



## THE REDUCED NITROGEN BUDGET OF AN OROGRAPHIC CLOUD

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**Abstract**—Field data collected during the GDF 93 project indicated that during polluted conditions ( $\text{SO}_{2(g)} > 2$  ppbv,  $\text{NH}_3(g) > 0.5$  ppbv), sulphate and ammonium concentrations in air increased through cloud chemistry by as much as 25%. Similarly, ammonia was seen to be consumed by cloud processing and decreased by up to 20%. In comparatively clean conditions ( $\text{SO}_{2(g)} < 0.5$  ppbv,  $\text{NH}_3(g) < 0.5$  ppbv), the sulphate loading of the aerosol was seen to remain constant, and ammonium was lost from the aerosol and outgassed as ammonia, increasing ambient ammonia concentrations by as much as 0.5 ppbv.

An ideal cloud chemistry model predicted up to 20% more sulphate production than is implied by the bulk aerosol data set. A non-ideal cloud chemistry model was used to estimate the final ammonium loading of the aerosol, which is determined by the transformation from wet cloud droplet to dry aerosol particles below their deliquescence point. The non-ideal model showed that in three of the four cases ammonia outgassed from evaporating cloud droplets, consistent with field observations, but at variance with the ideal chemistry model. The results indicate that in low pollution conditions clouds act to re-equilibrate reduced nitrogen in the aerosol phase with gaseous ammonia. The outgassed ammonia will then be rapidly deposited to semi-natural ecosystems downwind of such clouds. © 1997 Elsevier Science Ltd.

*Key word index:* Ammonia, ammonium, outgassing, non-ideal chemistry.

### 1. INTRODUCTION

Unlike the gaseous pollutants sulphur dioxide and the nitrogen oxides, ammonia ( $\text{NH}_3$ ) gas is not rapidly oxidised in the atmosphere. However,  $\text{NH}_3$  dissolves readily in rain and cloud water, and determines the acidity of water droplets, neutralizing any acidity produced during the solution and reaction of sulphur and nitrogen oxides. Reduced nitrogen also exists in the atmosphere as ammonium ( $\text{NH}_4^+$ ) salts, with dynamic equilibria being established between the gas and particle phase for the more volatile salts, ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ). Conversion of  $\text{NH}_3$  to ammonium sulphate,

$(\text{NH}_4)_2\text{SO}_4$ , or to a mixed salt such as  $\text{NH}_4\text{HSO}_4$ , occurs through gas-to-particle reactions of  $\text{NH}_3$  with sulphuric acid ( $\text{H}_2\text{SO}_4$ ), or by dissolution and reaction of  $\text{NH}_3$  in a water droplet and subsequent droplet evaporation. Formation of ammonium sulphate particles is essentially an irreversible reaction, as the sulphate salts are not volatile under atmospheric conditions.

As an air mass, containing both  $\text{NH}_3$  (gas) and  $\text{NH}_4^+$  (particle), is advected into and through a cloud, both gas and particles will dissolve and may react with other dissolved species to produce new ionic solutions which determine the composition of the aerosol and gas phase as cloud droplets evaporate.

This paper describes field observations of the budget of reduced nitrogen ( $\text{NH}_3$  and  $\text{NH}_4^+$ ) as an air mass is advected through a stationary cap cloud, and presents results from a detailed model of the cloud chemistry involved, as a first step in interpreting the observations.

## 2. METHODOLOGY

The field measurements were made during April and May 1993 at Great Dun Fell, Cumbria, in northwest England. Measurement sites below cloud (upwind or downwind) were at Wharley Croft (WC) and Moor House (MH), one site was near cloud base (Mine Road, MR) and one site was at the summit (SU). Details of the experiment are given in Choulaton *et al.* (1996), which also provides information on the methods used to sample reduced nitrogen as gas, particle and dissolved in cloud water.

### 2.1. Measurement methods

In brief, gaseous  $\text{NH}_3$  was measured using annular denuders, either by a continuous rotating wet denuder (Wyers *et al.*, 1993; Sutton *et al.*, 1996) with time resolution of 2 min, or by both wet and dry batch denuders, with 1 and 8 h sampling periods, respectively. Ammonia is very soluble in acidic solutions and modelling verifies that less than 2% of the ammonia is in the aqueous phase at the summit.  $\text{NH}_4^+$  particles were sampled using a high-volume Rotheroe-Mitchell sampler in which air is sampled isokinetically, then drawn at  $15 \text{ m}^3 \text{ h}^{-1}$  through Whatman 41 filter paper. The properties of Whatman 41 filter paper are well-documented (Hinds, 1982); the fibre diameter varies from 3–20  $\mu\text{m}$ , and the paper is approximately 0.19 mm thick.  $\text{NH}_4^+$  particles were also sampled in a four-stage Berner impactor. The MH impactor had a cut-off of 5  $\mu\text{m}$  diameter, and so excluded the largest particles. Cloud water was sampled using 2 independent active collectors (designated IEP and MOH) with hourly time resolution at both SU and R, and at site SU also by a passive sampler from which cloud water was continuously pumped to a  $\text{NH}_4^+$  analyser. Filter papers from the Rotheroe-Mitchell sampler were extracted in deionized water, and analysed by ion chromatography; cloud water was analysed directly by ion chromatography.

### 2.2. Modelling

The computer model is based upon the model of Bower (1991) which has been modified to use an observed aerosol spectrum. The explicit model has 28 categories or bins for particles, which are given an initial dry radius, number of aerosol particles in that size bin, the hygroscopic fraction, and a description of their ionic composition. Dry radius and number are taken from the hourly average spectra, observed by the Differential Mobility Particle Scatterer (Wiedensohler *et al.*, 1996). The aerosol particle distribution was divided into 2 modes, with diameter greater or less than 1  $\mu\text{m}$ . The Tandem Differential Mobility Analyser (Martinsson *et al.*, 1996) indicated that small aerosol particles had a lower hygroscopic fraction than larger aerosol particles. Particles in the smaller mode were assigned a hygroscopic mass fraction of 0.4, and the ionic fraction was assumed to be pure ammonium sulphate. In the presence of gas-phase ammonia, small aerosol particles are assumed to be fully neutralised. A hygroscopic fraction of 0.6 was assigned to the larger mode, with ion composition which most closely reproduced cloud droplet concentrations at the summit.

The cloud model advects air over GDF using FLOWSTAR (Wobrock *et al.*, 1996). Once aerosol particles exceed their critical supersaturation they grow to cloud droplets, scavenge gaseous species and sulphate chemistry

proceeds. Two output concentrations for reduced nitrogen are deduced, from ideal chemistry and non-ideal chemistry. The transition from wet cloud droplet to dry aerosol particle is not well understood, and previous models (Bower *et al.*, 1991; Sander *et al.*, 1995) are restricted to ideal chemistry, where the liquid water content (LWC) remains above  $0.01 \text{ gm}^{-3}$ . This ensures that the ionic concentration in each cloud droplet is less than 1 M; typically cloud droplets are considerably more dilute ( $\sim \text{mM}$ ). In the non-ideal model wet cloud droplets are evaporated to wet aerosol particles at 90% relative humidity and held here for 55 s, an approximate time for the air-parcel to reach the downwind sampling site. The time that the aerosol is held at 90% relative humidity determines the post cloud ammonia and ammonium levels. If the aerosol was to dry rapidly less ammonia would be outgassed. If the time was extended more ammonia would be outgassed. For example equilibrium between the aerosol and the gas phase was achieved in the model after 155 s, yet 90% of the reduced nitrogen that could be outgassed has been lost after only 55 s (see case 2, Table 3).

Wet aerosol particles have concentrations typically in excess of 2–3 M. At such strengths, electrostatic and short-range intermolecular forces between electrolytes form clusters of electrolytes in the solution, which reduces the effective mole fraction of solutes. To model the non-ideal chemistry that occurs in wet aerosol particles the Pitzer parameterisation has been employed (Pitzer, 1991), where the effective mole fraction of ionic solutes  $X'$  is given by equation (1).

$$X' = f_x [X] \quad (1)$$

where  $f_x$  is the activity coefficient of the electrolyte  $X$ , and  $[X]$  is the molal concentration. For neutral molecules the activity coefficient is represented by equation (2), where  $I$  is the molality and the salting coefficient has been set to 0.1:

$$X' = 10^{0.1I} \quad (2)$$

The Pitzer model evaluates activity coefficients that describe the effective fraction of species in solution (ions or molecules). The effective concentration (activity) of hydrogen ions is reduced (Wells *et al.*, 1996), making the solution less acidic than expected, and encouraging the transformation of  $\text{NH}_4^+$  ions to  $\text{NH}_3(\text{aq})$ . When the model attempts to set up an equilibrium between  $\text{NH}_3(\text{aq})$  and  $\text{NH}_3(\text{g})$ , the concentration of  $\text{NH}_3(\text{aq})$  exceeds the equilibrium value and  $\text{NH}_3(\text{g})$  is outgassed. The transformation from wet cloud droplet, through to wet humid aerosol (100 to 73% relative humidity), and then to solid aerosol is undoubtedly a more complex procedure than that which has been presented. However, this study gives an insight to the physical processes which are likely to take place. The effect of non-ideal solutions is to enhance the effective concentration of  $\text{NH}_3(\text{aq})$ , and to encourage outgassing and loss from the aerosol.

