

Sulphate production in summer cloud over Ontario, Canada

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ABSTRACT

The contribution of in-cloud oxidation of S(IV) to the cloudwater SO_4^- concentration is examined using airborne measurements made in and around summer clouds over central Ontario. The measurements include SO_2 , H_2O_2 , aerosol and cloud droplet size distribution, cloud liquid water content, HNO_3 , NH_3 , particulate SO_4^- and NH_4^+ , and cloudwater SO_4^- , NH_4^+ and H^+ . The quantity of SO_4^- produced in cloud is determined by subtracting the SO_4^- due to nucleation scavenging from the total cloudwater SO_4^- . The nucleation scavenged SO_4^- is estimated by 3 methods: (1) using NH_4^+ as a tracer of particulate SO_4^- ; (2) using the number of accumulation mode particles (generally the SO_4^- bearing particles) activated in cloud; (3) using the volume of the accumulation mode particles activated in cloud. The NH_4^+ method gives detectable in-cloud SO_4^- production for 20 of 36 data points, ranging from 8% to 83% of the total, with a median of 27%. The aerosol number approach yields detectable production for 6 of the 36 data points, ranging from 39% to 71%, with a median of 55%. The aerosol volume method gives no detectable production. The ammonium and aerosol number method results are consistent with the observations of the precursors for S(IV) oxidation. The difference between the ammonium and aerosol number methods is reasonable in so much as the number method results are considered overestimates because the nucleation-scavenged SO_4^- mass may be underestimated, while the ammonium method results may underestimate the production due to the scavenging of NH_3 by the acidic cloudwater. The lack of detectable sulphate production provided by the aerosol volume method is explained if the aerosol sulphate is preferentially distributed among the particles of sizes smaller than the accumulation mode mass modal size.

1. Introduction

Particulate sulphate is one of the more important chemical species in the atmosphere. It can dominate the acidity of clouds and precipitation, and in doing so exert a significant control on atmospheric chemistry. For example, the aqueous-phase destruction of ozone by O_2^- in cloud droplets is lowered when the pH of the droplets is low, due to a reduction in the dissociation of HO_2 ($\text{H}^+ + \text{O}_2^-$) in acidic solutions (Lelieveld and Crutzen, 1990). Sulphate particles also have a significant role in global climate through their direct and indirect effects on solar radiation. For example, Charlson et al. (1991) have shown that

clear-air scattering by sulphate aerosols may currently cool the Northern Hemisphere by about 1.1 W m^{-2} . Leitch et al. (1992) have shown for eastern North America that the anthropogenic influence (measured as sulphate) on cloud droplet number concentrations may have a negative radiative forcing on that region of $2\text{--}3 \text{ W m}^{-2}$ due to corresponding increases in cloud albedo. Wigley (1991) suggests that these factors may dictate the degree of warming expected from greenhouse gases over the next century.

There are two major pathways for the production of sulphate in the atmosphere as considered in regional and global scale models: bimolecular homogeneous gas-phase production of small sulphuric acid particles and in-cloud aqueous-phase oxidation of dissolved SO_2 (S(IV)). The latter is a very important path for the production

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of sulphate: global models suggest in-cloud aqueous-phase oxidation accounts for between 40% and 95% of the SO_4^{2-} formed in the global atmosphere (see Langner and Rodhe, 1991 and references therein); regional models for North America suggest 50% to 80% of the SO_4^{2-} deposited as precipitation is produced in cloud (Fung et al., 1991; McHenry and Dennis, 1991).

Laboratory studies of the aqueous-phase oxidation of S(IV) (see Findlayson-Pitts and Pitts, 1986 and Seinfeld, 1986 for reviews) suggest the major aqueous-phase oxidants are H_2O_2 , O_3 or O_2 , where aerobic oxidation is catalyzed by iron and manganese. The relative importance of each oxidant depends on the concentrations and the pH of the aqueous solution. For solutions which are quite acidic, H_2O_2 , if present at a sufficient level appears to be the dominant aqueous-phase oxidant. For higher pH, but still acidic solutions, metal-catalyzed aerobic oxidation (Martin and Good, 1991), O_3 and possibly $\text{H}_2\text{O}_2\text{-Fe}^{++}$ (Ibusuki et al., 1990) may be important and perhaps the dominant aqueous-phase oxidants; however, little is known about the concentrations of the metal catalysts in the atmosphere. During cloud condensation, cloud droplets are initially smaller and these less dilute droplets can have

relatively low values of pH if strong acids are present in the pre-cloud air. As the droplets grow larger and become more dilute, the pH may increase. Therefore in clouds present in relatively acidic environments, it is likely that H_2O_2 will be the first aqueous-phase oxidant. In such a situation, the other mechanisms become increasingly important as the pH of the droplets rise. Of course individual droplet chemistry may vary considerably, and it is probable that the different sized droplets will possess varying values of pH (e.g., Perdue and Beck, 1988; Noone et al., 1988; Ogren et al., 1989; Seidl, 1989; Twohy et al., 1989; Ayers and Larson, 1990; Hegg and Larson, 1990; Pandis et al., 1990).

A number of field studies have used a variety of methods to determine the importance of in-cloud production of sulphate. However, detecting sulphate production in cloud is a difficult task considering the many uncertainties associated with measurements and the variability of the atmosphere (Kelly et al., 1989). The results of some studies are tabulated in Table 1. As seen from this table, there are few quantitative results for this process in the natural atmosphere.

Many different conditions can be encountered in the field which will affect the ability to detect

Table 1. *Summary of previous field studies for the investigation of aqueous-phase sulphate formation*

Cloud type	Approach	SO_4^{2-} produced	Cloudwater SO_4^{2-} $\mu\text{g m}^{-3}$	Ref.
supercooled stratus/ rain band		negligible	1.92–3.29	Scott and Laulainen (1979)
wave cloud	upwind-downwind	0.31–4.2 $\mu\text{g m}^{-3}$	filter data	Hegg and Hobbs (1981)
wave cloud	upwind-downwind	0–10.9 $\mu\text{g m}^{-3}$	filter data	Hegg and Hobbs (1982)
stratiform	$[\text{H}^+]/[\text{NO}_3^-] + [\text{SO}_4^{2-}]$	significant amount		Lazrus et al. (1983)
small cumulus	aerosol number as tracer	negligible	0.5–9.4	Leaitch et al. (1983)
cumuliform and stratiform	mass difference	0–4.4 $\mu\text{g m}^{-3}$	0.1–5.6	Hegg et al. (1984)
stratiform	$[\text{H}^+]/[\text{NH}_4^+]$	significant amount		Daum et al. (1984)
cumulus and stratocumulus	mass difference	0–5.8 $\mu\text{g m}^{-3}$	0.2–5.9	Hegg and Hobbs (1986)
cumulus and stratocumulus	aerosol number as tracer	not detectable	0.2–9.2	Leaitch et al. (1986)
supercooled stratus	aerosol number and mass difference	negligible	0.86–5.53	Daum et al. (1987)
cumuliform and stratiform	mass difference	0–9.3 $\mu\text{g m}^{-3}$	0.04–14	Hegg and Hobbs (1988)
stratiform	$[\text{NH}_4^+]/[\text{SO}_4^{2-}]$	negligible	2.14–6.85	Strapp et al. (1988)
orographic cloud	artificial injection of SO_2	negligible	1.0–1.3	Gervat et al. (1988)
orographic cloud	artificial injection of SO_2	negligible		Chandler et al. (1988)
orographic clouds	Se used as tracer	8–22 %	(no LWC)	Husain (1989)
orographic cloud	artificial injection of SO_2	0.96–1.15 $\mu\text{g m}^{-3}$	1.0–5.8	Clark et al. (1990)
orographic clouds	Se used as tracer	0–39 %	(no LWC)	Husain et al. (1991)

in-cloud sulphate production. For example, in the winter period the concentration of H_2O_2 may be relatively low, thus lowering the likelihood of detection of in-cloud SO_4^- production (e.g., Strapp et al., 1988). Whereas, during the summer months, when oxidant levels are higher (e.g., Van Valin et al., 1990; Isaac et al., 1992; Ray et al., 1992), sulphate production in cloudwater is more likely to be detectable. The contrast in potential S(IV) oxidation between seasons has been demonstrated by Mohnen and Kadlec (1988). Kelly et al. (1989) suggest that it is possible to detect S(IV) oxidation by H_2O_2 in a wide variety of cloud conditions, but the oxidation by O_3 is much less likely to be detected. Still, some experimental studies have suggested the importance of O_3 as an aqueous-phase oxidant (Hegg and Hobbs, 1986; Clark et al., 1990). The use of comprehensive modelling in concert with observations is potentially a powerful tool for diagnosis of this issue (e.g., Barth et al., 1992; Pilinis et al., 1992).

This study examines airborne measurements conducted in and around clouds over central Ontario during the first intensive measurement period of the Eulerian Model Evaluation Field Study (EMEFS I) from 21 July–29 August 1988. Three methods are applied to this data set to estimate the contribution of in-cloud oxidation of S(IV) to sulphate during this study.

2. Instrumentation

The observational platforms were the National Research Council of Canada DHC-6 Twin Otter and the Innotech Aviation DC-3. The airspeed for both aircraft was $50\text{--}60\text{ m s}^{-1}$. Both aircraft sampled cloudwater and made microphysical and chemical measurements, although the Twin Otter was used primarily for cloud observations and the DC-3 primarily for clear-air observations.

The measurements used here include SO_2 , H_2O_2 , aerosol and cloud droplet size distribution, cloud liquid water content (LWC), particulate SO_4^- (pSO_4^-), particulate ammonium (pNH_4^+), particulate nitrate (pNO_3^-), HNO_3 and NH_3 , as well as measurements of SO_4^- , NH_4^+ , NO_3^- and H^+ in cloudwater samples (hereafter cSO_4^- , cNH_4^+ , cNO_3^- , cH^+ respectively). The measurement techniques are described below.

Filter-based measurements of HNO_3 , SO_2 , NH_3 , pSO_4^- , pNO_3^- and pNH_4^+ were made with a triple filter pack system. Aerosol particles were collected on the front filter ($1\text{ }\mu\text{m}$ teflon) and HNO_3 on the middle filter ($1\text{ }\mu\text{m}$ nylon). For the first half of the study, SO_2 was collected on the third filter (K_2CO_3 -impregnated Whatman 41) and for the second half of the study, NH_3 was collected on the third filter (citric acid-impregnated Whatman 41). Sulphate extracted from the nylon filters was assumed to be SO_2 . Concentrations of all species were measured by ion chromatography using a Dionex-2000i. The uncertainties in these measurements are estimated at $\pm 0.4\text{ }\mu\text{g m}^{-3}$.

