cover the full variability of NH<sub>3</sub> concentrations, with a dense network (e.g. >2-4 sites per 100 km x 100 km) the main regional patterns for most countries could be detected (For the UK this equates to 50-100 sites). A primary need for maps of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations is to help model patterns and total budgets of dry deposition. In this respect, detailed spatial coverage is more important than high time resolution. As a consequence, sampling methods that can be implemented cheaply at many sites with low time-resolution would be highly attractive. For this purpose, monthly sampling is sufficient to detect seasonal variation. A number of passive methods have been applied to measure NH<sub>3</sub> concentrations (e.g. Hargreaves and Atkins 1987, Ferm and Rodhe 1997, Thijssse et al. 1998). However, these do not provide NH<sub>4</sub><sup>+</sup> concentrations and their implementation has often proved to be unreliable and subject to large correction factors (RGAR 1997).

Given the increasing concern related to NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> (collectively NH<sub>x</sub>), the UK Department of the Environment, Transport and the Regions has initiated a new National Ammonia Monitoring Network. The first task was to select a sampling method capable of monitoring NH<sub>3</sub> both in polluted areas (>5 µg m<sup>-3</sup>) and in very clean areas (<0.1 µg m<sup>-3</sup>). For this purpose it was found that classical diffusion tube samplers were insufficiently sensitive, and an improved method was needed (Sutton et al. 1997). This paper reports the design and

application of a new low cost diffusion denuder system, which was developed to meet this need, referred to as the DENuder for Long Term Ammonia (DELTA). The denuder is based on the original design of Ferm (1979), but is optimized for long-term sampling and distribution to site operators through the normal postal service. The method is simple to implement at a large number of sites, and should be of particular relevance as countries seek to monitor long-term changes (over 5-10 years) in  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations in relation to new  $\text{NH}_3$  emission abatement policies agreed by the UNECE and EC (Sutton et al. 2001).

## METHODS

### *Denuder design*

The classical denuder of Ferm (1979) consists of a 0.5 m denuder, which is not convenient for posting to remote sites. By contrast, shorter annular denuder or honeycomb variants of this approach are widely available, but are much more expensive (Allegrini et al. 1984; Sioutas et al. 1999). Each of these approaches is designed for short-term sampling of typically 1-24 hours. A key point in the design of a denuder system, as explained by Ferm (1979), is that the length of the denuder required to obtain near complete capture of a reactive gas is a function of the diffusion rate of the gas and the air-sampling rate. Ferm (1979) showed that:

$$\chi_a^{\text{out}}/\chi_a^{\text{in}} = 0.819 e^{-14.6272 \Delta} + 0.0976 e^{89.22 \Delta} + 0.01896 e^{-212 \Delta} \quad (1)$$

where  $\chi_a^{\text{in}}$  is the concentration of  $\text{NH}_3$  in the air entering the denuder, and  $\chi_a^{\text{out}}$  is the concentration of air leaving the denuder, and where:

$$\Delta = \pi DL/(4F) \quad (2)$$

given that  $D$  is the diffusion coefficient of  $\text{NH}_3$   $2.09 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  (Hargreaves and Atkins 1987),  $L$  is the length of the tube (m), and  $F$  is the flow rate ( $\text{m}^3 \text{ s}^{-1}$ ) through the tube. This shows that tube diameter is not important, since the residence time rate through a wider denuder at a given  $F$  is proportionately slower. (This applies within the range necessary to maintain laminar flow according to the Reynolds number, although Murphy and Fahey 1987 note that diameter can become important at high flow rates when capture is inefficient).. The internal diameter of the denuder can therefore be selected for convenience and robustness, and here 6 mm i.d. borosilicate glass tubes are used. Increasing the sampling rate implies a requirement for a longer denuder sampling section for a given fractional collection of the gas. Since monthly sampling is able to collect sufficient  $\text{NH}_3$  with a much lower sampling rate than with daily sampling, a much shorter denuder can be used. Here a target airflow rate of

0.35 l min<sup>-1</sup> is used, and from equation 1 it can be calculated that 97% of the NH<sub>3</sub> should be captured by a perfectly absorbing surface (such as an acid coating) in 8 cm.