Four case studies were modelled: cases 1 and 2 were on 22 April for the periods 1600–1900 and 1900–2400 BST, respectively, and cases 3 and 4 were on 9–10 May, from 2300 to 0600 and from 1800 to 2400 on 10 May, respectively.

## 3. RESULTS AND DISCUSSION OF FIELD MEASUREMENTS

### 3.1. Measured budget of reduced nitrogen across the hill

Sufficient measurements were obtained to construct detailed budgets for three periods during the experimental period, on 22 April and on 9–10 May. The weather conditions were very different on these days (Colville *et al.*, 1996), with relatively polluted air in a southwesterly flow on 22 April, and less polluted easterly flow on 9–10 May. On 22 April, therefore, site WC was upwind, and site MH was downwind of the

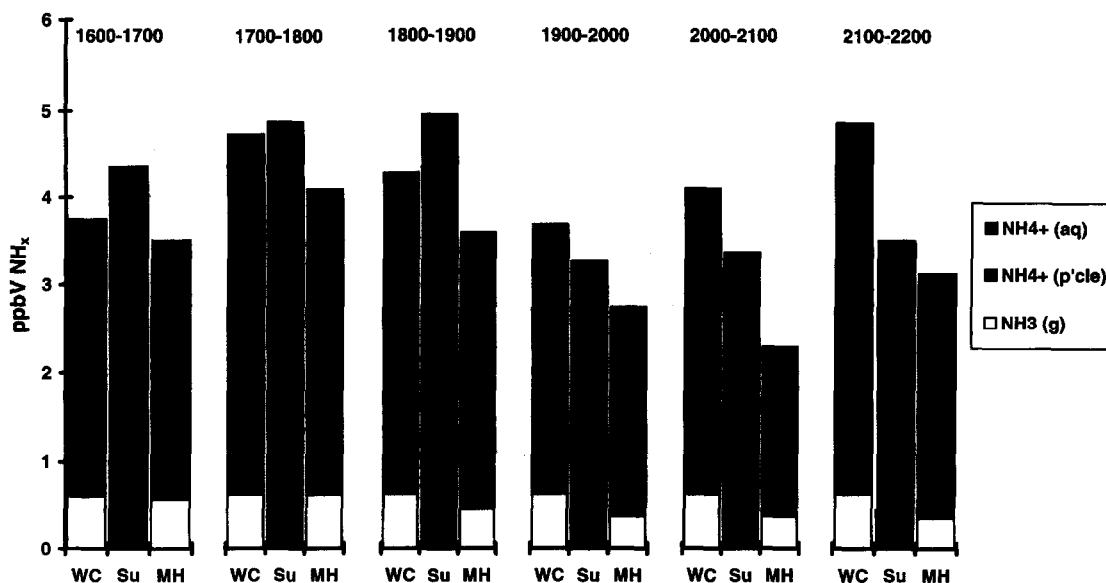


Fig. 1. Measurements of  $\text{NH}_x$  budget for case study 1 (16:00–19:00) and case study 2 (19–23:00) on the 22nd of April 1993. Concentrations of  $\text{NH}_3$  gas (open bars),  $\text{NH}_4^+$  particles (grey bars) and  $\text{NH}_4^+$  ions (black bars) in cloud water, expressed as a mixing ratio in air (ppbV), at the upwind site (Wharley Croft = WC), Summit (SU) and downwind site (Moor House = MH). Particle data are from Rotheroe-Mitchell high volume samplers. Gas measurements were made using one 8 h batch denuder over the whole period. No  $\text{NH}_3$  was detected at the Summit ( $< 0.3$  ppbv), which was in cloud.

cloud. On 9–10 May, in reversed flow conditions, site MH was upwind, and sites MR and WC were downwind of the cloud.

Figure 1 shows the total reduced nitrogen budget on 22 April, where all concentrations have been expressed as equivalent gas-phase concentrations in ppbV (parts in  $10^9$  by volume). For cloud water (IEP) this measurement combines data on aqueous-phase concentration with cloud liquid water content on an hourly basis. The gas and particle (from Rotheroe-Mitchell, RM, samplers) concentrations are given for the sites below cloud (WC and MH). Between 16:00 and 22:00 BST,  $\text{NH}_x$  concentrations upwind (WC) were within 15% of the summit cloud water values, which is within the combined measurement uncertainties, but thereafter were increasingly greater than in cloud. Light drizzle was noted at the Summit and at the downwind site (MH), which may have washed out droplets and led to a loss of  $\text{NH}_x$  across the hill. The uncertainty caused by use of an 8 h average  $\text{NH}_3$  concentration upwind is not sufficient to account for the discrepancy. The loss of  $\text{NH}_3$  downwind was also seen in the data for total aerosol mass, and all other chemical species in aerosol. As there was little evidence for dilution of the air mass by entrainment (Colville *et al.*, 1996), the most likely explanation is a miscalibration of the air flow through the RM aerosol samplers.

Figure 2 shows the measured data for the night and morning of 9–10 May, when air was flowing from MH to WC. In general, the pattern repeats that shown in Fig. 1, with cloud water estimates of  $\text{NH}_x$  being larger

than upwind and downwind measurements during the early part of the measurement period, and a move towards increased  $\text{NH}_x$  concentration upwind towards the end of the period. The small contribution (around 10%) of  $\text{NH}_3$  to total  $\text{NH}_x$  upwind means that any small systematic underestimate in  $\text{NH}_3$  concentrations will also make only a small contribution to the overall uncertainty. The upwind site was close to cloud base for much of the period, so  $\text{NH}_4^+$  particle concentrations may have been underestimated if particles were activated and grew too large for the sampling inlet. Cloud water mixing ratios derived from cloud concentrations and LWC measurements at both sites (SU and MR) were within the combined uncertainties for LWC measurements ( $\pm 20\%$ ). The large contribution (around 60%) of  $\text{NH}_3$  to total  $\text{NH}_x$  downwind (WC) also leads to a large uncertainty in  $\text{NH}_x$  downwind. The systematic smaller value downwind compared to the summit could be the result of an underestimate of  $\text{NH}_3$  (Section 3.2.1).

Figure 3 shows the measured data for the evening of 10 May, when air was flowing from MH to WC. Towards the end of the period the agreement in total  $\text{NH}_x$  across the three sites was within the experimental error around  $\pm 20\%$ , although earlier in the period there was an apparent deficit in  $\text{NH}_x$  upwind. This may have been caused by loss of droplets at the sampling inlet to the aerosol sampler, as the upwind site (MH) was in cloud initially, and came out of cloud after 23:00. There was significant entrainment of dry air (Colville *et al.*, 1996), which led to the total evaporation of smaller cloud droplets close to cloud base.