SO_2 was monitored in real time using a TECO 43-S instrument. The instantaneous detection limit for SO_2 is 0.3 ppb. A 67% response is obtained after 1 minute, and near full response is obtained after about 2 min. The instrument was calibrated approximately every 2nd day. The uncertainty in the measurement at 1.0 ppbv is estimated at 37%. Filter and instrumental SO_2 measurements, based on approximately 45 minute averages, were highly correlated, but the TECO 43-S measurements were biased higher by about 30%.

Gas-phase hydrogen peroxide was monitored using the enzyme fluorometric method described by Lazrus et al. (1986). The detection limit is approximately 0.1 ppbv with an uncertainty of $\pm 10\%$. Instrument response time was about 90 seconds. Calibrations were performed on the ground prior to each flight. In-flight zeros and spans were done and usually an additional calibration and zero followed each flight. Based upon 32 flights of data, the average organic fraction of the total peroxides was 23%, and ranged between 18% and 42%.

The size distributions of aerosol particles and cloud droplets were measured with a Particle Measuring Systems (PMS) ASASP-100X and a PMS FSSP-100 respectively. In the case of the Twin Otter, these probes were mounted under one wing. In the case of the DC-3 they were suspended from a pylon, about 1 m above the fuselage. The calibration for these ASASP-100X probes against latex spheres and nearly monodisperse NaCl particles has been discussed in detail by Liu et al. (1992). The calibrated size range of the ASASP-100X is about $0.17\text{ }\mu\text{m}$ to $2\text{ }\mu\text{m} \pm 5\%$. The uncertainty in counting is estimated at $\pm 15\%$. For the FSSP, the calibration of Dye and Baumgardner

(1984) is used. Routine checks with glass beads were performed to ensure maintenance of the calibration. For the flights discussed here, the FSSP-100 were operated on the size range between about $2\text{ }\mu\text{m}$ and $35\text{ }\mu\text{m}$. The FSSP measurements have been corrected for probe dead time and coincidence according to the procedure of Baumgardner et al. (1985). The uncertainty in counting is estimated to be $\pm 20\%$.

LWC was measured with a PMS King probe. The King probe is a hot-wire type device found to be more accurate and reproducible than the more common Johnson-Williams probe (King et al., 1985). The King probe was calibrated in the National Research Council of Canada icing wind tunnel in February 1988. The uncertainty of the LWC is estimated at $\pm(0.02 + 0.15 \times \text{LWC})\text{ g m}^{-3}$.

Cloudwater was collected using slotted-rod type collectors. Two designs were employed: a copy of the style described by Winters et al. (1979; hereafter referred to as the standard collector); and a modified design with narrower rods, one-half the standard collector diameter, in an attempt to improve the collection efficiency of smaller droplets. The modified design is similar to that described by Hubert et al. (1988). On both aircraft, the collectors were deployed out of openings in the top of the fuselage near the top edge of the windscreen. Simultaneous deployment of two collectors was possible on both aircraft, and most samples were collected in pairs using a standard collector and a modified collector. Comparisons of the quantity of water collected with each collector against the theoretical quantity computed from the collection efficiencies evaluated according to Langmuir and Blodgett (1961) were done for the Twin Otter collectors in each of two locations: port and centre. The modified collector compared favourably with the theoretical collection efficiency (within 20% on average) when situated in the port location. The total water collected in the centre location was much lower than the theoretical quantity (30%–50% on average). The reason for this discrepancy is not known, but it is suspected that when in the centre location the collector may not have been oriented directly into the airstream. The standard collector was more consistent between the two locations; however, the total quantity of water collected was on average higher than the theoretical

quantity by 10%–35%. The reason for this is unknown.

All cloudwater samples were analyzed by ion chromatography (Dionex 2000i) for Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , and K^+ . The uncertainties in these measurements were estimated at $0.1\text{ }\mu\text{g ml}^{-1}$. H^+ was measured by colourimetry. Ion concentrations measured with the two collectors during simultaneous deployment were compared as a function of the mean volume diameter of the cloud droplets. This was done in an attempt to determine if these collectors were biased relative to one another because of droplet size. For the Twin Otter samples used here, 27 of 30 pairs of samples had SO_4^{2-} concentrations within 30% of each other. For NO_3^- , 15 of 17 pairs had concentrations within 20%, and for NH_4^+ , 17 of 20 were within 25%. For none of these ions was a significant bias with respect to droplet size indicated.

Forty-one cloudwater samples collected on flights between 15 August and 29 August were analyzed for dissolved H_2O_2 via the derivatization technique described by Kok et al. (1986). In this technique, peroxides in a cloudwater sample react with p-hydroxyphenylacetic acid (POPHA) in the presence of horseradish peroxidase to form a stable dimer. Samples were fixed on the aircraft within minutes of collection and later analyzed.

Inlets for filter sampling on the Twin Otter were mounted in a small aerodynamic pylon set atop the fuselage, about mid-way along the aircraft. The air intake consisted of a 1 cm diameter teflon tube protruding out the front of the pylon enclosed by a near-isokinetic nozzle. The end of the nozzle was slightly blunt. The filter was mounted about 15-cm straight behind the nozzle inlet. On the DC-3, the filter intake consisted of a teflon block with a 2 cm diameter channel milled through it and fitted with an isokinetic teflon nozzle. Comparisons of the filter sampling systems on the two aircraft and between the aircraft and ground are quite good (Leitch et al., 1991a).

Trace gas intakes on the Twin Otter consisted of teflon-lined aluminum tubes protruding vertically out of the top of the fuselage. The top of the inlet was capped by a teflon hat to keep out rain and eliminate contact with metal surfaces. On the DC-3, the trace gas inlets were open-ended teflon-lined tubes protruding from the fuselage pylon. Calibration gases were introduced to the inlets.

3. Observations

The observations were made over a region of south-central Ontario, Canada between two ground measurement sites, Dorset and Egbert, separated by about 125 km. The flight plans centred on collecting data for evaluation of the Canadian and US regional Eulerian models (ADOM and RADM respectively) and typically consisted of collecting vertical profile data over each ground site, and filter and instrumental data at multiple levels between Dorset and Egbert. When cloud was present, cloud sampling was substituted for one or more of the filter samples. Ideally on cloudy days vertical profile data were collected at Dorset and Egbert, cloudwater was sampled at one or more levels between Dorset and Egbert, and filter samples were collected at one or more altitudes below cloud between Dorset and Egbert. As an example, Fig. 1 illustrates the

flight profile of 6 August, when a layer of thick stratocumulus was present. All flights discussed here have similar measurements. Altogether, 117 cloudwater samples were collected on the Twin Otter and 29 on the DC-3. Of these, 51 collected on 11 different flights are used for this study. The remainder are excluded because the conditions were inappropriate for this study: some cloudwater samples had rain mixed in with them, some flights did not have sufficient observations for the present analysis, some had instrument problems, and for some there was no sampling of cloud-base air. The Twin Otter cloudwater samples are identified by TO x - y (Twin Otter) or DC3 x - y , where x indicates flight number, y indicates the sequential cloudwater sample. Of the 51 samples, all, except TO 24-1, were duplicates. The duplicates, except for flight TO 13, were averaged to give 25. 4 samples from flight TO 13 were averaged to give 1 result because the concentrations were very

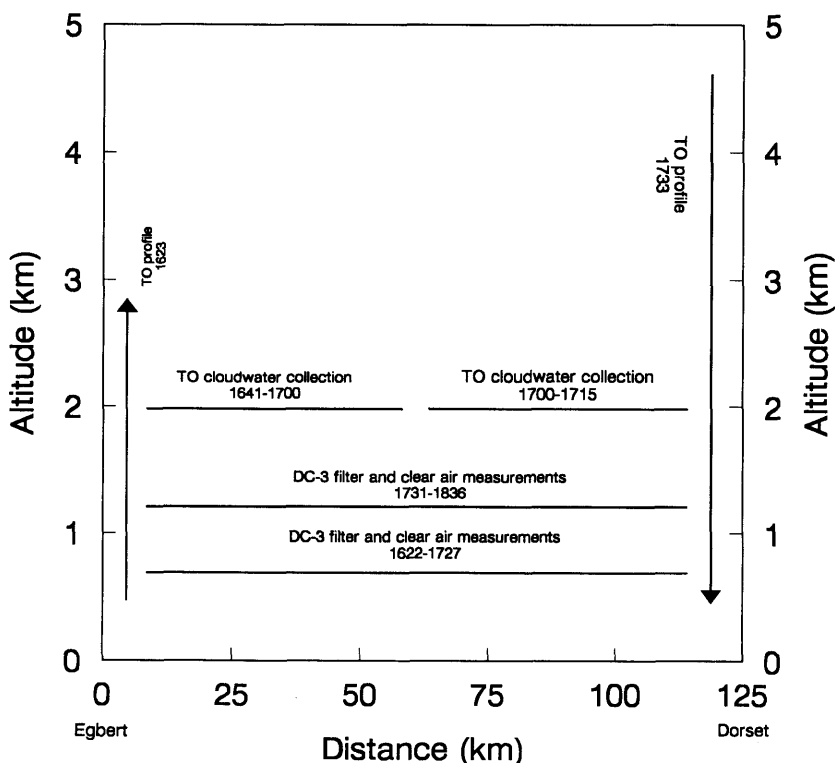


Fig. 1. Flight plans followed for 6 August. The Twin Otter collected profile data over Egbert, followed by cloudwater collection toward Dorset and finally profile data over Dorset. The DC-3 collected filter samples and made clear-air measurements at two altitudes below cloud.

similar. Cumuli or stratocumuli were sampled on 8 of the 11 flights. Stratus were sampled on DC3-7, TO 32, and TO 48.

In all cases there is similarity between the below-cloud air, where the filter samples were collected, and the in-cloud air, where the cloud water samples were collected. In some cases the cloud was topped by a strong temperature inversion below which the air was well mixed down to the surface. An example of such a case is flight TO 25 (Aug. 6). Stratocumuli were sampled just below the top of this mixed layer. The ASAP total concentration profile for this case is shown in Fig. 2a. The temperature inversion varied between 1800 and 2100 m. Below this layer the ASAP concentration is about 400 cm^{-3} , similar to the out of cloud ASAP concentration measured during cloud-

water collection (Fig. 2b; the greatest variations represent the in-cloud periods). In some cases, the clouds were based in a relatively well-mixed surface layer and then grew out of the surface layer. In this case, the air feeding the base of the clouds is still represented by the below-cloud filters. An example of this situation (TO 24) is discussed in some detail in Leitch et al. (1991b) who use pseudo-conservative quantities to link the in-cloud air with that at cloud base. Details of other cases are given in Section 5.