A further requirement is to minimize the capture of aerosol in the denuder. In order to achieve this, the air should be under laminar flow in the sampling portion of the denuder. Laminar flow in the tube is obtained when  $Re < 2000$  and  $L > 0.05 d Re$ , where  $Re$  is the Reynolds number (Ferm 1979). For the tube sampling conditions applied here,  $Re$  may be calculated (Ferm 1979) as 73, resulting in a tube length required to develop laminar flow of 2 cm. In order to ensure laminar flow, in the study here 2 cm of denuder is left uncoated at the inlet, allowing 10 cm long denuders to be used which are convenient for posting to local site operators. In addition, at the front of the 10 cm glass denuder an additional 2 cm glass tube length is added to ensure laminar flow is complete even if sampling rates should increase slightly.

### ***Preparation of the denuders for sampling***

A range of acids may be used to coat the denuder wall in order to capture NH<sub>3</sub>. In preliminary tests, 5% phosphoric acid was used (Sutton et al. 1997). However, citric acid was found to be preferable for low blanks and greater capture efficiency, and has been used for the network since May 1997.

To prepare the glass denuders for sampling, these are first soaked in 0.1% NaOH, then rinsed several times with deionized water and dried in an oven at 100 °C. Finally, a solution of 5% citric acid in methanol is taken up by suction 8 cm into the tube and then left to drain. The tubes are dried in NH<sub>3</sub> free air that has been passed over silica gel. The coated denuders are stopped with polyurethane end caps.

### ***Filter sampling for NH<sub>4</sub><sup>+</sup> containing aerosol***

Having removed NH<sub>3</sub> from the air stream in the denuder, a post denuder filter may be used to capture NH<sub>4</sub><sup>+</sup> containing aerosol. This aerosol is potentially volatile, especially when sampling over long periods and in the NH<sub>3</sub>-free atmosphere after the denuder. In order to avoid volatilization losses, a cellulose fibre filter is used (Whatman No. 1, 25 mm diameter), impregnated with 50 µl of 13% citric acid in methanol. The impregnated filters are prepared and dried in a vacuum dessicator, and then loaded with one per holder into filter packs (Gelman Sciences).

### ***Combined air sampling system***

The denuder plus filter pack combination is oriented vertically during sampling, to minimize particle capture by sedimentation, and mounted in a plastic field box. When the box is mounted outdoors, a cut-down 80 mm diameter polyethylene filter funnel is used as an air inlet to prevent sampling of rain (The denuder inlet is fitted into the stem of the filter funnel, which is placed open face down). When indoor boxes are used, 6mm i.d. polyethylene tubing (preferably < 2m long) is used to join the sampling inlet to the denuder in the sampling box, connected using an external silicone tubing sleeve. The air sampling rate is measured using a sensitive G1.6 gas meter (UGI, London) This meter reports the volume of air sampled at actual atmospheric pressure and is rated with a minimum air flow of 16 l hour<sup>-1</sup> ( $\equiv 0.0267$  l min<sup>-1</sup>), at which it is accurate to  $\pm 3\%$  within the temperature range  $-5$  to  $35$  °C. Tests with a bubble meter showed that the G1.6 meter actually operates down to  $< 0.1$  l min<sup>-1</sup>. Normally, air is sampled using a mains electricity piston air pump (Medcalfe Bros, Herts. UK.), which supplies air at the desired flow rate. At sites where mains electricity is not available, a 12-volt air pump is used (Campbell Scientific, Loughborough, UK) with a regulated rotameter, powered by a suite of lead acid batteries, and recharged by a wind generator and/or photovoltaic cells.

### ***Chemical analysis and calculation of NH<sub>x</sub> air concentrations***

Denuders and filters are extracted in 3 and 4 ml deionized water, respectively, and analyzed for NH<sub>4</sub><sup>+</sup> using flow injection analysis and membrane diffusion. In this approach, NaOH is mixed in a continuous flow carrier of deionised H<sub>2</sub>O and samples replacing the carrier in a flow injection system. The carrier and sample is continuously passed over a Teflon membrane. At pH>12, all NH<sub>x</sub> is converted to NH<sub>3</sub> and this diffuses across the membrane in to a counter flow of deionized water, where the NH<sub>x</sub> converts to NH<sub>4</sub><sup>+</sup>, which is subsequently detected by conductivity. An automated system referred to as AMFIA (ECN, Petten, The Netherlands) including autosampler datalogging and calibration software is used. The system is normally calibrated with aqueous NH<sub>4</sub><sup>+</sup> standards of 0, 0.1, 1 and 10 mg l<sup>-1</sup>.