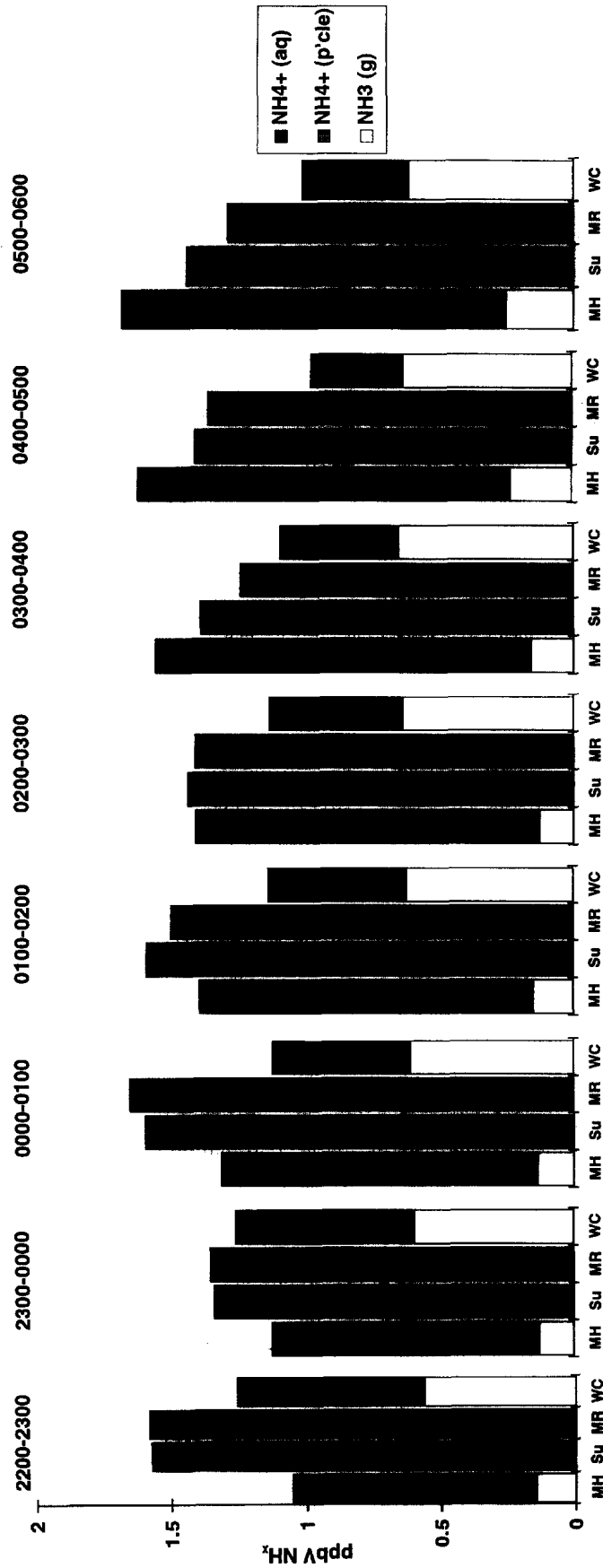


Fig. 2. Measurements of NH<sub>3</sub> budget for case study 3 (9–10 May 1993). Concentrations of NH<sub>3</sub> gas (open bars), NH<sub>4</sub><sup>+</sup> particles (grey bars) and NH<sub>4</sub><sup>+</sup> ions (black bars) in cloud water, expressed as a mixing ratio in air (ppbv), at the upwind site (Moor House = MH), Summit (SU), near cloud base (Mine Road = MR) and downwind site (Wharley Croft = WC). Particle data are from Rotheroe-Mitchell high volume samplers. Gas measurements were made using a continuous wet denuder (MH and WC), or one hour denuder (SU and MR). No NH<sub>3</sub> was detected at sites SU or MR (< 0.3 ppbv), which were in cloud.

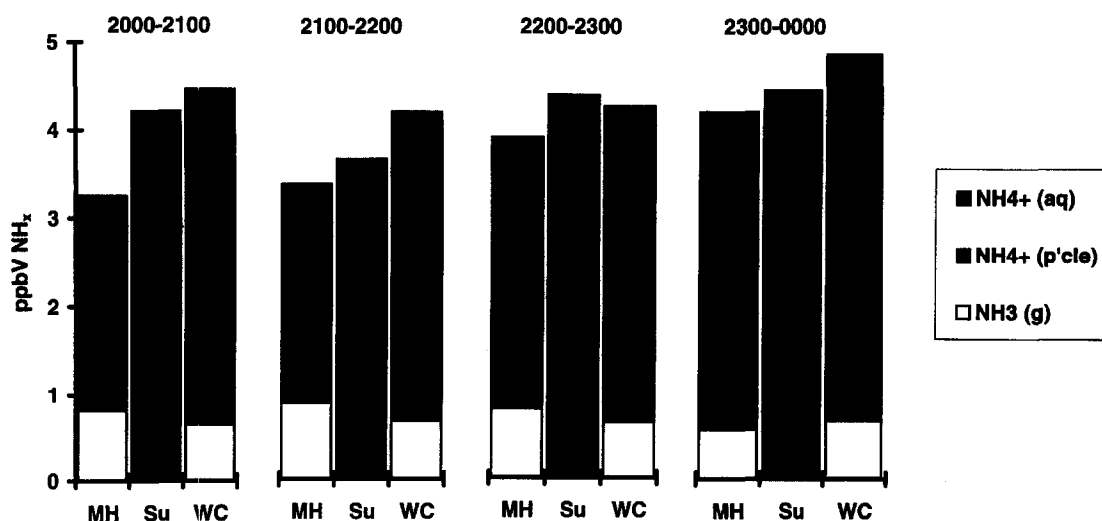


Fig. 3. Measurements of  $\text{NH}_x$  budget for case study 4 (10 May 1993). Concentrations of  $\text{NH}_3$  gas (open bars),  $\text{NH}_4^+$  particles (grey bars) and  $\text{NH}_4^+$  ions (black bars) in cloud water, expressed as a mixing ratio in air (ppbv), at the upwind site (Moor House = MH), Summit (SU) and downwind site (Wharley Croft = WC). Particle data are from Rotheroe-Mitchell high volume samplers. Gas measurements were made using a continuous wet denuder (MH and WC), or 1 h denuder (SU and MR). No  $\text{NH}_3$  was detected at site SU or MR ( $< 0.3$  ppbv), which were in cloud.

The particulate  $\text{NH}_4^+$  produced was not measured at site MR, and therefore not included in Fig. 3. Although no  $\text{NH}_3$  gas was detected at cloud base (measured concentration  $< 0.2 \mu\text{g m}^{-3}$ ) concentrations at site WC ( $0.49 \mu\text{g m}^{-3}$ ) were around 15% of total reduced nitrogen, and similar to concentrations upwind (site MH).

### 3.2. Discussion of measurements

3.2.1. *Analysis of reduced nitrogen data.* Uncertainties in concentration were around 0.1 ppbv for continuous  $\text{NH}_3$  data, after comparing aqueous standards between sites. However, the data systematically underestimate the concentration appropriate to the budget study, by as much as 35% because of pronounced vertical gradients in concentration caused by dry deposition to the moorland surface (Sutton *et al.*, 1997).

There was generally good agreement between the two particle sampling devices at MH. Given the upper cutoff for particle size in the Berner impactor, the agreement between the samplers suggests that most of the particulate  $\text{NH}_4^+$  was in the small size fraction, as expected. Uncertainties in particle measurements can arise from analytical errors ( $< 5\%$ ), from under-capture of large particles ( $> 5 \mu\text{m}$  diameter), and from errors in measuring the volume of air passing through the samplers. In case studies 1 and 2, the volume flow measurement was thought to be in error, leading to systematic underestimation of particle concentrations at Moor House. Systematic under-capture of particles would also occur if particles had been activated in cloud droplets close to cloud base. This may have

occurred during case studies 3 and 4 at the upwind site (Moor House).

Effective concentrations of  $\text{NH}_4^+$  in air, derived from concentrations in the two independent cloud samplers, and average cloud liquid water content (LWC) derived from concentrations were generally in good agreement on both occasions, and for both sites on 9–10 May, but not on the evening of the 10th May, when the Mine Road site was close to cloud base, and LWC was highly variable over small spatial scales ( $\sim 10$  m) (Pahl *et al.*, 1996). The error introduced by combining time-averaged concentrations with time-averaged cloud LWC can be assessed by comparison with the continuous cloud measurements.  $\text{NH}_4^+$  concentrations were calculated as 10 min averages before combination with 10 min average cloud LWC data (Fig. 4). The data show considerably more structure on the shorter time scale, as expected, but overall good agreement. If anything, the 10 min concentrations are slightly smaller than the 1 h averages, as expected on the basis of taking a product of hourly means (mean concentration  $\times$  mean LWC) rather than a mean value of the product (concentration  $\times$  LWC). If concentration and LWC were uncorrelated, the resultant hourly mean air concentration would be similar regardless of averaging time, but as, in general, concentration is inversely proportional to LWC, it can be shown that the mean of (concentration  $\times$  LWC)  $<$  (mean concentration)  $\times$  (mean LWC), as shown in Fig. 4. The measurement uncertainty from the two independent active cloud collectors is also illustrated. Uncertainties in LWC measurement are discussed in Colville *et al.* (1997), and are of the order of 10%.

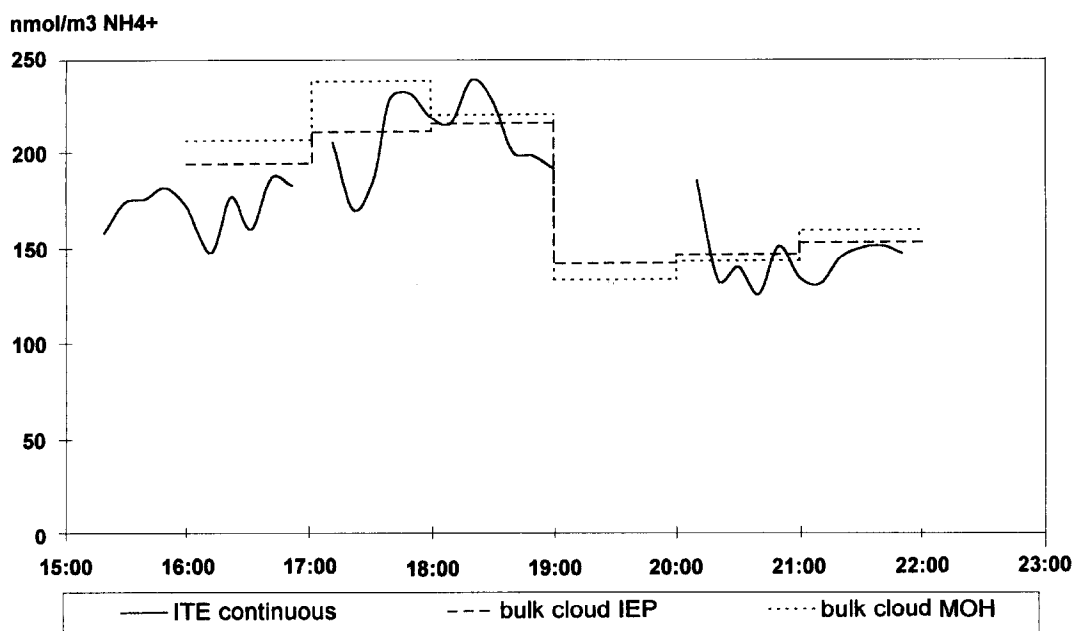


Fig. 4. Ammonium in the aqueous phase at the summit, cases 1 and 2.