The summaries of the cloudwater and filter ion concentrations for the cases used here are listed in Table 2. All cloudwater concentrations have been referenced to air volume concentrations by multiplication with the liquid water content. Further, all concentrations are expressed at standard tem-

Table 2. Summaries of the cloud water ion concentrations and filter-based measurements of HNO_3 , NH_3 , $p\text{SO}_4^-$, $p\text{NH}_4^+$ and $p\text{NO}_3^-$; all concentrations are in nEq m^{-3} ; blanks indicate no measurements taken; A, B refers to filter A and B

Date-Flight	Cloud water ions			Twin Otter filter concentration					DC-3 filter concentration				
	SO_4^-	NH_4^+	NO_3^-	SO_4^-	NH_4^+	NO_3^-	HNO_3	NH_3	SO_4^-	NH_4^+	NO_3^-	HNO_3	NH_3
7-25 TO 7	29	26	24	65	51	BDL	22		61	55	6	29	
7-30 TO 13-A	78	76	36						142	119	1	27	
7-30 TO 13-B	78	76	36						111	90	BDL	31	
8-01 DC3 7-1	214	158	308						169	179	2	77	
8-01 DC3 7-2	130	83	102						169	179	2	77	
8-01 DC3 7-3	158	131	144						169	179	2	77	
8-01 DC3 7-4	250	189	241						169	179	2	77	
8-01 DC3 7-5	19	13	29						169	179	2	77	
8-03 DC3 9-1	224	132	179						557	398	BDL	191	
8-03 DC3 9-2	186	121	179						557	398	BDL	191	
8-03 DC3 9-3	472	309	441						557	398	BDL	191	
8-04 TO 20-1	221	111	132	651	432	23	186		592	391	BDL	189	
8-04 TO 20-2	117	61	92	651	432	23	186		592	391	BDL	189	
8-05 TO 24-1	668	216	350	795	342	7	282						
8-05 TO 24-2	378	128	137	795	342	7	282						
8-05 TO 24-3	303	101	185	795	342	7	282						
8-06 TO 25-1A	19	35	21						20	25	BDL	33	
8-06 TO 25-1B	19	35	21						16	22	BDL	19	
8-06 TO 25-2A	12	15	11						20	25	BDL	33	
8-06 TO 25-2B	12	15	11						16	22	BDL	19	
8-13 TO 31	133	120	189	176	173	18	92	63					
8-15 TO 32	38	3	3						44	21	BDL	8	39
8-17 TO 37	60	13	9	43	51	2	23	2					
8-28 TO 48-1	58	32	46	84	83	BDL	53	3	48	59	6	41	10
8-28 TO 48-2	27	14	23	84	83	BDL	53	3	48	59	6	41	10
8-28 TO 48-3	42	21	25	84	83	BDL	53	3	48	59	6	41	10
8-28 TO 48-4	35	18	26	84	83	BDL	53	3	48	59	6	41	10
8-28 TO 48-5	14	9	13	84	83	BDL	53	3	48	59	6	41	10

BDL: Below detection limit.

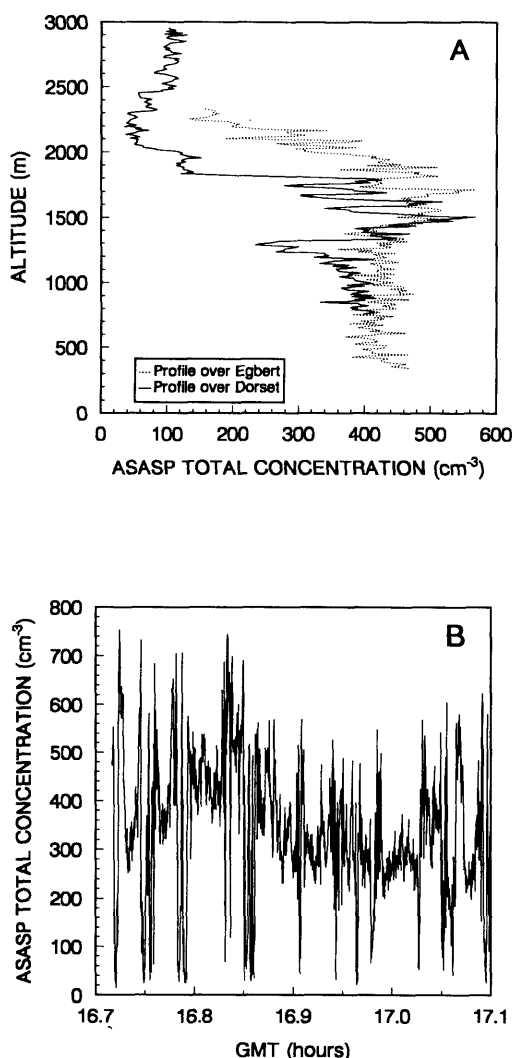


Fig. 2. (a) Profiles of ASASP total number concentration over Egbert and Dorset for Flight TO 25. (b) Time series of ASASP total number concentration measured in and out of cloud.

perature (273 K) and pressure. In general, $c\text{SO}_4^-$ is lower than the below-cloud $p\text{SO}_4^-$, suggesting that SO_4^- production in the clouds is negligible. However, factors such as spatial and temporal gradients and incomplete nucleation scavenging must be considered. To account for these and other factors, the following methods to estimate in-cloud SO_4^- production are used.

4. Estimation of SO_4^- production

The methods for estimating sulphate production use variables assumed to be conserved from aerosol to cloud as an indicator of the quantity of SO_4^- in the cloudwater due to nucleation scavenging. These approaches are described below.

4.1. NH_4^+ as a tracer for nucleation scavenging

This method estimates the sulphate formed in cloudwater by examining the difference between the ratio of SO_4^- to NH_4^+ in the cloudwater to that of the below-cloud filter. NH_4^+ is used because its concentration in the aerosol is sufficiently high, it has been used in the past as a tracer to indicate nucleation scavenging of aerosol SO_4^- (e.g., Daum et al., 1984; Strapp et al., 1988), and because it is highly correlated with SO_4^- , as shown in Fig. 3a. In this figure, the data are from filters collected during the flights discussed here. For a log-log regression the coefficient of variation (r^2) is 0.95, while for a linear regression r^2 equals 0.91.

The amount of sulphate formed in cloud using NH_4^+ as a tracer is calculated using the following equation:

$$\frac{\text{aqSO}_4^-}{c\text{NH}_4^+} = \left(\frac{c\text{SO}_4^-}{c\text{NH}_4^+} - \frac{p\text{SO}_4^-}{p\text{NH}_4^+} \right), \quad (1)$$

where aqSO_4^- is the amount of SO_4^- produced in cloud. Rearranging eq. (1) gives

$$\frac{\text{aqSO}_4^-}{c\text{SO}_4^-} = 1 - \left(\frac{p\text{SO}_4^-}{p\text{NH}_4^+} \right) \left(\frac{c\text{NH}_4^+}{c\text{SO}_4^-} \right), \quad (2)$$

which represents the fraction of SO_4^- produced in cloud. The use of NH_4^+ assumes it has the same size distribution as SO_4^- , it is scavenged with the same efficiency by cloudwater, and that NH_3 is not scavenged by cloud. The implications of these assumptions are discussed in Section 5.

4.2. Aerosol number as tracer for nucleation scavenging

This method has been previously used to examine S(IV) oxidation (Leaith et al., 1986a), and some assumptions are inherent with this method also. First is the assumption that the aerosol is monodisperse. Although this is clearly not the case, the size distribution of particles in the 0.1–1.0 μm size, where the mass of SO_4^- is concen-

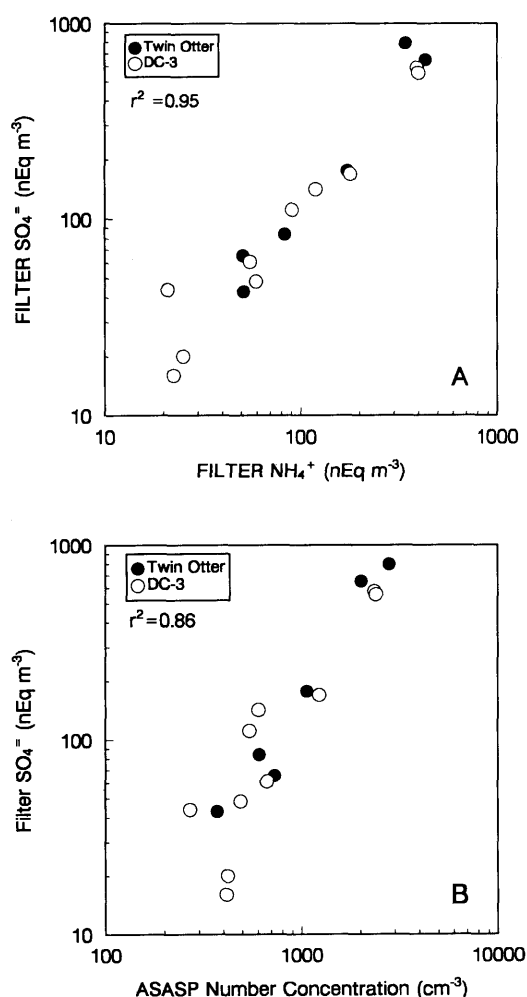


Fig. 3. (a) Relationship between $p\text{SO}_4^{2-}$ and $p\text{NH}_4^+$ for the 16 filter samples used for the NH_4^+ method. (b) Relationship between $p\text{SO}_4^{2-}$ and ASASP total number concentration for the 15 filter samples used for Aerosol number method.

trated, does indicate a quite narrow distribution (e.g., Leaitch and Isaac, 1991). Fig. 3b shows $p\text{SO}_4^{2-}$ plotted against ASASP number concentration on logarithmic scale. For this plot, the regression has a r^2 value of 0.86 and r^2 for the linear regression is 0.95, indicating that $p\text{SO}_4^{2-}$ is largely associated with these particles. It is also assumed that the aerosol is uniformly and internally mixed (i.e., each particle contains the same relative fraction of sulphate), and that the sulphate is con-

centrated in this size range. The issue of uniformity of distribution is discussed with the results. The assumption that sulphate is internally mixed within the accumulation-mode aerosol is probably justified (e.g., Ferek et al., 1982).