Air concentrations ( $\chi_a$ ) of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> aerosol in  $\mu\text{g m}^{-3}$  are calculated by:

$$\chi_a = (M_e - M_b) / V \quad (3)$$

where  $M_e$  is the mass of NH<sub>x</sub> on an exposed denuder or filter,  $M_b$  is the average mass of NH<sub>x</sub> in the blank samples of a given batch of denuders or filters, and  $V$  is the volume of air sampled.

In order to establish complete capture of NH<sub>3</sub> for each denuder (see QA/QC below), two glass denuders are used in series joined by a 50 mm length of silicone tubing. Tests have shown only trace levels of NH<sub>3</sub> are adsorbed to this connector. According to equation (1), 99.9% of the sampled NH<sub>3</sub> should be captured within the resulting 16 cm length of denuder coating. However, to allow for possible imperfect capture of NH<sub>3</sub> by the denuders, a correction factor is applied where the total NH<sub>3</sub> concentration is given by:

$$\chi_a^{\text{total}} = \chi_a^{\text{Den1}} / (1 - \chi_a^{\text{Den2}} / \chi_a^{\text{Den1}}) \quad (4)$$

At a typical capture efficiency, where 90% of the NH<sub>3</sub> captured by the two denuders is in the first denuder, this equates to a correction factor of 1%.

### ***Quality Assurance /Quality control***

Ammonia is well known to be a difficult gas to measure accurately. It is therefore essential that sound Quality Assurance and Quality Control (QA/QC) procedures be established in order to estimate concentrations reliably. The general principles of good laboratory practice for quality assurance (QA) follow those recommended by EMEP (1996). In particular, key QA elements include: wearing of disposable gloves whenever handling samples (including by site operators), clearly labelling the inlet and outlet of denuders, and storing denuders in grip sealed polythene bags (the bag protected from NH<sub>3</sub> by acid impregnated paper), checking the coating of citric acid by observation and matching samples to blanks for the same batches. At least 15 blanks are prepared for each batch of samplers.

Quality control (QC) of the samples is achieved by filtering the data according to a) capture efficiency in the first of the two denuders compared with the total captured, b) assessment of the air flow rate. Of the total NH<sub>3</sub> captured by the two denuders, a value of 75% in the first denuder (calculated as  $100\chi_a^{\text{Den1}} / (\chi_a^{\text{Den1}} + \chi_a^{\text{Den2}})$ ) is taken as a threshold that near complete sampling of the air has been achieved. This equates to a maximum acceptable correction factor from that measured ( $\chi_a^{\text{Den1}} + \chi_a^{\text{Den2}}$ ) of 11%. At less than 75% capture, it is possible that most of the NH<sub>3</sub> has been captured, but this is not certain. Therefore, the correction factor is still applied, but these rejected results treated with caution. At <60% capture the correction factor becomes highly uncertain and is not applied. The airflow rates of the denuders are relatively stable within the range 0.25-0.38 l min<sup>-1</sup>. A low flow rate may indicate that the pump needs to be oiled, that an extended power cut has occurred, or that there is a leak in the system. Data with an air flow rate <0.23 l min<sup>-1</sup> are therefore rejected and the sampling system serviced.

By distinguishing between runs with this standard data filtration, a comparison may be made of the effect acceptance/rejection on the mean air concentration estimate for each site. This also provides a means, to identify the most reliable estimates when exploring monthly variability. In addition to the above tests, the full dataset is investigated for outliers in relation to the functioning of the equipment. This is designed to identify the small number of runs where there was clearly a sampling malfunction.

## RESULTS AND DISCUSSION

### *Performance of the system*

The performance of the systems in relation to the standard quality control criteria was found to be very temporally variable, depending largely on the quality of the denuder acid coating. Overall, 74% of the data passed the QC filtering. By contrast only 1% of the data were removed by the manual identification of problems. Reasons for manual removal of a data point included: tube blockage, one occasion of contamination immediately after setting up a system (detected as an outlier), air pump failure ( $<0.07 \text{ l min}^{-1}$ ) or water in the denuder system. It was noted that denuders mounted indoors failed more than those outdoors, which may be an effect of increased temperature in the denuder boxes. **(INSERT FIG 1)**

An initial six-month field inter-comparison was made of the DELTA system against  $\text{NH}_3$  reference estimates at three sites in the Scotland and three in the Netherlands (Sutton et al. 1997). The reference estimates consisted of either continuous monitoring (e.g. Burkhardt et al., 1998; Buijsman et al., 1998), daily sampling (Ferm 1979) or combination of model estimates and campaign based continuous monitoring. The results of the inter-comparison are shown in Figure 1. Although there is a reasonable scatter, overall, the comparison with the reference estimates is almost 1:1. Temporal changes in concentrations between runs contribute substantially to the standard errors of both the DELTA and reference estimates for each of the six sites.