Independent cloud water devices and analytical methods were in good agreement (e.g. Fig. 4), suggesting that concentration measurements were within analytical uncertainty ( $<5\%$ ). The overall uncertainty in equivalent mixing ratios of  $\text{NH}_x$  for cloud water are therefore dominated by the uncertainty in LWC.

**3.2.2. Phase transformation of reduced nitrogen through cloud processing.** It was highlighted above that the Rotheroe-Mitchell bulk aerosol filters suffered from a flow rate problem for cases 1 and 2 and this explains the non-conservation of reduced nitrogen (Fig. 1). Normally, the chemical modification of the aerosol is examined by comparing pre-cloud, in-cloud and post-cloud aerosol loadings (as for cases 3 and 4). However, the flow rate error leads to more mass being sampled before cloud than after. This may be resolved by taking ratios of ions to a conserved species, typically sodium. However in these two case studies, the aerosol is principally composed of ammonium sulphate, with some nitrate but very little sodium chloride.  $\text{NO}_x$  gas data showed that  $\text{NO}_x$  may have been lost through the cloud (Cape *et al.*, 1996), which may or may not have led to increased nitrate but is unlikely to have led to a decrease in nitrate. Therefore an increase in the  $\text{SO}_4/\text{NO}_3$  ratio may indicate sulphate production. If nitrate had increased this may lead to an underestimate of  $\text{SO}_4$  production, but is unlikely to lead to an overestimate.

Figure 5 presents the output sulphate to nitrate ratio divided by the input sulphate to nitrate ratio. It can be seen that sulphate production varies significantly throughout the two case studies. Case 1 has an average of  $21 \pm 21\%$  sulphate production, and case 2

has  $25 \pm 10\%$  production. The  $\text{SO}_4/\text{NO}_3$  ratio greater than 1 early in the period in Fig. 5 indicates sulphate production in case 1. It is possible that the increase (Fig. 6) in acidity, associated with a change in aerosol composition entering the cloud reduces the efficiency of ozone oxidation of S(IV) to S(VI) and therefore lowers the sulphate production (and hence  $\text{SO}_4/\text{NO}_3$  ratio). The sulphate production increase later on (Run 2) may be attributed to a change of oxidant. An increase in hydrogen peroxide entering the cloud combined with elevated sulphur dioxide levels could account for the rising sulphate production as the run progressed.

The ammonium to nitrate ratio (Fig. 5) presents a more complex picture. The ammonium loading of the aerosol increases by  $13 \pm 13\%$  for case 1, while for case 2 the fraction of the aerosol that is composed of ammonium has decreased by  $9 \pm 4\%$ . The  $\text{NH}_4/\text{NO}_3$  ratio for case 2 indicates that ammonia is outgassed or there was an increase in nitrate relative to ammonium. Since gaseous ammonia was observed in the lee of the cloud, it is deduced that this indicates ammonia outgassing.

The uncertainty in the ammonia input, a single data point for an 8 h period ( $0.4 \mu\text{g m}^{-3}$ ) from the batch denuders, leaves us in doubt about the small-scale (here hourly) fluctuations of input gaseous ammonia. The cloud becomes more acidic from case 1 to case 2 (Fig. 6), and this indicates that ammonia entering the cloud may have decreased throughout the evening of the 22nd of April. Gaseous ammonia in the lee of the cloud drops from  $0.35 \mu\text{g m}^{-3}$  for case 1 to  $0.2 \mu\text{g m}^{-3}$  for case 2 (Fig. 12). In summary, the annular denuder

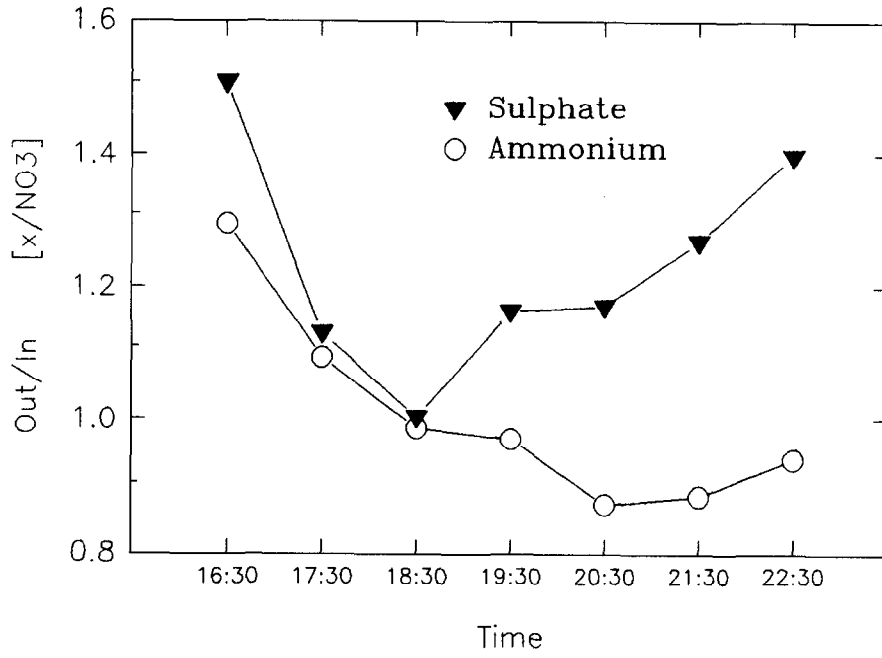


Fig. 5. Sulphate and ammonium ratio to nitrate: case 1 (16:00–19:00) and case 2 (19:00–23:00) observed on the 22nd April 1993.

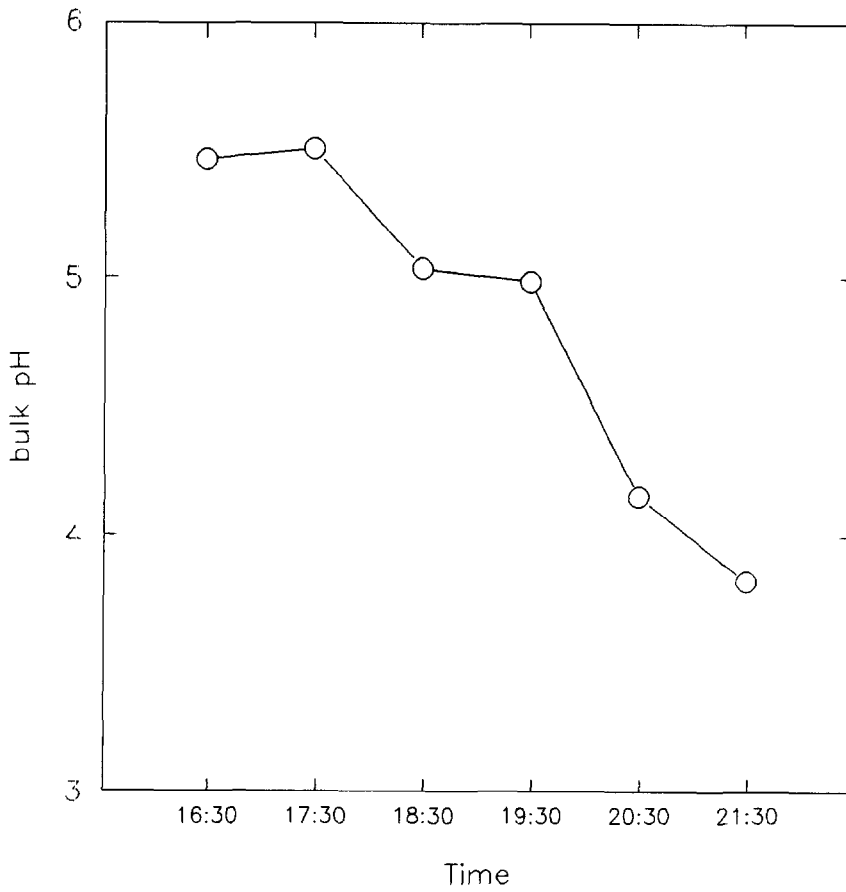


Fig. 6. Acidity of cases 1 and 2: 22nd April 1993.