If indeed sulphate is internally mixed and concentrated in these particles, then they will be good cloud condensation nuclei (CCN). Aerosol particles in this size range have previously been shown to act as CCN (e.g., Leaitch et al., 1986b; Ahr et al., 1989). This is shown for the present study by comparing the interstitial aerosol particle number concentration (IAPNC) and the cloud droplet number concentration (CDNC) each with the cloud-base APNC (CBAPNC). Ratios of these quantities are given in Table 3. The data shows

Table 3. Ratios of interstitial aerosol particle number concentration (IAPNC) to cloud base aerosol particle number concentration (CBAPNC) and cloud droplet number concentration (CDNC) to CBAPNC; the last column is the sum of the two ratios

Flight #	IAPNC/CBAPNC	CDNC/CBAPNC	SUM
TO 7	0.45	0.92	1.37
TO 13-A	0.69	0.54	1.23
TO 13-B	0.69	0.54	1.23
DC3 7-1	0.87	0.26	1.13
DC3 7-2	0.73	0.56	1.29
DC3 7-3	0.74	0.57	1.31
DC3 7-4	0.63	0.67	1.30
DC3 7-5	0.93	0.09	1.02
DC3 9-1	0.52	0.25	0.77
DC3 9-2	0.54	0.21	0.75
DC3 9-3	0.49	0.33	0.82
TO 20-1	0.37	0.29	0.66
TO 20-2	0.46	0.22	0.68
TO 24-1	0.26	0.45	0.71
TO 24-2	0.30	0.34	0.64
TO 24-3	0.50	0.27	0.77
TO 25-1A	0.60	1.00	1.60
TO 25-1B	0.60	1.00	1.60
TO 25-2A	0.61	1.00	1.61
TO 25-2B	0.61	1.00	1.61
TO 31	0.56	0.40	0.96
TO 32	0.31	0.86	1.17
TO 37	0.96	0.54	1.50
TO 48-1	0.73	0.81	1.54
TO 48-2	0.49	0.85	1.34
TO 48-3	0.67	0.59	1.26
TO 48-4	0.44	0.96	1.40
TO 48-5	0.61	0.57	1.18

that in every case except TO 25, the CDNC are a fraction of the CBAPNC, and in every case the IAPNC are some fraction of the CBAPNC. The sum of these 2 ratios ranges between 0.64 and 1.61 with a median of 1.23. Entrainment of air with lower aerosol concentrations reduces the sum of these ratios. Double counting by the aerosol probe, which dries or partially dries cloud droplets, and activation of particles smaller than the detection limit of the ASASP raises the sum of these ratios. On days with more pollution and when the clouds tower out of the boundary layer (e.g., TO 24), the effect of entrainment dominates because of the relatively low particle-scavenging ratio. On relatively clean days coupled with the clouds contained by the boundary layer (e.g., TO 25), the effect of entrainment is reduced, and the activation of smaller particles leads to a much higher scavenging ratio. Combined with the double-counting this results in much higher sums of the above ratios. Double-counting by the ASASP in cloud is an effect which depends on the size of the droplets and the continuous time spent in cloud. The TO 25 case shown in Fig. 2 is a good example. The APNC concentrations almost double when sampling in the edges of the clouds where the droplet diameters are smallest and the probe heaters are able to dry the cloud droplets. In the centres of the clouds, where the diameters are the largest, the APNC drop very low because the particles are inside the droplets and the droplets are not sufficiently dried to be detected by the ASASP. This aspect of the ASASP is discussed in more detail by Strapp et al. (1992).

The sulphate produced in cloud, aqSO_4^- , is then estimated from the following

$$\frac{\text{aqSO}_4^-}{\text{cSO}_4^-} = 1 - \frac{\text{pSO}_4^-}{\text{cSO}_4^-} \left(\frac{\text{CBAPNC}}{\text{FAPNC}} \right) \left(\frac{\text{CDNC}}{\text{CBAPNC}} \right), \quad (3)$$

where FAPNC is the filter aerosol particle number concentration. The $(\text{CDNC}/\text{CBAPNC})$ represents the aerosol fraction scavenged by nucleation, and the $\text{pSO}_4^- (\text{CBAPNC}/\text{FAPNC})$ estimates the fraction of pSO_4^- sampled during filter collection which is present at cloud base. The CBAPNC is estimated either from the profile obtained nearest the cloud or from ascent or descent near the cloud. However, with the exception of the TO 25 samples,

for which CDNC/CBAPNC was set to unity, the two CBAPNC in equation 3 nullify each other. This results in a slightly reduced experimental error for these samples, but more importantly eliminates the unquantifiable uncertainty due to estimating the CBAPNC. For the TO 25 case, the right-hand bracket is set equal to 1 since the CDNC exceeds the CBAPNC and most of the mass is in particles $>0.17 \mu\text{m}$. The uncertainty due to this is estimated at $<10\%$. The FAPNC is the averaged number concentration of aerosol particles for the period of the filter collection (about 1 h).

4.3. Aerosol volume as tracer for nucleation scavenging

The use of aerosol volume, in place of number, as a tracer for nucleation scavenging of sulphate removes the assumption of monodispersity, but retains the assumption of an internally- and uniformly-mixed sulphate aerosol. The nucleation scavenged mass ratio is estimated from cumulative volume and cumulative number versus diameter plots of the cloud-base and clear-air measurements. The mass of sulphate activated is proportional to the activated volume (ACTVOL) of the cloud-base aerosol. It is obtained by locating the diameter corresponding to the number of particles equal to CDNC¹ on the cumulative number plot. At this diameter on the cumulative volume plot, the ACTVOL is obtained. The cloud-base aerosol volume (CBVOL) and the filter aerosol volume (FVOL) are the average volumes measured with the ASASP at cloud base and during the period of filter sampling respectively. The sulphate produced in cloud is then estimated from the following expression

$$\frac{\text{aqSO}_4^-}{\text{cSO}_4^-} = 1 - \frac{\text{pSO}_4^-}{\text{cSO}_4^-} \left(\frac{\text{CBVOL}}{\text{FVOL}} \right) \left(\frac{\text{ACTVOL}}{\text{CBVOL}} \right), \quad (4)$$

where the sulphate scavenged by nucleation is subtracted from the cSO_4^- concentration. This approach, as will be shown, leads to an over-

¹ This assumes that larger particles are scavenged first and field evidence supports this assumption (e.g., Ogren et al., 1989). More strictly speaking the scavenging will be most efficient for those particles with the greatest mass of water-soluble material.

estimation of nucleation scavenged sulphate and has important implications concerning the distribution of sulphate in the aerosol.

5. Results and discussion

5.1. Production estimates

The in-cloud sulphate production estimated using NH_4^+ is shown in Fig. 4. The results and their experimental errors are tabulated in Table 4. The experimental errors were derived from the combination of the individual measurement uncertainties in quadrature (Taylor, 1982). The individual uncertainties are those due to the LWC and the measurements of all the chemical species indicated in eq. (2). These uncertainties are given

in the section describing instrumentation. One of the benefits of using ammonium as a tracer is that the use of it as a reference eliminates the uncertainty associated with the LWC measurement (often the greatest source of uncertainty) when estimating the relative quantity of sulphate produced. To derive the error estimate for aqSO_4^- , the uncertainty in the right-hand side of eq. (2) was first obtained. This is the error in the fraction of cloudwater sulphate which is due to in-cloud production, and does not include the LWC uncertainty. To obtain the absolute error in aqSO_4^- the error in the above fraction and that in cSO_4^- , which includes the LWC, were combined in quadrature to give an uncertainty in the aqSO_4^- concentrations.

The concern here is to derive the cases of sulphate production with the greatest confidence. To

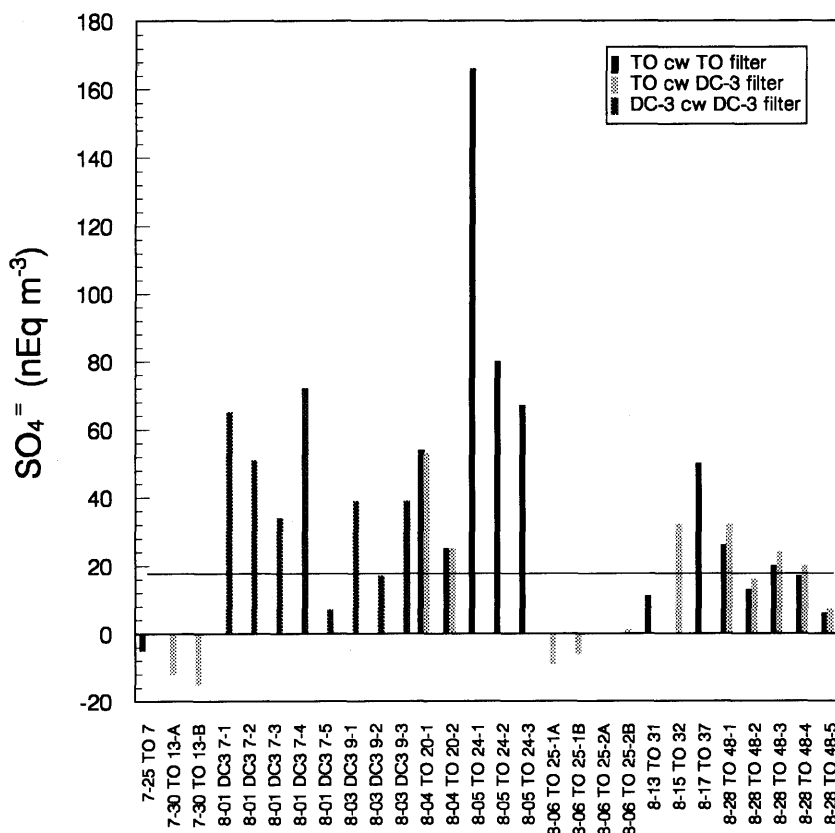


Fig. 4. Sulphate produced in cloud as estimated by NH_4^+ method. The line at 18 nEq m^{-3} represents 2 standard deviations of those values bounded by the absolute of the most negative value indicated.