In subsequently implementing the method in the UK network, it was found that the temporal course of the acceptance under the standard QC filter varied with time. (Figure 2). The highest data rejection occurred during the initial 6-month of the network, and was found to be due to ageing of the glass surface of the denuders. The pre-soaking of denuders with NaOH before for every sample exposure reactivates polar groups on the glass, and ensures good capture efficiency. For the period since September 1997, 81% of the samples have passed the QC criteria. In Italy, Perrino and Gherardi (1999) have found citric acid unsuitable, due to potential remobilization and recommend the use of phosphorus acid. This may be a reason for

lower capture efficiency sometimes observed here with indoor sampling equipment at high temperatures. In the cooler climate of the UK compared with Italy this problem is avoided when mounting denuders outdoors, or by ensuring that indoor boxes are well ventilated.

The QC filter was used to test whether the less certain data were systematically biased compared with the selected data. In Figure 3, the mean  $\text{NH}_3$  concentration for each site in the network is reported for the full dataset (excluding manual filtration) compared with the data passing the QC criteria. Linear regression of both the actual data and log-transformed data showed no significant divergence ( $P=0.05$ ) from 1:1 with zero intercept. For each site, the % root mean square difference between the two estimates was calculated. The average for all sites was 5.7%. Figure 3 illustrates that, although the rejected data are expected to be less precise than accepted data, there is no substantial bias in these data. As a consequence all the data (with the exception of those deleted by manual filtration) are used for calculation of annual averages, while the distinction between data passing and failing the QC filtration helps in the assessment of seasonal trends. **(INSERT FIG 2)**

It is important to note that no screening of the monthly results was made in relation to sampler detection limit, so as to avoid bias of the results toward larger numbers. The detection limits expressed as the median of different individual monthly values ( $3 \sigma$  of blanks) are  $0.009 \mu\text{g m}^{-3}$  for the DELTA for  $\text{NH}_3$  and  $0.011 \mu\text{g m}^{-3}$  for  $\text{NH}_4^+$ . **(INSERT FIG 3)**

#### ***Application of the method: $\text{NH}_3$ and $\text{NH}_4^+$ concentrations at selected sites***

The performance of the DELTA system is demonstrated here by measurements at four sites in Scotland: Inverpolly (national grid reference: NC187088), Halladale (NC902488), Ellon Ythan (NJ945304) and near CEH Edinburgh at Bush (NT243639). Inverpolly is in the north west highlands of Scotland, in a region with very low livestock density; Halladale is in north east Scotland, in a remote area, but with some sheep farming, while Ellon Ythan and Bush are in mixed agricultural areas of east and southern Scotland, respectively. Sampling for  $\text{NH}_3$  started in 1996, while that for  $\text{NH}_4^+$  aerosol started in 1999 (Figure 4). **(INSERT FIG 4).**

At Inverpolly, duplicate denuders have been run for much of the time and the comparison indicated that the method is sufficiently precise to show the main seasonal trends even at air concentrations of  $<0.1 \mu\text{g m}^{-3}$ . At this site, concentrations are somewhat larger during the summer than the winter, with larger concentrations during warm years. By contrast, the seasonal pattern in  $\text{NH}_4^+$  aerosol is much less pronounced, with only slightly larger concentrations in the summer. This is expected to reflect a combination of higher rates of



conversion of  $\text{NH}_3$  to  $\text{NH}_4^+$  in winter coupled with the contribution of long-range transport of  $\text{NH}_4^+$  from areas where  $\text{NH}_3$  emission is still high during winter. The duplicate  $\text{NH}_3$  sampling at Inverpolly (mean concentration  $0.07 \mu\text{g m}^{-3}$ ) demonstrates the precision of the approach. The difference between the replicates from the monthly mean was on average  $\pm 9.5\%$ , while for the average of all the data the value was  $\pm 1.5\%$ .