Table 1. Observed upwind and downwind ammonia concentrations

Case study	Time	Pre-cloud ( $\mu\text{g m}^{-3}$ )	Post-cloud ( $\mu\text{g m}^{-3}$ )
Run 3	00:30	0.09	0.44
	01:30	0.10	0.45
	02:30	0.11	0.46
	03:30	0.09	0.47
	04:30	0.12	0.48
	05:30	0.17	0.46
	06:30	0.18	0.45
	07:30	0.12	0.46
	Avg.	0.12	0.46
	Std.	0.03	0.01
Run 4	20:30	0.61	0.51
	21:30	0.62	0.50
	22:30	0.65	0.49
	23:30	0.59	0.48
	Avg.	0.62	0.49
	Std.	0.02	0.01

observes ammonia downwind of the cloud. This is unexpected, given the large amount of sulphate production inferred. Therefore not all the gaseous ammonia is being fixed as ammonium. Indeed in case 2, it is

possible that the ammonia concentration entering the cloud is much smaller than the average suggests, as indicated by the acidity of the cloud, i.e. in case 2 the aerosol particles may act a source of ammonia, and cloud processing has increased the ammonia loading of the airstream.

Field case 3 is characterised by evidence of ammonia outgassing. More ammonia was observed after the cloud ( $0.45 \mu\text{g m}^{-3}$ ) than observed entering ( $0.1 \mu\text{g m}^{-3}$ ) (Table 1). The cloud became less acidic as this run progressed (Fig. 7), but is still too acidic for ozone to become a significant contributor to S(IV) oxidation. The Rotheroe-Mitchell data (Fig. 8) present a clear picture of aerosol composition before and after cloud processing. Equivalent aerosol loadings calculated from the cloud samples compare well with input sulphate and ammonium loadings, while there is a clear difference between input and final particulate ammonium, with  $0.6 \mu\text{g m}^{-3}$  of  $\text{NH}_4^+$  lost from the aerosol after passage through the cloud. Very little sulphur dioxide was present ( $< 0.5 \text{ ppbv}$ ), although this was enough to provide the  $0.25 \pm 0.5 \mu\text{g m}^{-3}$  of sulphate production implied by the Rotheroe-Mitchell aerosol measurements. The low upwind gaseous ammonia concentration ( $0.1 \mu\text{g m}^{-3}$ ) in case 3 could be attributed to the atmospheric conditions

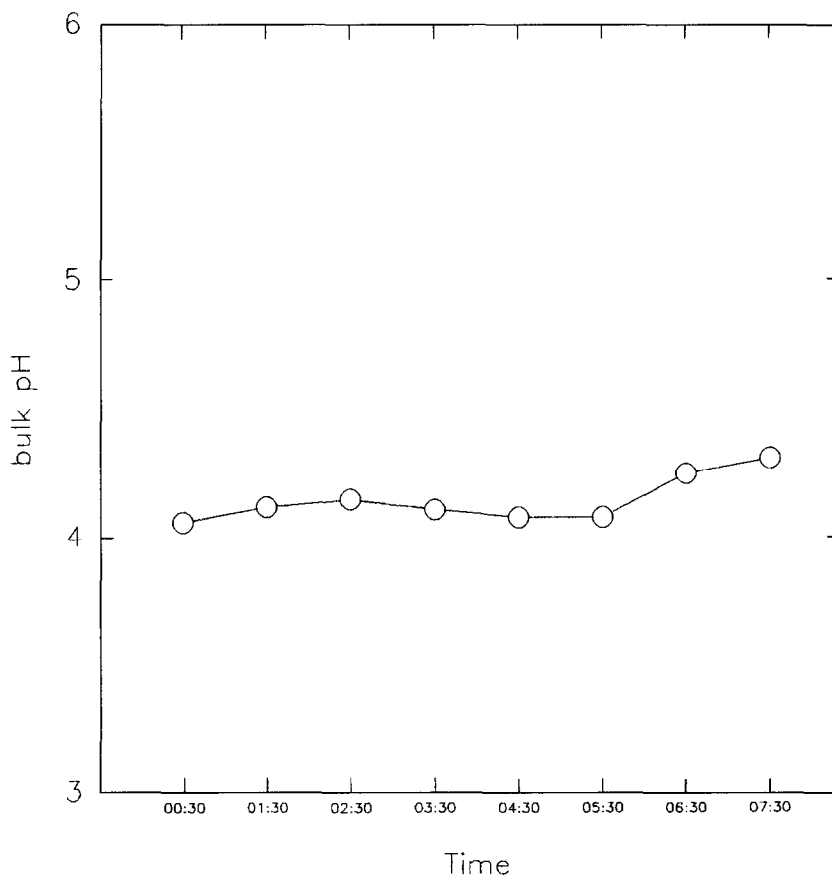


Fig. 7. Acidity of case 3: 10th May 1993.



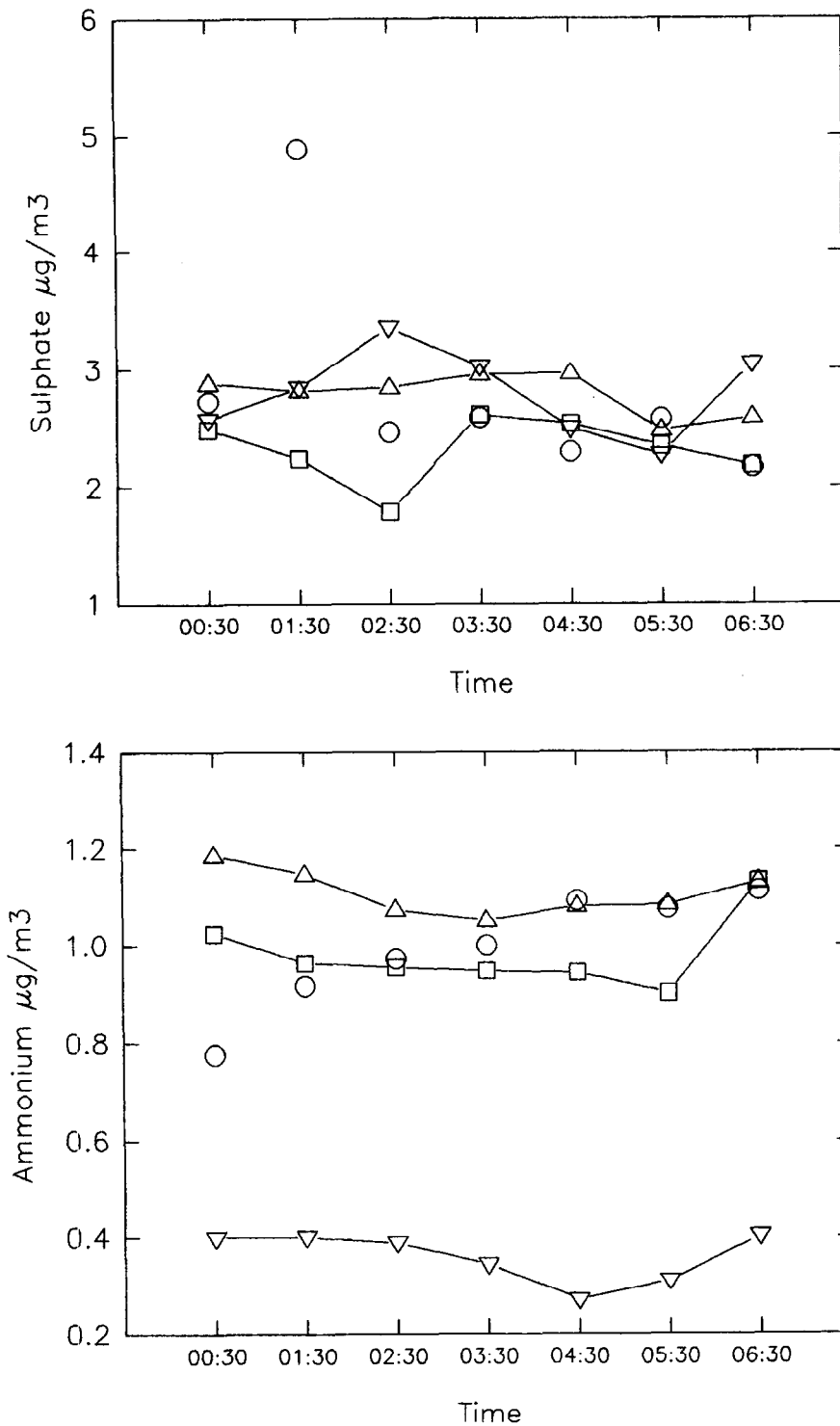


Fig. 8. Rotheroe-Mitchell aerosol filter samples case 3.

encountered at the upwind field site, which led to the presence of cloud at what was intended to be a pre-cloud sampling site. The Rotheroe-Mitchell aerosol samplers might have been expected to perform poorly in such conditions, yet the agreement with total  $\text{NH}_4^+$  in cloud is good. In case 4, the upwind site (MH) was

similarly affected by cloud, yet ammonia was nevertheless detected in significant quantities ( $0.6 \mu\text{g m}^{-3}$ ). Field case study 4 is an example of cloud chemistry acting as a mechanism to neutralise acidic aerosol. Gaseous ammonia was fixed as particulate ammonium, and  $0.7 \pm 0.4 \mu\text{g m}^{-3}$  reduced nitrogen changes