Table 4. Results of NH_4^+ method and number method. TO and DC-3 columns indicate the filters used as sampled by that particular aircraft; the last column is the measured cloudwater SO_4^{2-} concentration; asterisk indicates cases identified for in-cloud production of sulphate

Flight #	$\text{aqSO}_4^{2-} \text{ nEq m}^{-3}$ NH_4^+ method		$\text{aqSO}_4^{2-} \text{ nEq m}^{-3}$ aerosol number method		cSO_4^{2-} (nEq m^{-3})
	TO	DC-3	TO	DC-3	
TO 7	-5 ± 11	0 ± 8	-34 ± 21	-35 ± 21	29 ± 12
TO 13-A		-11 ± 13		-18 ± 32	78 ± 21
TO 13-B		-15 ± 17		-6 ± 30	78 ± 21
DC3 7-1		$*65 \pm 55$		170 ± 176	214 ± 130
DC3 7-2		$*51 \pm 24$		35 ± 63	130 ± 38
DC3 7-3		$*34 \pm 19$		61 ± 77	158 ± 61
DC3 7-4		$*72 \pm 33$		$*136 \pm 105$	250 ± 77
DC3 7-5		7 ± 37		3 ± 98	19 ± 65
DC3 9-1		$*39 \pm 24$		84 ± 134	224 ± 77
DC3 9-2		17 ± 15		71 ± 157	186 ± 101
DC3 9-3		$*39 \pm 25$		$*289 \pm 228$	472 ± 147
TO 20-1	$*54 \pm 17$	$*53 \pm 17$	15 ± 81	65 ± 74	221 ± 63
TO 20-2	$*25 \pm 12$	$*25 \pm 12$	-37 ± 65	0 ± 60	117 ± 52
TO 24-1	$*166 \pm 55$		$*365 \pm 140$		668 ± 117
TO 24-2	$*80 \pm 24$		$*149 \pm 99$		378 ± 81
TO 23-3	$*67 \pm 28$		117 ± 124		303 ± 115
TO 25-1A		-9 ± 19		-3 ± 13	19 ± 10
TO 25-1B		-6 ± 19		1 ± 13	19 ± 10
TO 25-2A		0 ± 8		-10 ± 10	12 ± 5
TO 25-2B		1 ± 8		-6 ± 9	12 ± 5
TO 31	11 ± 12		$*63 \pm 45$		133 ± 42
TO 32		$*32 \pm 15$		-15 ± 23	38 ± 17
TO 37	$*50 \pm 29$		$*43 \pm 36$		60 ± 35
TO 48-1	$*26 \pm 10$	$*32 \pm 11$	1 ± 21	17 ± 18	58 ± 15
TO 48-2	13 ± 6	16 ± 7	-33 ± 20	-16 ± 16	27 ± 11
TO 48-3	$*20 \pm 10$	$*24 \pm 12$	0 ± 22	12 ± 20	42 ± 19
TO 48-4	17 ± 7	$*20 \pm 8$	-33 ± 22	-13 ± 18	35 ± 12
TO 48-5	6 ± 5	7 ± 6	-26 ± 15	-14 ± 13	14 ± 11

achieve this, 2 criteria are used to define sulphate production. The first criterion considers that some negative values are indicated. Although the negative values are generally within the errors associated with the measurements, they may also reflect uncertainties associated with the method. For example, although pSO_4^{2-} and pNH_4^+ are strongly correlated, as shown by Fig. 3a, the size distribution of pNH_4^+ will not of course exactly mimic that of pSO_4^{2-} . Further, some differences may be ascribed to changes in $\text{pSO}_4^{2-}/\text{pNH}_4^+$ between the point of filter sampling and the cloud base. It is assumed here that such differences are not systematic, and that the negative values indicate the detection limit for the method. This is

defined as two standard deviations of all the values which fall within the absolute of the most negative value. For this method, -15 nEq m^{-3} is the most negative value and there are 13 points bounded by [15]. The mean of the 13 points is 0 nEq m^{-3} and two standard deviations is 18 nEq m^{-3} . Thus, the first criterion is that all indications of production must exceed $+18 \text{ nEq m}^{-3}$. The second criterion is that only cases for which the lower limit of each uncertainty is above zero are considered. With both criteria considered together, there are 20 of a possible 36 data points indicating in-cloud SO_4^{2-} production. These points are marked by an asterisk in Table 4. For these cases, the relative amount of sulphate produced ranges between 8%

and 83% with a median of 27% (mean = 37%). Because of these criteria, the possibility of very low or no in-cloud sulphate production is excluded.

The absorption of NH_3 by the cloud droplets will increase the cNH_4^+ and therefore reduce the amount of sulphate indicated from eq. (1). This could also be a factor contributing to the presence of negative values in Fig. 4. The NH_3 could enter the cloud through the base during adiabatic ascent, or be entrained with air from outside the cloud. Hegg and Larson (1990) have shown that for certain situations the use of interstitial cloud NH_4^+ may result in an overestimation of H^+ produced in cloud, as a result of partitioning of NH_3 among the gas-phase, the cloud droplets and the interstitial aerosol particles. Here, the below-cloud rather than interstitial aerosol is used for

comparison, and it is unlikely that any NH_4^+ from NH_3 absorption will transfer out of the cloud droplets, since HNO_3 (not considered by Hegg and Larson) is a very significant species here (Table 2). HNO_3 will partition to the cloud droplets rather than to the aqueous aerosol particles, resulting in increased acidification of the solution droplets during condensation and inhibit the transfer of NH_4^+ out of the droplets. Therefore, it is expected that the presence of NH_3 will generally be such as to make these results slight underestimates. In any case, this effect is probably small as the ammonia concentrations measured during filter collections in the second half of the study (Table 2) are relatively low.

Fig. 5 shows the estimated in-cloud sulphate production using aerosol number concentration as

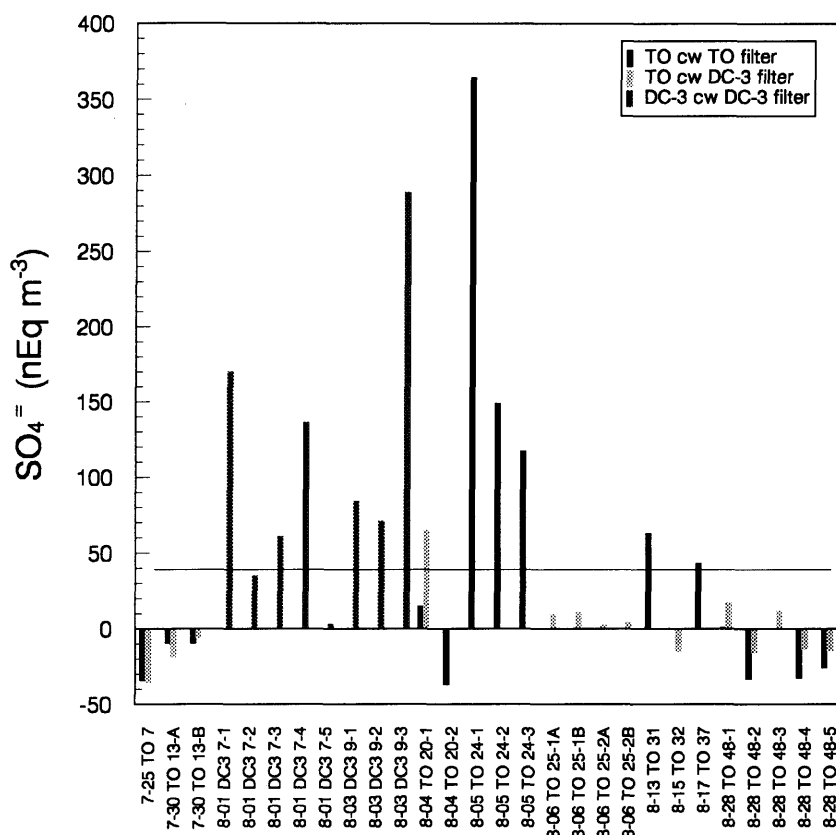


Fig. 5. Sulphate produced in cloud estimated by accumulation mode aerosol number concentration method. The line at 39 nEq m^{-3} represents 2 standard deviations of those values bounded by the absolute of the most negative value indicated.

a tracer. These results are also given in Table 4. The experimental errors were calculated in quadrature using the uncertainties for those quantities included in eq. (4) (LWC is part of $c\text{SO}_4^-$). The errors in the number method results are larger than for the ammonium method because on the right-hand side of eq. (3) the $p\text{SO}_4^-$ is compared with the $c\text{SO}_4^-$, resulting in an additional contribution from the LWC uncertainty. In the same way as for the ammonium method, the baseline uncertainty was estimated to be 38 nEq m^{-3} . Applying the same two criteria as discussed above, 6 of a possible 36 points are identified as indicating in-cloud production of sulphate. The relative quantity of sulphate produced in cloud ranged from 39%–71% with a median of 55% (mean = 55%).

The aerosol volume method should improve on the results obtained using the aerosol number method since the assumption of monodispersity is removed. The improvement should take the form of generally lower estimates for the level of sul-

phate production as demonstrated by the following example. The cumulative number distribution and cumulative volume distribution for 5 August case TO 24–2, identified by cross and open triangle symbols, respectively are plotted in Fig. 6. The cumulative volume distribution has been multiplied by a constant fraction (0.4 to represent a reasonable value for the fraction of sulphate present in the atmospheric aerosol), but this has no bearing on this discussion. For a high number scavenging fraction of say 90%, the volume scavenged fraction (proportional to the mass) is about 92% of that of the number approach. For a lower number scavenging fraction of say 20%, the volume scavenging fraction is about 48%, considerably higher than the number approach. Therefore, the volume method should provide a higher estimate for the nucleation scavenging fraction, and result in a lower estimate for aqSO_4^- .

The results using the volume approach are shown in Fig. 7 and do indicate less production than the number method. In fact, applying the

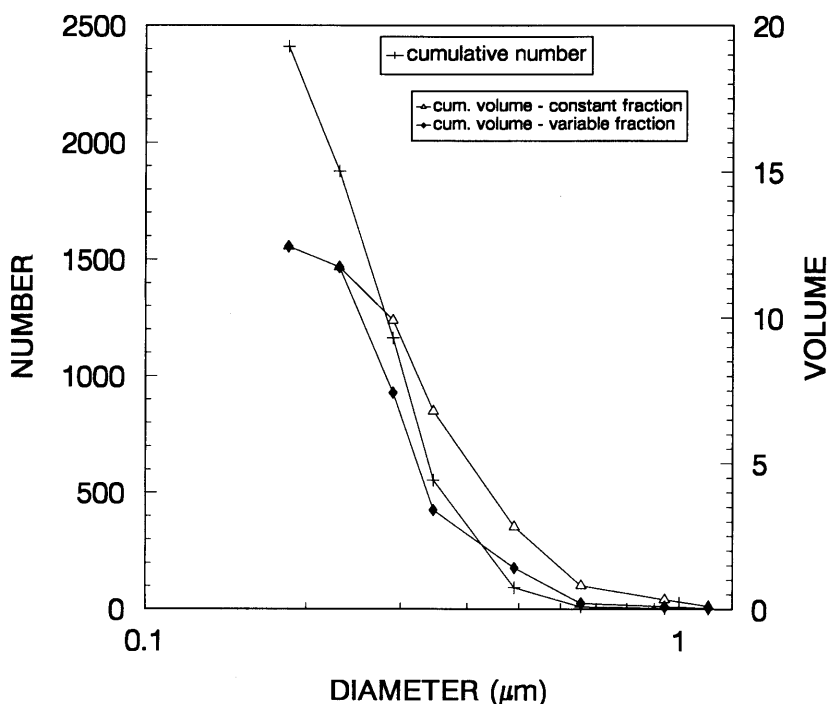


Fig. 6. Cumulative ASASP number and volume versus diameter plots for TO 24. Open triangles represent a constant fraction of cumulative volume arbitrarily chosen as 0.4. The solid diamonds represent sulphate distribution of the same mass, but one which is skewed towards particles of smaller size.