At Halladale an even stronger seasonal cycle in  $\text{NH}_3$  is observed. Winter concentrations are comparable with those at Inverpolly, while summer monthly mean concentrations reach between 2 and  $9 \mu\text{g m}^{-3}$  for different years. This much larger concentration is believed to relate to the presence of sheep in the area and illustrates the highly temperature dependent nature of emissions from sheep pastures, as has been observed elsewhere (e.g. Loubet et al. 2001). The inter-year differences are believed to be related to changes in nearby grazing.

At Ellon Ythan and Bush, the seasonal patterns in  $\text{NH}_3$  concentrations are much less clear, although concentrations are highest in spring and summer. This reflects the mixed nature of  $\text{NH}_3$  sources in these areas, including grazing animals, livestock housing, manure spreading and other sources. Most manure spreading occurs in spring, which is thought to be the main reason for the high concentrations during these months. Comparing the different sites, it is clear that the  $\text{NH}_3$  seasonal patterns vary greatly between sites, reflecting the local nature of  $\text{NH}_3$  sources. By contrast, some correlation between sites for  $\text{NH}_4^+$  aerosol is seen which may be related to the much longer atmospheric residence time of  $\text{NH}_4^+$

These results illustrate both the precision of the method and its suitability for long-term monitoring of seasonal and inter-annual changes in  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations.

## CONCLUSIONS

A new diffusion denuder system has been developed here, tuned for weekly to monthly sampling, referred to as the DENuder for Long Term Ammonia (DELTA). By sampling at a flow rate of approximately  $0.3 \text{ l min}^{-1}$ , the system is able to use 10 cm denuders, which are sufficiently robust to be supplied to sites through the normal postal service. In addition, by using two denuders in series, capture efficiency can be established, providing an important means of quality control. Comparison against reference estimates showed a close agreement within the range of concentrations that was tested (site means of  $0.07\text{-}15 \mu\text{g m}^{-3}$ ). Although filtered data (<75% of total capture in the first denuder or air flow rate too low) are less certain than selected data, there is no evidence of a systematic bias in the data, and therefore

all results (with the exception of <2% rejection due to system failure or contamination etc) are used in the calculation of annual averages.

The results of 4 years monitoring at 4 Scottish sites show clear seasonal and inter-annual differences. Duplicate sampling at the cleanest site ( $0.07 \mu\text{g m}^{-3}$ ) illustrates the precision of the approach for monthly samples ( $\pm 9.5\%$ ) and the whole period ( $\pm 1.5\%$ ). It is concluded that the method provides a robust approach for regional monitoring of  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations, with sampling at many sites. By using a postal exchange with local site operators, the UK Ammonia Monitoring Network has been established with DELTA systems at >50 sites, enabling spatial patterns at a country scale to be assessed at relatively low cost. Ammonia emission controls have recently been agreed in Europe, with a target date under the UNECE Gothenburg Protocol and EU National Emissions Ceilings Directive of 2010. The monitoring will allow the changes in regional  $\text{NH}_3$  and  $\text{NH}_4^+$  to be quantified, which will be necessary to assess compliance with these international agreements.