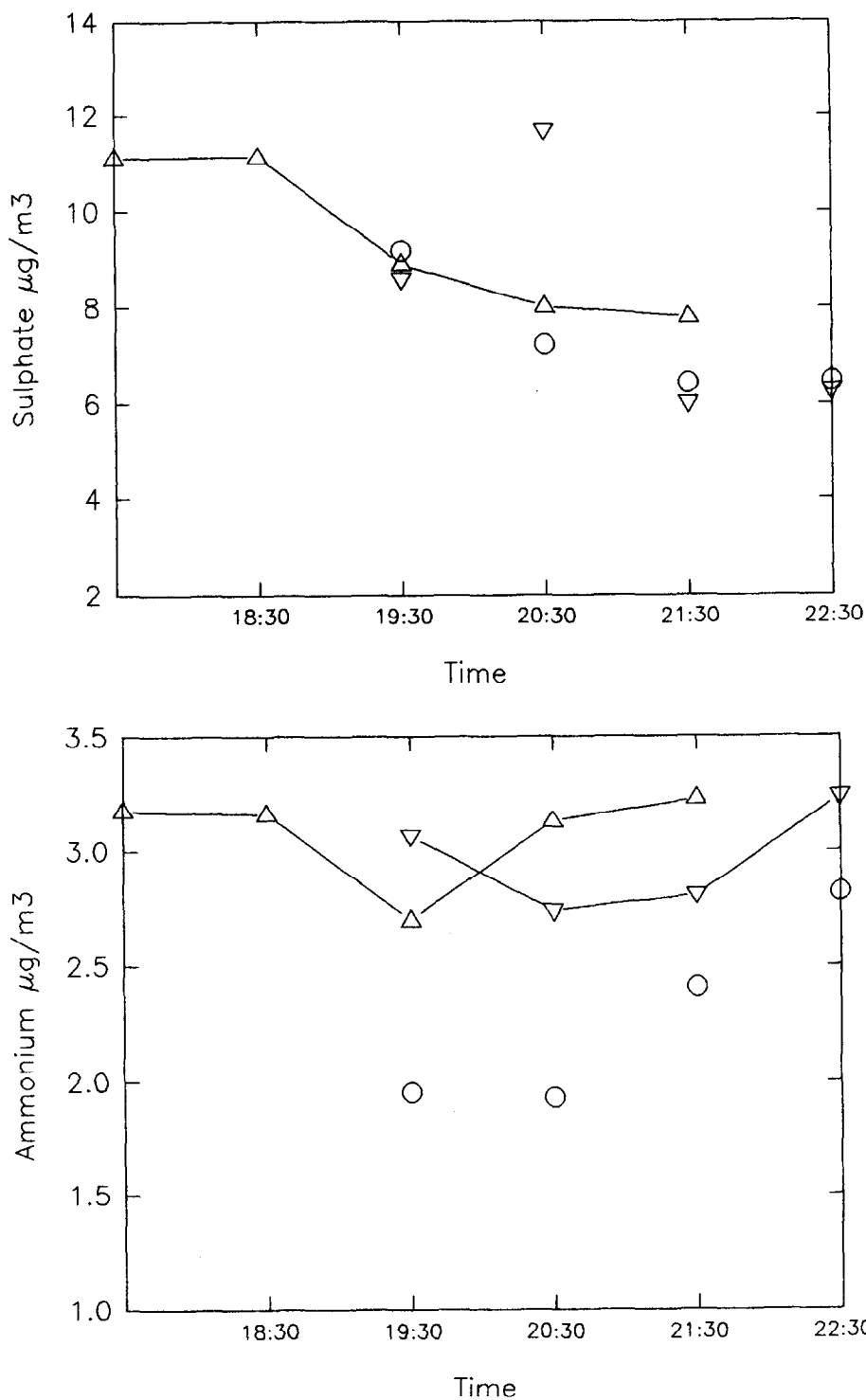


Fig. 9. Rotheroe-Mitchell aerosol filter samples case 4.

phase. Minimal sulphate production occurred ( $0.4 \pm 0.1 \mu\text{g m}^{-3}$ ; Fig. 9) from comparison of Rotheroe-Mitchell filters. However, this case study is complicated by the microphysical conditions under which the cloud was produced. The northeasterly air flow led to a complex updraught profile with multiple activation

points (Bower *et al.*, 1996), giving rise to the preferential growth of large cloud droplets. The cloud remained acidic throughout this run (Fig. 10), indicating that any sulphate production occurred through reaction with hydrogen peroxide. The aerosol data set indicated little sulphate production, implying that

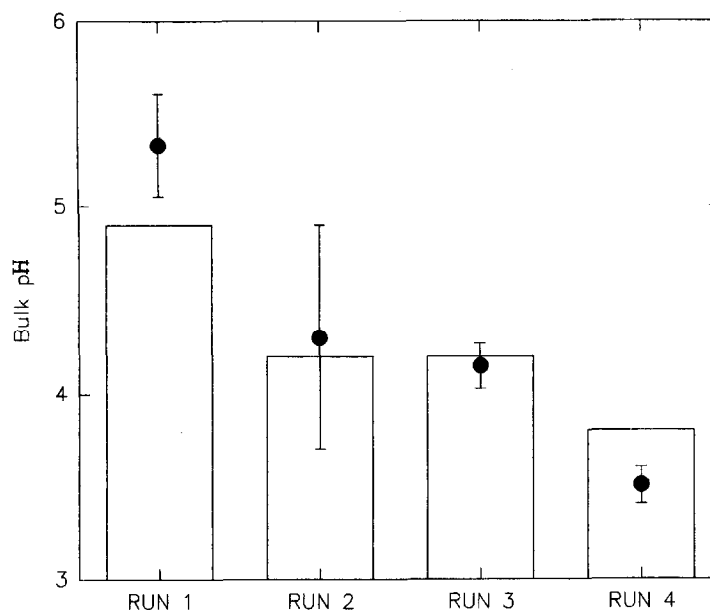


Fig. 10. Comparison of modelled and observed bulk cloud droplet acidity at the summit—observed bulk cloud droplet acidity with error bars and—bar charts represent bulk acidity of model.

hydrogen peroxide was not entrained into the cloud. Little aqueous hydrogen peroxide was measured at the summit, and even less at site MR close to cloud base on the lee of the hill ( $<7$  and  $<0.7 \mu\text{M}$ , respectively). Approximately  $0.7 \pm 0.1 \mu\text{g m}^{-3}$  of reduced nitrogen was fixed as ammonium. Table 1 indicates that only  $0.1 \mu\text{g m}^{-3}$  of ammonium was lost from the gas phase. As in case 3, however, cloud was present at the upwind sampling site and  $\text{NH}_3$  may have been scavenged into cloud droplets. The difference between total  $\text{NH}_4^+$  at the summit and downwind is approximately equal to the gas-phase  $\text{NH}_3$  detected at the post-cloud sampling site, MR.

### 3.3. Summary of field observations

Four field case studies have been presented, and they highlight the ammonium–sulphate relationship caused by chemical reactions in cloud.

#### (A) Ammonium fixing and sulphate production—Run 1

Ozone and hydrogen peroxide oxidation of S(IV) to S(VI) act as mechanisms to increase the total mass of the aerosol. Reduced nitrogen is transferred from the gas-phase to the particulate phase to neutralise the increased acidity associated with sulphate production.

#### (B) Ammonium fixing to neutralise an acidic aerosol—Run 4

The aerosol that entered the cloud was sufficiently acidic to remove reduced nitrogen from the gas-phase. It was therefore not in equilibrium with species in the gas-phase before it entered the cloud, and the cloud acted to re-equilibrate the aerosol with species in the gas phase.

#### (C) Ammonia out-gassing—Run 3

Almost no sulphate production is implied by the filters, and as a result of cloud processing reduced nitrogen is transferred from particulate ammonium to gaseous ammonia.

#### (D) Ammonia outgassing with sulphate production—Run 2

Gaseous ammonia is observed downwind of the cloud at  $\sim 2 \mu\text{g m}^{-3}$ . This is the smallest downwind ammonia concentration observed in a case study. It indicates that even with sulphate production ammonia is outgassed from evaporating cloud droplets, and not all gaseous ammonia is converted to ammonium to neutralise sulphate production.

## 4. COMPUTER MODEL CASE STUDIES

Of particular importance in reproducing the observed cloud droplet chemistry of the preceding four case studies, is that the model should give a good estimate of cloud liquid water content (Table 2), bulk cloud droplet acidity (Fig. 10) and the mean ion loadings of the cloud water at the summit (Fig. 11).