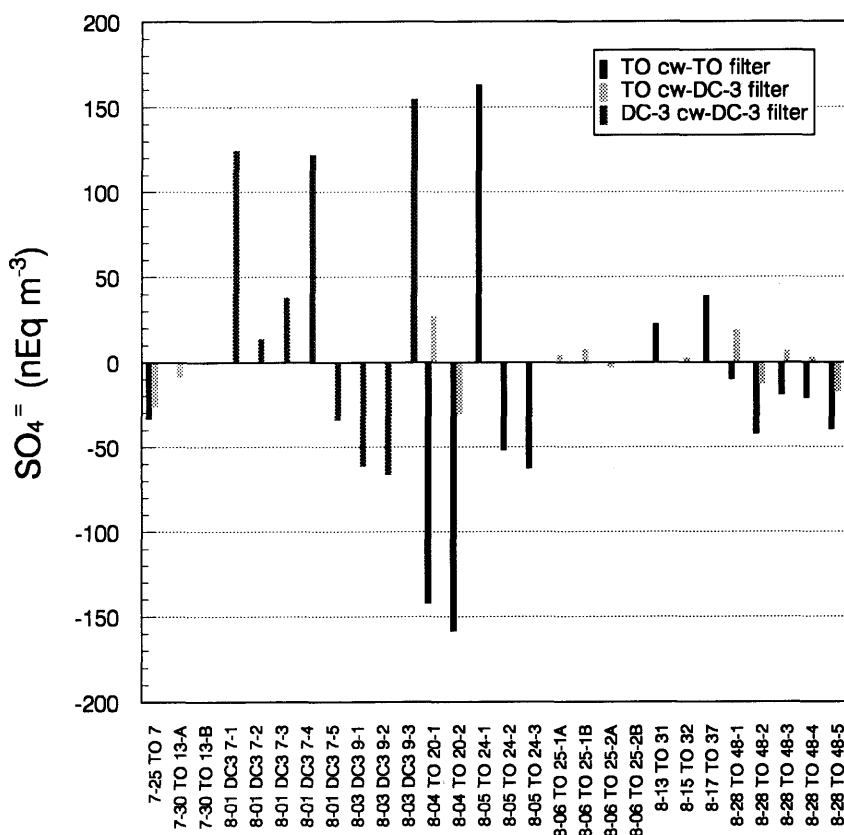


Fig. 7. Sulphate produced in cloud as estimated by accumulation mode aerosol volume concentration method.

same criteria as before to the volume method results in no sulphate production in cloud for any cases. One possible reason for this is that the pSO_4^- is preferentially distributed among the smaller particles. This is demonstrated with the use of the cumulative volume curves plotted in Fig. 6 for case TO 24-2. Using the constant fraction volume curve (open triangles) in eq. (4) results in an estimate of -52 nEq m^{-3} for $aqSO_4^-$, as shown in Fig. 7. If a sulphate distribution of the same mass, but one which is skewed towards particles of smaller size is used, and such an example is shown in Fig. 6 (filled diamonds; variable fraction), a higher estimate for $aqSO_4^-$ results. This skewed example when used in eq. (4) gives an estimate for $aqSO_4^-$ of 110 nEq m^{-3} , which is in much better agreement with the ammonium method results. The suggestion that the sulphate-mass-modal diameter is less than that of the

accumulation mode aerosol distribution agrees with the result of Leaitch and Megaw (1982), who, for the same study region, used CCN measurements to infer the bulk of the sulphate mass is narrowly distributed about $0.22 \mu\text{m}$ (the geometric volume mean diameter for the aerosol in this study was $0.29 \mu\text{m}$; Leaitch and Isaac, 1991). Thus the sensitivity of the volume method to the distribution of sulphate mass, relative to the total aerosol mass, may explain the apparent poor sensitivity of this method.

5.2. Interstitial measurements of SO_2 and oxidants

Further information concerning the in-cloud S(IV) oxidation process can be derived from examining the precursors of S(IV) oxidation and its governing factors.

The values of SO_2 , H_2O_2 , and O_3 at cloud base and in the cloud interstitial air during the time of

cloudwater sampling are given in Table 5 for the cases of detectable sulphate production indicated in Table 4. In 16 of the 17 cases, the interstitial SO_2 is lower than the cloud-base amount, and in 8 of the 16 cases the interstitial SO_2 is near zero or below detection limit. In the one remaining case (TO 37), a strong SO_2 plume (likely originating from near Sudbury, Ontario) was encountered in the cloud (fairweather cumulus based at 915 m and topped at 1220 m) which resulted in much higher SO_2 at this point. The general reduction in SO_2 from below cloud to in cloud offers reason to believe SO_2 was consumed in these clouds. In column 9 the amount of in-cloud $\text{SO}_4^{=}$ which would have been produced if the reduction in the SO_2 levels from cloud base to interstitial cloud was only due to consumption through aqueous-phase oxidation is given. These values are generally higher than the quantities determined using the NH_4^+ and number methods (column 10). Higher estimates based on the interstitial SO_2 are attributed to the entrainment of outside air with lower SO_2 levels than at cloud base, thus reducing

the actual amount of SO_2 supplied to the cloud in the case of cumulus. This is demonstrated using the vertical profile data of SO_2 , H_2O_2 and O_3 collected in the vicinity of the cumulus samples (DC3 9, TO 20, TO 24 and TO 31) shown in Fig. 8. The bases of the clouds and the sampling altitudes are marked. The SO_2 levels at the sampling altitude outside of cloud are much lower than at cloud base. In contrast, the oxidant levels (H_2O_2 and O_3) at the sampling altitudes outside of cloud are more similar to those at cloud base. This is consistent with the Table 5 data which show the cloud-interstitial and cloud-base oxidant levels to be more similar relative to SO_2 .

The higher estimates using the interstitial SO_2 in the case of stratiform cloud may occur because of difficulty in accurately determining "pre-cloud" values, or oxidant limitations. These points are discussed below in more detail.

Time series data of SO_2 and LWC for the DC3 7 case are plotted in Fig. 9. In this case, the samples were collected while flying level through the cloud. The cloudwater sampling times are also indicated

Table 5. Cloud interstitial and cloud-base oxidant levels for the cases identified for positive production of $\text{SO}_4^{=}$ (cases with asterisk in Table 4); the estimated SO_2 oxidized for cloud-base less the interstitial are given in column 9; column 10 is the amount of $\text{aqSO}_4^{=}$ estimated by NH_4^+ and number methods; the last two columns indicate the cloud water pH and LWC respectively

Flight #	Cloud Type	Cloud Base (ppb)			Interstitial (ppb)			Estimated SO_2 oxidized for CB-interstitial (nEq m^{-3})	$\text{aqSO}_4^{=}$ (nEq m^{-3})	Sample (pH)	LWC (g m^{-3})
		SO_2	H_2O_2	O_3	SO_2	H_2O_2	O_3				
DC3 7-1	S	2.3	NM	68	2.0	NM	73	27	65 ± 55	3.7	0.08
DC3 7-2	S	2.3	NM	68	0.9	NM	79	125	51 ± 24	3.6	0.17
DC3 7-3	S	2.3	NM	68	0.9	NM	78	125	34 ± 19	4.1	0.16
DC3 7-4	S	2.3	NM	68	0.4	NM	80	170	$72 \pm 33; 136 \pm 105$	3.2	0.20
DC3 9-1	C	2.3	NM	108	0.8	NM	81	143	39 ± 24	4.8	0.12
DC3 9-3	C	2.3	NM	108	0.8	NM	81	143	$39 \pm 24; 289 \pm 228$	6.0	0.16
TO 20-1	C	1.1	2.6	87	BDL	2.7	76	72	$54 \pm 17; 53 \pm 17$	4.5	0.41
TO 20-2	C	1.1	2.6	87	BDL	2.9	76	72	$25 \pm 12; 25 \pm 12$	5.0	0.18
TO 24-1	C	4.0	2.4	72	BDL	NM	60	333	$166 \pm 55; 365 \pm 140$	4.1	3.10
TO 24-2	C	4.0	2.4	72	BDL	NM	73	333	$80 \pm 24; 149 \pm 99$	3.5	0.87
TO 24-3	C	4.0	2.4	72	0.4	NM	71	324	67 ± 28	3.2	0.22
TO 31	C	1.3	2.5	48	BDL	2.1	49	90	63 ± 45	4.7	0.32
TO 32	S	4.0	0.4	10	1.3	0.3	20	241	32 ± 15	3.8	0.18
TO 37	C	BDL	1.6	55	5.2	NM	53	ENP	$50 \pm 29; 43 \pm 36$	3.6	0.12
TO 48-1	S	0.5	0.5	43	0.1	0.5	62	36	$26 \pm 10; 32 \pm 11$	4.6	0.73
TO 48-3	S	0.5	0.5	43	0.2	0.4	50	27	$20 \pm 10; 24 \pm 12$	3.7	0.18
TO 48-4	S	0.5	0.5	43	0.1	0.5	54	36	20 ± 8	3.8	0.30

NM: no measurement; BDL: below detection limit; ENP: estimate not possible.

C: cumuliiform; S: stratiform.