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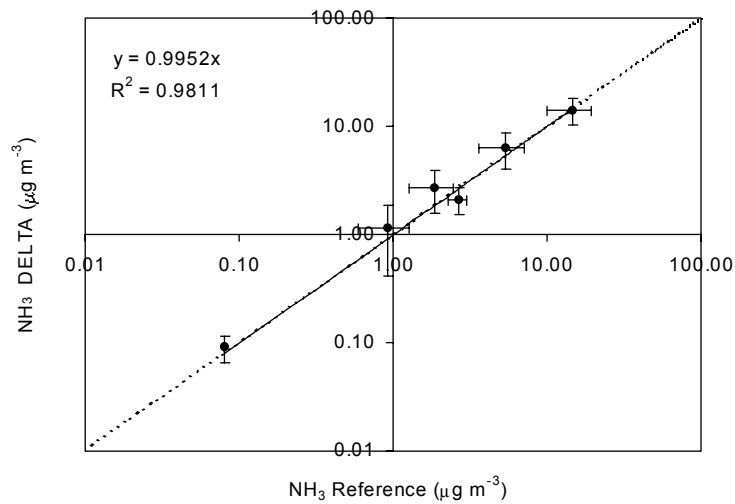
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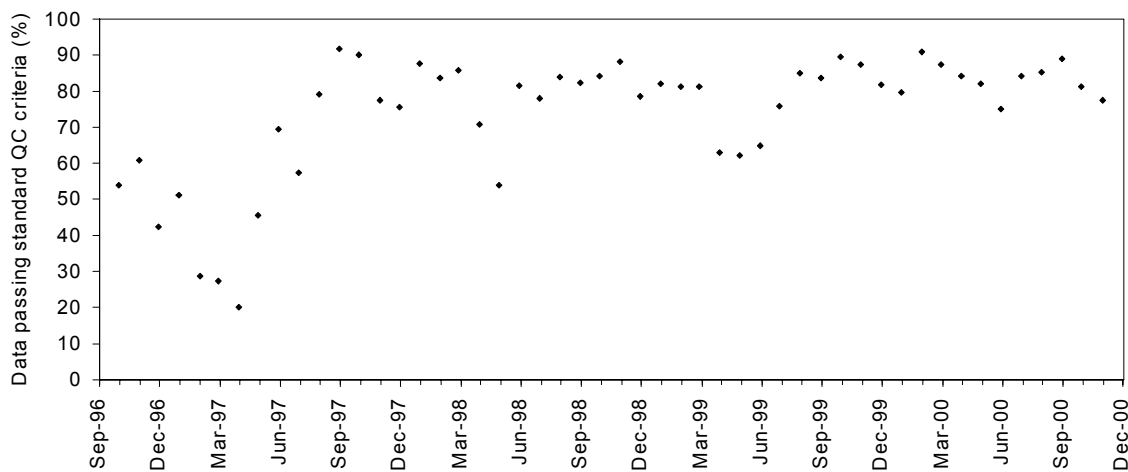
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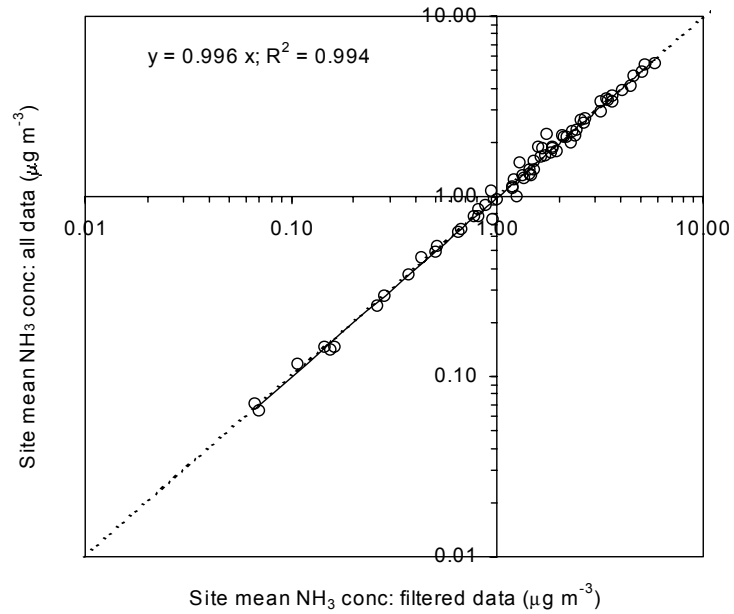
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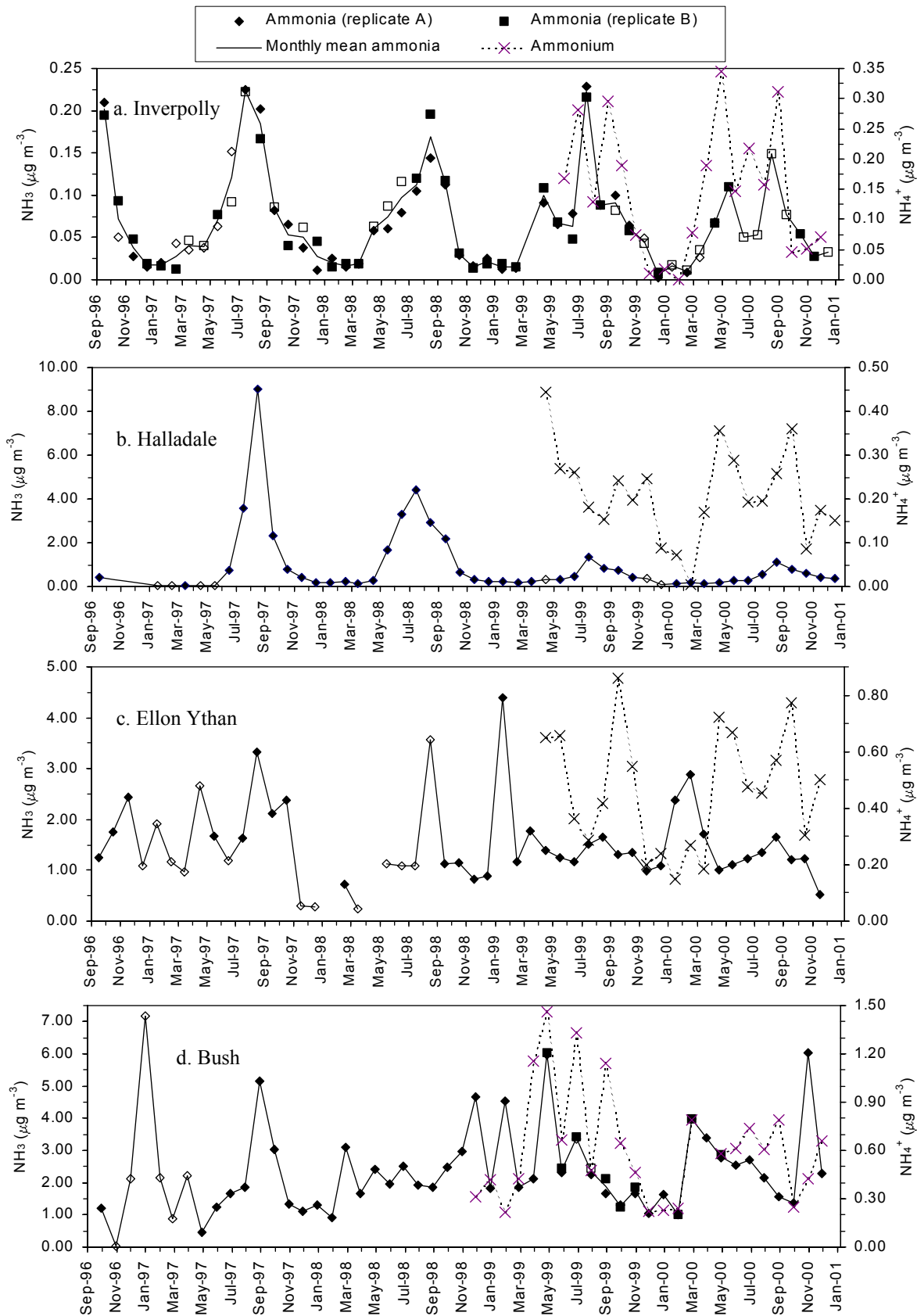
**Figure 1.** Comparison of the new DELTA system against reference estimates at six European sites. Points are the means  $\pm$  standard errors of between 3 to 7 analyses at each site for periods when both the DELTA and the reference estimate were available. At the cleanest site, the reference was provided by campaign data and model estimates (Sutton et al. 1997). The line fit is from linear regression of untransformed values.