Two values for final ammonium and gaseous ammonia are presented in Table 3, from ideal and non-ideal chemistry models. These represent the concentrations after cloud processing and after cloud evaporation, respectively. Ideal chemistry continues while the liquid water content is above  $0.01 \text{ g m}^{-3}$ . Once the liquid water content drops below this value chemistry is frozen and the cloud droplets are held for 30 s to equilibrate with species in the gas-phase. Non-ideal chemistry gives the reduced nitrogen loading in

Table 2. Comparison of observed and modelled liquid water content at the summit  $\text{mg m}^{-3}$ 

Run	LWC observed	LWC modelled
1	$448 \pm 40$	423
2	$540 \pm 110$	533
3	$643 \pm 60$	579
4	$703 \pm 168$	711

the aerosol phase after the aerosol has been held at 90% relative humidity. This simulates the early stages of cloud droplet evaporation to aerosol particles.

#### 4.1. Case 1

The modelled cloud is more acidic than observed (Fig. 10). This is an artifact of the explicit cloud droplet model where the largest category contains over

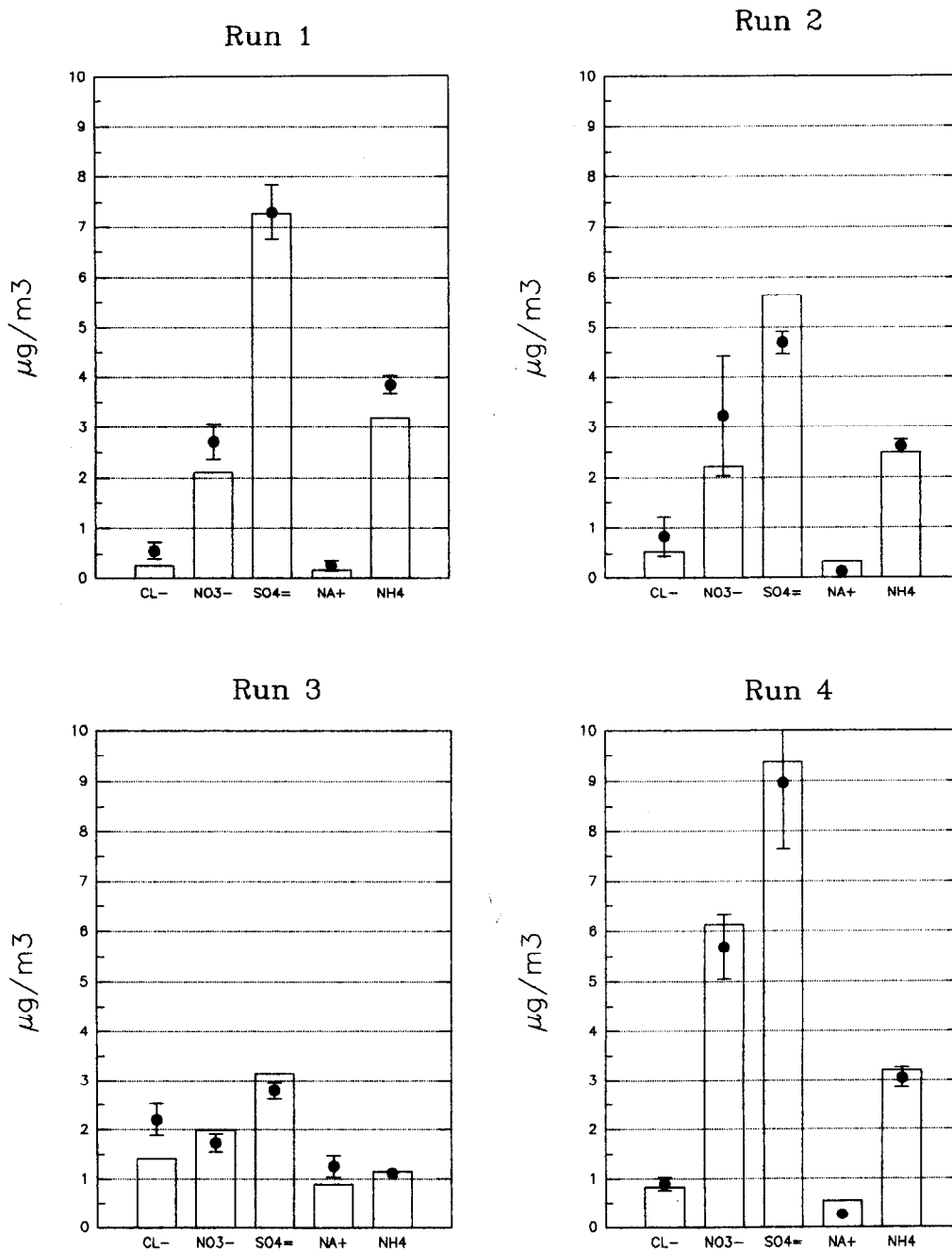


Fig. 11. Comparison of modelled and observed equivalent aerosol loadings calculated from the cloud samples. Legends as Fig. 10.

Table 3. Model input and output loadings for sulphate and ammonium

Case study:	1	2	3	4
Input: $\text{SO}_4^{-2}$	6.14	4.03	2.99	8.10
Output: $\text{SO}_4^{-2}$	7.28	6.46	3.28	9.30
Input: $\text{NH}_4^+$	2.82	2.11	1.04	2.78
Output: ideal $\text{NH}_4^+$	3.22	2.54	1.19	3.39
Output: non-ideal $\text{NH}_4^+$	2.68	2.11 <sup>a</sup> 2.06 <sup>b</sup>	1.13	2.86
Input: $\text{NH}_{3(g)}$	0.46	0.46	0.1	0.6
Output: ideal $\text{NH}_{3(g)}$	0.07	0.02	0.05	0.004
Output: non-ideal $\text{NH}_{3(g)}$	0.58	0.46 <sup>a</sup> 0.50 <sup>b</sup>	0.06	0.51

Output: ideal ammonium/ammonia concentrations in equilibrium with when  $\text{LWC} < 0.01 \text{ gm}^{-3}$ .

Output: <sup>a</sup>non-ideal ammonia/ammonium concentrations after wet cloud droplets have been evaporated to 90% relative humidity for 55 s (<sup>b</sup>case 2 evaporation for 155 s).

70% of the liquid water, while 99% of the cloud droplets have a  $\text{pH} \approx 5.5$ . Under these conditions ozone oxidises S(IV) to S(VI) rapidly, and the model estimates  $1.14 \mu\text{g m}^{-3}$  of S(VI) production. It is expected that after cloud processing ammonium will have been fixed in order to neutralise the increased acidity of the aerosol associated with sulphate production. Indeed the ideal model fixes  $0.4 \mu\text{g m}^{-3}$  of ammonium. However, too much ammonium has been fixed in the ideal model, and gaseous ammonia after cloud processing is much smaller than the observed value, less than  $0.1 \mu\text{g m}^{-3}$  compared to the observed  $0.35 \mu\text{g m}^{-3}$ . The evaporation of cloud droplets helps to address this problem. The non-ideal model outgasses ammonia, leading to a net increase in gaseous ammonia and a net decrease in ammonium after cloud processing. It is unlikely, given the large amount of sulphate production, that there will be less reduced nitrogen in the ammonium phase once the aerosol has dropped below its deliquescence point. Therefore, we can state that here the non-ideal model was run for too long, but gave within a factor of two a good estimate of the final gaseous ammonia concentration.

#### 4.2. Case 2

While case 2 is more acidic than case 1, more sulphate production occurs due to more sulphur dioxide present (4–6 ppbv). In total  $2.4 \mu\text{g m}^{-3}$  of sulphate is produced, and it might be expected that more ammonium would be fixed than case 1, in order to neutralise the associated increase in aerosol acidity. The ideal model fixes all gaseous ammonia as ammonium in case 1, i.e. ammonium fixing is limited by the amount of ammonia in the gas phase. After cloud processing only  $0.02 \mu\text{g m}^{-3}$  of ammonia remains in the gas-phase. Field data from case 2 (see Fig. 12) indicated that a small amount of gaseous ammonia was present at the downwind sampling site,  $0.2 \mu\text{g m}^{-3}$ , an order of magnitude more than the ideal

chemistry model predicted. The non-ideal model outgasses ammonia, returning the downwind ammonia concentration to the same concentration as entering the cloud,  $0.46 \mu\text{g m}^{-3}$ . The non-ideal model was run for a further 100 s (Table 3) and ammonia was outgassed from the aerosol, increasing gas-phase ammonia by  $0.05 \mu\text{g m}^{-3}$ . Therefore, the non-ideal model was able to reproduce field observations that aerosol could act as a source of gaseous ammonia.

#### 4.3. Case 3

Field data for this case study indicates that little sulphate production should occur, and the model predicts only  $0.29 \mu\text{g m}^{-3}$  of sulphate production. This case study is unusual in that the field data showed the final output ammonium loading observed is much lower than the input loading. The ideal chemistry model increased particulate reduced nitrogen by  $0.15 \mu\text{g m}^{-3}$ , and similarly the non-ideal chemistry gave a net increase in particulate ammonium after cloud processing ( $0.09 \mu\text{g m}^{-3}$ ). While the non-ideal chemistry model outgassed ammonia from evaporating cloud droplets, there was not a net increase in the gaseous ammonia concentration after cloud processing. This indicates that the acidic nature of the aerosol prohibits ammonia outgassing at 90% relative humidity. It appears that in this case the non-ideal model is not able to explain the large amount of ammonia outgassed.