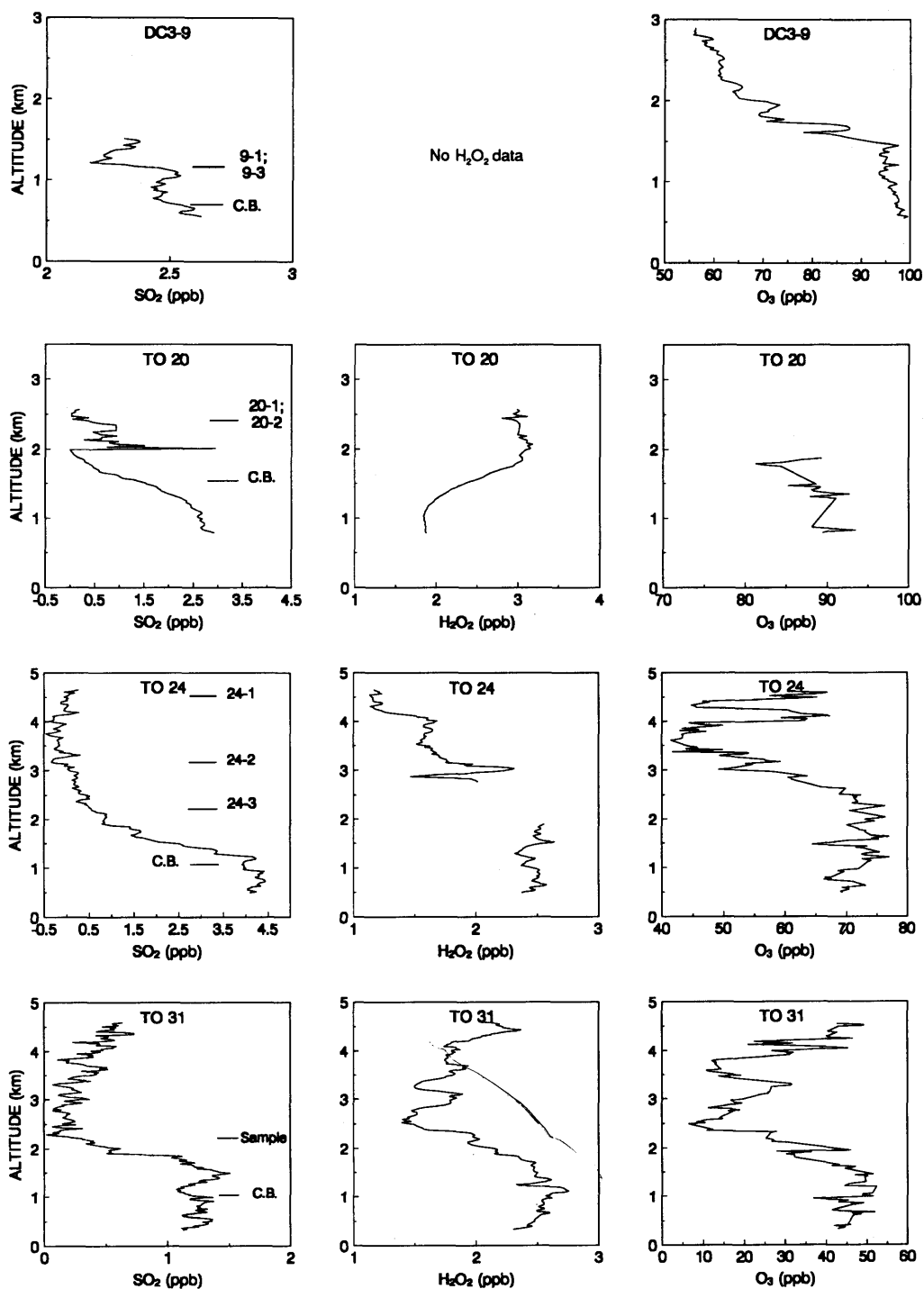


Fig. 8. Vertical profile data for SO_2 , H_2O_2 and O_3 collected in the vicinity of the cumulus samples.

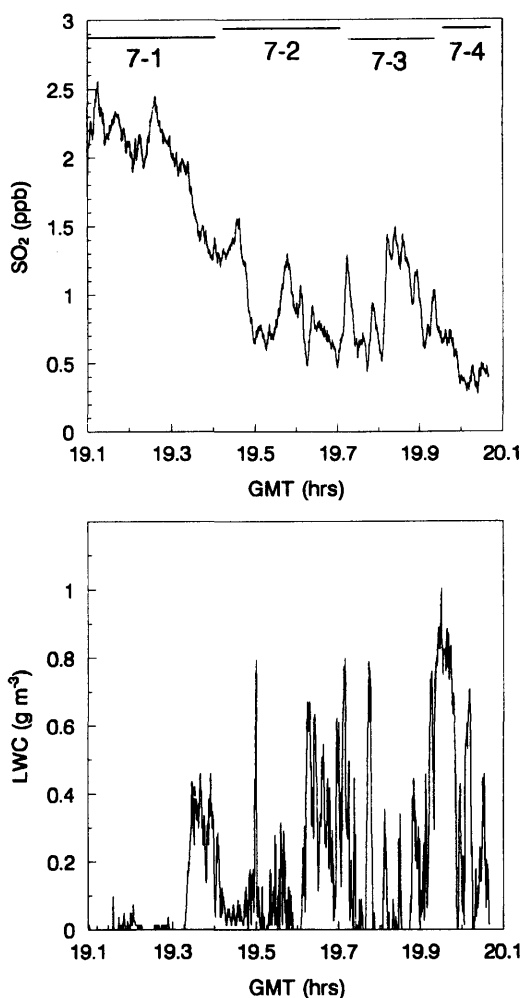


Fig. 9. Time series data of SO₂ and LWC for the DC3-7 samples.

in Fig. 9. There is a general decrease in SO₂ with increasing time, and during the out-of-cloud periods or times of relatively low LWC the SO₂ rises, but not as high as the cloud base level. For example, between 19.8 and 19.9 there is an increase in SO₂ to about 1.5 ppbv from about 0.7 ppbv as the LWC drops quite low for a few minutes. Thus, it may be for samples 7-2, 7-3 and 7-4 that the pre-cloud SO₂ was not as high as the cloud-base level indicated in Table 5, and this would account for the higher sulphate production estimated from the difference between cloud-base and interstitial SO₂.

The TO 48 cloudwater samples were collected during ascent and descent through cloud, and while level in cloud. In Fig. 10, vertical profile data of SO₂, H₂O₂, O₃, aerosol particle number concentration, LWC, and water vapour are plotted for both the ascent and descent. The ozone profiles indicate increasing ozone up to the top of the profile (about 4.7 km), suggesting a stratospheric influence. The H₂O₂ profile has a similar tendency as the ozone profile, except for depletion in the cloud (cloud indicated by LWC profile) and a sharp reduction at about 3.6 km. The water vapour data indicate a moist atmosphere up to about 3.6 km. The low H₂O mixing ratio above 3.6 km may explain the sharp reduction in H₂O₂ at this level, since reaction of water vapour with O(¹D) is an important step in the production of H₂O₂. The cloud was not continuous, but consisted of a layer between 1.6 km and 2.7 km, and a thinner layer above 3 km. The profiles of SO₂, ozone, aerosol number (the reductions in the number coincident with the cloud layers are due to nucleation scavenging) and water vapour suggest the air mass was continuous from cloud base to 3.7 km. The wind direction was steady at about 270° throughout the profile. Within the thickest cloud layer the SO₂ ranges between near zero and about 0.5 ppbv, thus the estimates in column 9 of Table 5 are reasonable, but possibly slightly high again.

Portions of samples TO 48-3 and 48-4 were analyzed for dissolved H₂O₂. In this case, a mass balance estimate of H₂O₂ is possible by comparing the H₂O₂ outside of cloud with the in-cloud gas-phase H₂O₂ plus the H₂O₂ dissolved in the cloudwater. This may indicate if H₂O₂ was consumed in the cloud, presumably due to oxidation of S(IV). While H₂O₂ may be lost by other mechanisms, recent field data suggest that H₂O₂ is conserved in cloud and dissolves approximately according to Henry's law in the absence of SO₂ (Macdonald et al., 1991; Noone et al., 1991). H₂O₂ dissolved in the cloudwater was 0.1 ppbv for sample 48-3 and 0.2 for sample 48-4. Interstitial H₂O₂ concentrations from Table 5 are 0.4 ppbv and 0.5 ppbv for 48-3 and 48-4 respectively; these values take into account the response time of the instrument. Therefore, the total in-cloud H₂O₂ is approximately 0.5 ppbv and 0.7 ppbv respectively. Although the cloud-base estimate is about 0.5 ppbv, the profile data suggests that the pre-

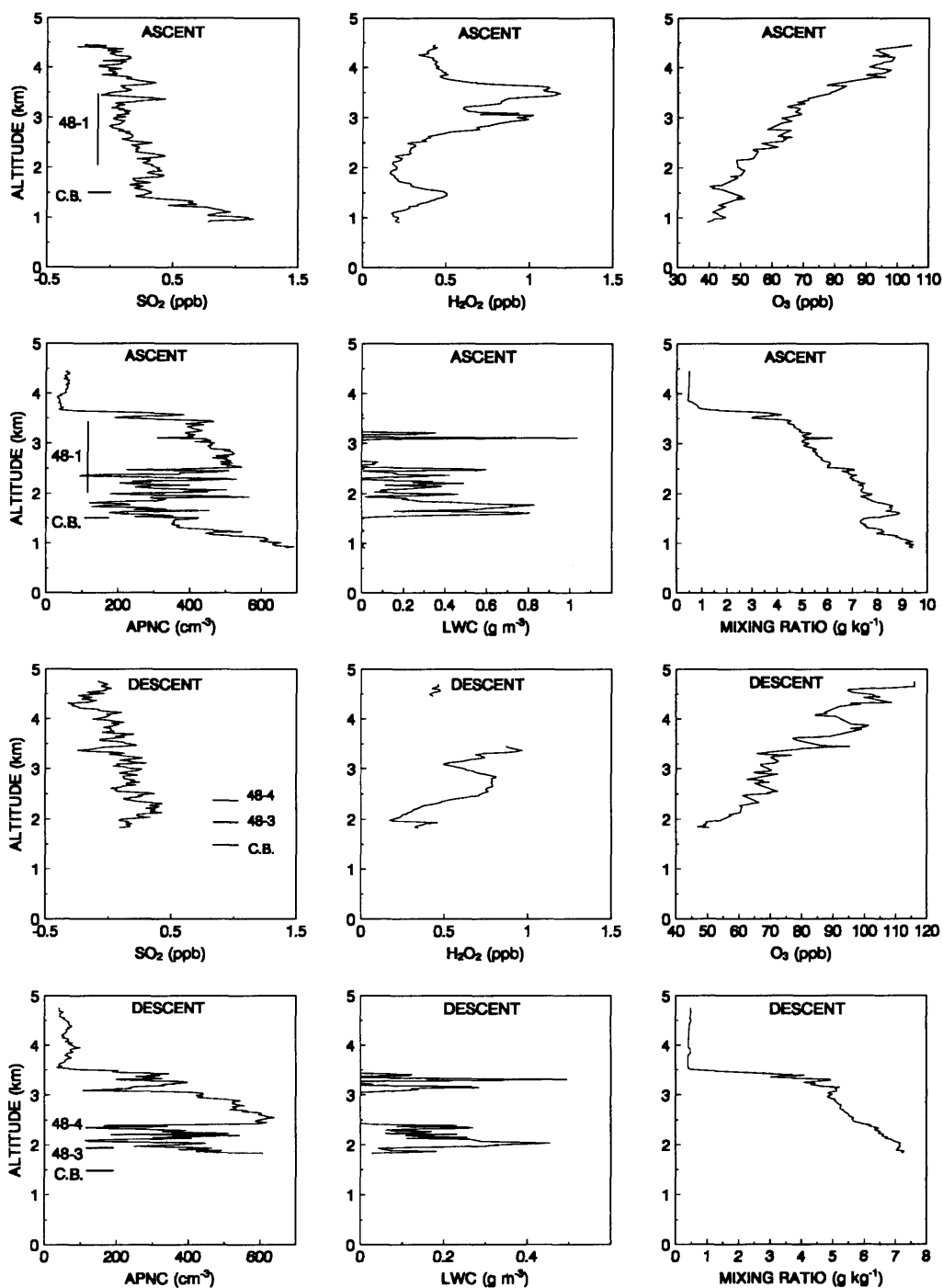


Fig. 10. Vertical profile data of SO₂, O₃, H₂O₂, aerosol number concentration, LWC, and water vapour for TO 48.

cloud H_2O_2 increased with altitude, in the same way as ozone, and by simple interpolation between the out-of-cloud peaks in the profile the pre-cloud H_2O_2 could well have been 0.7–0.9 ppbv for samples 48–3 and 48–4. For this pre-cloud H_2O_2 level, a loss of H_2O_2 of perhaps 0.2 ppbv is indicated. Such a result is low, but consistent with the other estimates of S(IV) oxidation for this case.