**Figure 2.** Percentage of samples passing the defined quality control criteria thresholds (capture efficiency of the first denuder  $>75\%$  of total capture; denuder sampling rate  $>0.23 \text{ l min}^{-1}$ ) for different sampling months. Data failing the QC are less certain than those passing. The lower QC pass rate at the start was largely due to imperfect acid coating of the denuders.



**Figure 3.** Comparison for each site in the national network of mean air concentration calculated for all data compared with that for runs passing the main QC data filtration criteria. Excludes 1% of the data removed by manual filtration due to system failure etc. The overall means are 1.80 (all data) and 1.79 (filtered data). The neither the intercept nor the slope of the regression is significantly different from 1:1 ( $P=0.05$ ). The regression and  $R^2$  shown are for the log-transformed data.



**Figure 4:** Temporal record of gaseous  $\text{NH}_3$  and  $\text{NH}_4^+$  aerosol at four sites in Scotland, measured using the DELTA system. a) Inverpolly, b) Halladale, c) Ellon Ythan and d) Bush. Runs passing the QC criteria are shown for  $\text{NH}_3$  using filled symbols. Runs not passing the criteria are shown with open symbols. Measurements of  $\text{NH}_3$  at Inverpolly and some at Bush were made with two replicate systems (A and B) until April 2000.