#### 4.4. Case 4

Cloud droplet acidity is modelled to be systematically lower (higher pH) than measured, and the model estimates  $1.2 \mu\text{g m}^{-3}$  of sulphate production. Ideal chemistry fixes  $0.61 \mu\text{g m}^{-3}$  of ammonium, and while the non-ideal model outgasses ammonia there is still a net increase of ammonium ( $0.08 \mu\text{g m}^{-3}$ ). The ideal model consumes all the gaseous ammonia, and the post-cloud ammonia concentration is too small compared to the  $0.49 \mu\text{g m}^{-3}$  observed at the downwind site. The non-ideal model outgasses ammonia, giving a more reasonable estimate of  $0.5 \mu\text{g m}^{-3}$ . Hence for this case study the non-ideal model is able to give a realistic description of ammonia observed after the cloud.

### 5. DISCUSSION OF MODEL

The model predicts sulphate production to occur in polluted cloud drops. Given an input gaseous ammonia concentration ideal chemistry in cloud droplets acts to convert reduced nitrogen from gaseous ammonia to particle ammonium. This is seen by the ideal chemistry model giving consistently very low post-cloud ammonia concentrations, and elevated ammonium concentrations. The non-ideal chemistry model of wet aerosol at 90% relative humidity was able to reduce the amount of reduced nitrogen fixed as ammonium, outgassing reduced nitrogen as gaseous

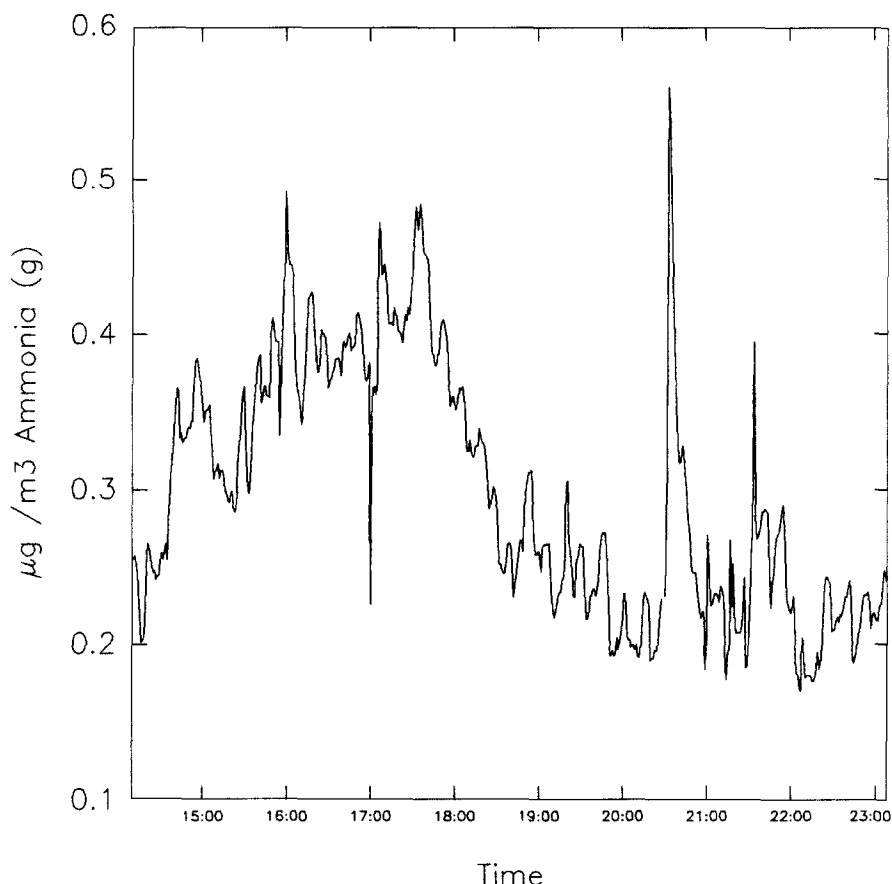


Fig. 12. Gas-phase ammonia observed at Moor house, 22nd April 1993.

ammonia. The non-ideal model was able to predict the final gaseous ammonia concentration to within 50% in three of the case studies. However, the non-ideal chemistry model was unable to reproduce the downwind ammonia concentration for case 3, and it is likely that some other mechanism apart from non-ideal chemistry at 90% relative humidity has a part to play in this case study.

#### 6. INTER-COMPARISON OF OBSERVATIONS AND MODEL

The model overestimates S(VI) production when compared to field observations (Table 4). The presence of cloud at the upwind site may influence estimates of sulphate production and the reduced nitrogen budget. Ammonia may have been undersampled at the upwind site, due to scavenging by cloud droplets, and particles may have been activated to cloud droplets (Section 3.2.1). This indicates that sulphate production and ammonium fixing may have been underestimated in these two cases.

The aqueous-phase transformation of reduced nitrogen is best shown through gaseous ammonia observed before and after the cloud. The ideal chemistry

Table 4. Comparison of model and observed change in sulphate and ammonium

	Sulphate	Ammonium
Observed 1	+ 25% ± 25%	+ 13 ± 13%
2	+ 25% ± 10%	- 9% ± 4%
3	+ 0.25 ± 0.5 µg m <sup>-3</sup>	- 0.6 ± 0.1 µg m <sup>-3</sup>
4	+ 0.4 ± 0.1 µg m <sup>-3</sup>	+ 0.7 ± 0.4 µg m <sup>-3</sup>
Modelled 1	+ 19%	- 5% → + 14%
2	+ 60%	- 3% → + 20%
3	+ 0.29 µg m <sup>-3</sup>	+ 0.09 → + 0.15 µg m <sup>-3</sup>
4	+ 1.2 µg m <sup>-3</sup>	+ 0.08 → 0.61 µg m <sup>-3</sup>

model consistently gave a gaseous ammonia loading that was much lower than observed, indicating that evaporation of wet cloud droplets to aerosol particles is an important mechanism in determining the final composition of aerosol particles and levels of gaseous ammonia. The effect of including activity coefficients to model wet aerosol at 90% relative humidity was to provide a more reasonable post-cloud gaseous ammonia concentration. The non-ideal model provided a good estimate of the after cloud ammonia for three

of the four case studies. Case study 3 was difficult to reproduce given the low loading of ammonium initially in the aerosol. A numerical study (Wells *et al.*, 1996) highlights that under more suitable conditions the cloud evaporation model can outgas significant quantities of ammonia from large aerosol particles in a similar manner implied by the field observations, if the aerosol contains large levels of ammonium. Presently, we have no means of estimating the time for aerosol particles to transfer from wet cloud droplets to dry aerosol particles. The Pitzer parameterisation is only valid for solutions of up to 4 molal, approximately 90% relative humidity. Therefore, the effects of activity for humidities in the range 73–90% is unknown, although it is likely that the aerosol spends little time in this regime (Phelps and Pond, 1971; DeLeeuw, 1988).

## 7. CONCLUSION

The field measurement of gaseous and particulate reduced nitrogen is not easy, and potential sources of error have been described. Although measurement of cloud water concentration of  $\text{NH}_4^+$  is inherently more precise, the uncertainties in generating effective air concentrations, by combining chemical concentrations with liquid water content, and the uncertainties in the capture efficiency of the cloud water samplers, lead to uncertainties of the order of  $\pm 20\%$ , similar to those for gas-phase and particles. Given these uncertainties, the budgets shown in Figs 1–3 are robust, but the data are not in themselves sufficiently precise or accurate to permit detailed interpretation of gas-to-particle conversion as the air mass moves through cloud. The detection of  $\text{NH}_3$  gas after cloud, however, in marked contrast to the predictions of cloud chemistry models which rely on ideal chemistry in cloud droplets, has shown that more complex cloud chemistry models need to be used. The non-ideal chemistry model developed here, although only semi-quantitative, has demonstrated that non-ideal chemistry in evaporating cloud droplets can lead to outgassing of  $\text{NH}_3$ , at concentrations consistent with those observed, even from acidic cloud water. This observation has implications for the long-range transport of reduced nitrogen; if  $\text{NH}_3$  gas is converted to  $\text{NH}_4^+$  in cloud, and released as  $\text{NH}_4^+$  particles when cloud droplets evaporate, the transport distance is effectively increased, because particles are much less efficiently dry-deposited than  $\text{NH}_3$  gas. If, however, the converse applies, and  $\text{NH}_4^+$  particles can be converted to  $\text{NH}_3$  gas by passage through cloud, the effective transport distance for reduced nitrogen is decreased. Moreover, the rapid dry deposition of  $\text{NH}_3$  gas (see Sutton *et al.*, 1997), produced as cloud droplets evaporate, may lead to detrimental effects in upland areas with ecosystems sensitive to deposition of nitrogen from the atmosphere.

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