The TO 32 case is a plume case with considerable variability in SO_2 , and low oxidant concentrations. Hydrogen peroxide was also measured in the aqueous-phase. The samples were collected in a stratus layer located at the top of a shallow, mixed surface layer. The aqueous-phase H_2O_2 was 0.05 ppb, and adding to this the interstitial H_2O_2 gives a total in-cloud H_2O_2 of about 0.4 ppb. This is very close to the cloud base estimate, suggesting little loss of H_2O_2 . The production indicated by the ammonium method is relatively low, much lower than suggested by the interstitial SO_2 , and is explained by the relatively low level of H_2O_2 . This case, along with TO 37, appears to be situations of oxidant limitation.

11 of the 17 cases in Table 5 have sample $\text{pH} \leq 4.1$. H_2O_2 was measured in 7 of these cases at levels sufficient to account for the estimated sulphate production. For the measured levels of H_2O_2 and O_3 , the oxidation rate by H_2O_2 at lower pH is much higher compared with that by O_3 , and it is likely that H_2O_2 was the primary oxidant in these cases. Of course contributions from metal-catalyzed aerobic oxidation can not be ruled out. Of the 6 cases with $\text{pH} > 4.1$, at least one (TO 48–1), and possibly two more (TO 20–1; TO 31), have pH which are significantly affected by dilution due to condensed water, as evidenced by the higher LWC. In these cases H_2O_2 is also a candidate for the primary aqueous-phase oxidant. The cases for which O_3 and O_2 (metal-catalyzed) have the greatest likelihood of contribution to the sulphate production are DC3 9–1; DC3 9–3; TO 20–2. These data tend to follow the expected pattern that when both reduced sulphur and oxidants are higher, the amount of S(IV) oxidation is higher. Also, the cases with the greatest absolute amount of sulphate produced in cloud are among the cases with the lowest relative production (DC3 7–4, 9–3; TO 24). This may explain why it is extremely difficult to detect this process in this region.

5.3. Comparisons with other work

The number of observations of sulphate production as a function of the percent sulphate produced is shown in Fig. 11. The majority of the observations are between 20–60%. The difference between the median for the ammonium and number methods (27% and 55%, respectively) is consistent with previous discussion which shows the number method to be an upper estimate, and suggests the ammonium method could be a lower estimate. For all data points combined, the median is 39% (mean = 41%). These estimates are somewhat higher than the estimates of Husain (1989) and Husain et al. (1991) of <40% with a median of about 16% for in-cloud SO_4^{2-} production in summer clouds. On the other hand, the present estimates are considerably lower than those of Hegg et al. (1984), Hegg and Hobbs (1986), and Hegg and Hobbs (1988). Analyzing Hegg's results in a manner similar to that done here (i.e., cases within noise eliminated) gives a range of 66% to 150% with a median of 90% for samples collected in the western US. Hegg and Hobbs (1988) report seven observations made over North Carolina for which the range of sulphate production is 73%–88%. Similarities between the results of Husain and Husain et al., with the present results are expected because their data are for a region in relatively close proximity to the present study region and during the same time of year. Thus, the differences between their results and the present results may be more related to technique. Husain and Husain et al., use $\text{SO}_4^{2-}/\text{Se}$ to determine excess SO_4^{2-} in cloud. One possible reason for the difference may be due to the larger mass median diameter of selenium (0.68 μm , Milford and Davidson, 1978) compared to mass median diameter of SO_4^{2-} (0.52 μm , Milford and Davidson, 1985), which would result in a lower value of SO_4^{2-} to Se scavenged. The difference may also be explained by the fact that cases of no and very low production have been excluded by the present analysis. Greater differences between the present results and those of Hegg et al., and Hegg and Hobbs may be due at least in part to the different geographical locations and conditions of measurements, but the techniques are also different. In addition, it should be noted that these estimates compare favourably with estimates for a few cases made using a cloud chemistry model and this data set (De Valk, 1992).

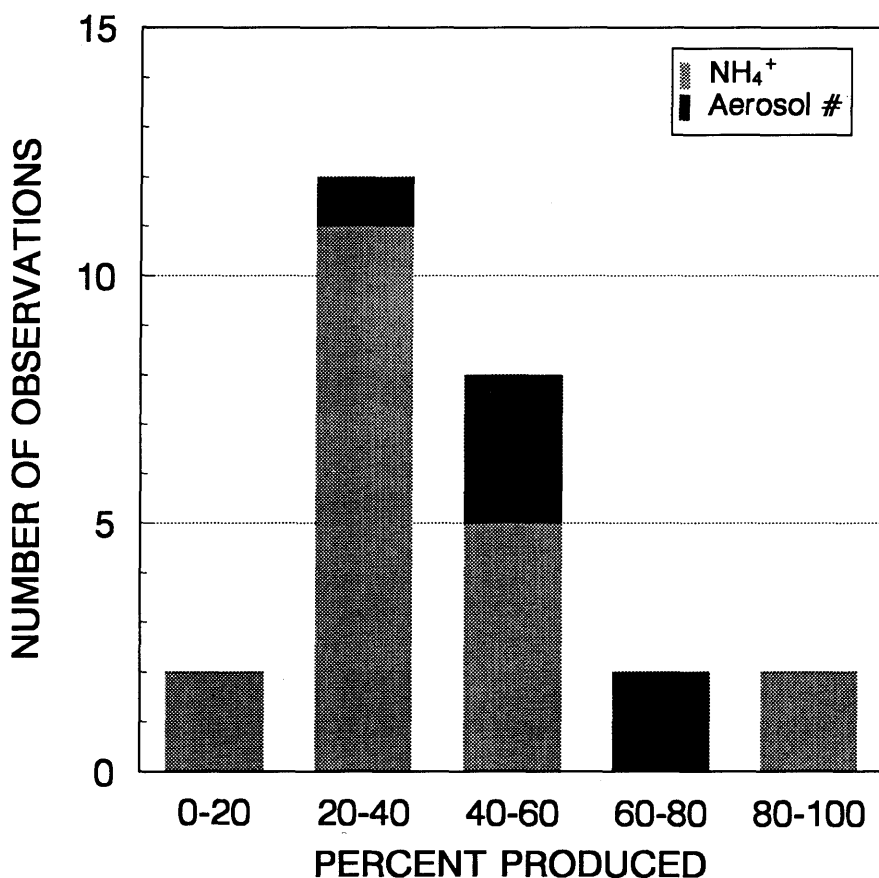


Fig. 11. The distribution of the observations of in-cloud SO_4^{2-} produced as a function of percent of total cloudwater sulphate.

Finally, these results estimate the sulphate produced at the point of time in the history of the cloud when the samples were collected. It is possible that had the sampling been conducted some time later the results would have been different. Consider the interstitial levels of SO_2 relative to the cloud base estimates given in Table 5. In all of the TO cases, with the exception of the plume cases (i.e., TO 32 and 37), the interstitial SO_2 is much reduced from the cloud base level, and either near zero or below detection limit. Thus, in these 9 instances the potential for further SO_2 oxidation is relatively low compared to that estimated. The DC3 cases indicate somewhat more interstitial SO_2 , and in these instances, as well as the plume cases, potential for further conversion of S(IV) exists. The potential for such oxidation also

depends on the lifetime of the cloud. Cumuli are relatively short-lived with lifetimes of tens of minutes (e.g., Schemenauer and Isaac, 1984), while the lifetime of stratiform cloud can be hours. In the latter case, it is more likely for an additional strong contribution to in-cloud sulphate to be made if significant SO_2 is present.

6. Summary and conclusions

Airborne observations of air and cloud chemistry and microphysics have been examined to determine the contribution of S(IV) oxidation to sulphate measured in summer clouds sampled over central Ontario, Canada.

The relative amount of the cloudwater SO_4^{2-} produced in cloud was estimated using ammonium as a conservative tracer of the cloudwater SO_4^{2-}

due to nucleation scavenging. Detectable production is indicated for 20 of 36 data points from which the fraction of the total cloudwater SO_4^- due to in-cloud oxidation was determined. The median (mean) SO_4^- production for these 20 data points was 27% (37%), and ranged from 8% to 83%. Due to NH_3 scavenging, these results may be slight underestimates.

Detectable production was found for 6 of 36 data points using the number concentrations of aerosols and cloud droplets to indicate nucleation scavenging. The relative quantity of sulphate produced is 39%–71% with a median (mean) of 55% (55%). Because of the nature of the aerosol size distribution this method may overestimate the quantity of sulphate produced.

The aerosol volume was substituted for the number concentration as a tracer for nucleation scavenging. In doing so, no sulphate production was indicated. It was shown that this could indicate the mass of sulphate is preferentially distributed among the particles of sizes smaller than the total aerosol accumulation-mode mass modal size.

The combined results give the estimated range of detectable sulphate produced in these clouds at

8%–83%, with the majority of the cases between 20%–60%. The median for the 26 observations is 39% (mean = 41%). Because of the difficulty of detection, these results are generally for situations with higher concentrations of species, and do not include the possibility of very low or no in-cloud SO_4^- production.

The pH of the samples for which in-cloud SO_4^- production is indicated ranged from 3.2 to 6.0, with a median of 3.8. Where measured, H_2O_2 was present at levels sufficient to account for the S(IV) oxidation in many of the cases. Contributions from other oxidants are also possible, and in a few cases might dominate.

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