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Cloud droplet nucleation and cloud scavenging of aerosol sulphate in polluted atmospheres

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ABSTRACT

Aircraft investigations of the microphysical and chemical properties of mildly to moderately convective clouds and stratiform clouds were conducted during the summer of 1982 and the early winter of 1984 over Algonquin Park, Ontario, Canada. Similar studies were carried out during the autumn of 1984 over upper New York state. Varying degrees of polluted conditions were observed. For the situation where the cloud liquid water content was close to the adiabatic value and the particle concentration was <750 cm^{-3}, the concentration of cloud droplets was directly proportional to the number concentration of cloud-base aerosol particles. For particle concentrations above 750 cm^{-3}, the cloud droplet concentration did not increase as fast as the particle numbers. An adiabatic model describing the condensational growth of cloud droplets predicted this apparent non-proportionality and indicated it to be the result of increasing competition for water vapour by increasing numbers of cloud condensation nuclei. The best quantitative agreement with the observations was obtained for the accommodation coefficient for condensation of water equal to unity and low values of the updraft speed at cloud base. Comparisons between cloud-averaged number concentrations of cloud droplets and number concentrations of cloud-base aerosol particles behaved in a very similar manner to the comparisons of near adiabatic cloud droplet concentrations with aerosol concentrations. Comparisons of the mass concentrations of cloudwater $SO_4^=$ with that of aerosol $SO_4^=$, measured at ground level, appeared to follow a similar behaviour as the cloud droplet concentrations, but with a much larger uncertainty.

1. Introduction

The nucleation of cloud droplets is fundamental to the chemistry as well as the physics of clouds. Submicron particles in the atmosphere are good sources of cloud nuclei because hygroscopic sulphate compounds frequently compose a large fraction of their mass (e.g. Twomey, 1977). Thus, nucleation is a major pathway for the scavenging of aerosol sulphate ($SO_4^=$) by cloudwater (CW). Observations of this process in moderate convective cloud by Hegg and Hobbs (1983) have shown it to be typically quite efficient, with an average of $\approx 63\%$ (based upon twelve cases) of the aerosol $SO_4^=$ incorporated into the CW.

Aerosol pollution may modify the cloud droplet size spectrum (e.g. Barrett et al., 1979) which, in turn, may influence the onset of precipitation (e.g. Lee et al., 1980). Such modification may also alter the transfer of radiation in the cloud. For instance, Twomey et al. (1984) have suggested that continued increase in the anthropogenic cloud nuclei loading of the atmosphere could lead to a severe increase in the cloud albedo, through the changing of the droplet spectra, and this might result in a cooling of the atmosphere which could potentially offset the "greenhouse effect".

Changes in the cloud droplet size spectrum are directly related to the number concentration of cloud droplets for a constant liquid water content. In any given parcel of cloudy air, the number of

cloud droplets will depend upon the spectrum of the cloud condensation nuclei (CCN) and upon the supersaturation history of that cloud parcel. Twomey (1959) derived an analytical approximation to determine the number of cloud droplets formed during adiabatic cloud formation. Subsequently, Twomey and Warner (1967) used measurements of cumulus over Australia to verify the use of this approximation for conditions of relatively low particle concentration (with respect to the eastern North American continent) and moderate cloud updraft speeds (assumed to be 3 m s^{-1}). However, for more polluted conditions, as often found in eastern North America, or for less convective cloud (i.e. stratus, stratocumulus, fairweather cumulus), cloud supersaturations may be lower, owing to stronger competition for water vapour or lower updraft speeds. Leaitch et al. (1984) found that for light to moderately convective cloud, the measured concentration of cloud droplets was apparently not continuously linear with respect to the concentration of nuclei measured below cloud. Jensen and Charlson (1984) have modelled the nucleation scavenging of NH_4HSO_4 aerosol in adiabatic updrafts. For small constant updraft speeds, as might be found in stratiform cloud, they found that the fraction of aerosol $SO_4^=$ scavenged by the cloud will decrease with increasing aerosol $SO_4^=$ concentration.

In this paper, data collected from three field programs is used with an adiabatic model to examine the nucleation of cloud droplets and scavenging of aerosol $SO_4^=$ with increasing levels of pollution. This is done first by considering how cloud droplet number concentrations measured in near adiabatic situations vary with below-cloud concentrations of aerosol particles and CCN. Secondly, numerical computations are performed for the determination of the concentration of cloud droplets produced in an adiabatic updraft. The effect of model variables on the calculated droplet concentrations and on comparisons with the observed values are examined. It is shown that a physically and chemically reasonable adiabatic model can approximate the near adiabatic observations. Finally, variations of cloud-averaged droplet number concentrations and CW $SO_4^=$ concentrations are compared with respective below-cloud observations of aerosol number and aerosol $SO_4^=$ concentrations.

2. Experimental

The data discussed herein were collected during studies carried out in the summer of 1982, the winter of early 1984 (hereafter referred to as 1984a) and the autumn of 1984 (hereafter referred to as 1984b). During 1982 and 1984a, microphysical measurements and samples of cloudwater were collected over regions of central Ontario, Canada, in non-precipitating cumuliform and stratiform cloud, respectively. During 1984b, microphysical measurements were made over upper New York state in both cumuliform and stratiform cloud. All microphysical data and several cloudwater samples were collected from a deHavilland Twin Otter, operated by the National Research Council of Canada. During 1984a, some cloudwater samples were collected from a DC-3, operated by Energy, Mines and Resources Canada.

Cloud droplets and supermicron aerosol particles were measured with a Particle Measuring System (PMS) forward scattering spectrometer probe (FSSP). The cloud droplet concentrations (CDC) were corrected for probe dead time and coincidence error according to the theoretical analysis of Baumgardner et al. (1985). Submicron aerosol particle concentrations (APC) were measured with a PMS active scattering aerosol spectrometer probe (ASASP-100X). Calibrations of the ASASP with latex particles and nearly monodisperse particles of pure NaCl have shown the minimum detectable size for this particular probe to be reliably between 0.17 and 0.18 μm diameter. This is supported by the findings of Pinnick and Auvermann (1979) who measured a lower limit for the ASASP of ≈ 0.16 μm for particles with real indices of refraction between 1.5 and 1.6. Further, this particular ASASP is equipped with heating elements in the sampling nozzles to reduce icing problems encountered when flying in supercooled cloud. These heaters were routinely kept on, whether in cloud or not. Field measurements of aerosol size distributions at various altitudes under convective cloud with relative humidities ranging from ≈ 55 to $\approx 95\%$ have indicated no change in the size spectra. This is taken to mean that aerosol solution droplets are almost completely dried before measurement. Additional support for this claim has been derived from tests with laboratory aerosols,

which have shown that the heat generated by the de-icing elements will dry NaCl solution droplets at relative humidities up to at least 95%.

During 1984a aerosol particles were also measured from the aircraft with a Thermo-Systems Incorporated (TSI) CN counter. The aerosol was filtered with a TSI diffusion battery before counting. Aerosol was sampled from three stages of the diffusion battery with measured 50% concentration cut-off diameters of 0.03, 0.11 and 0.20 μm.

Cloud liquid water concent (LWC) was measured with a Johnson-Williams (JW) liquid water content probe. The calibration procedure for the JW probe is recorded by Strapp and Schemenauer (1982). All measurements onboard the aircraft were recorded at 1 second intervals. With this frequency, spatial variations over $\approx$ 70 m path lengths can be examined.

Warm cloudwater samples were collected from the aircraft with slotted rod collectors designed at the State University of New York at Albany and described by Winters et al. (1979). Supercooled cloudwater was collected by riming onto polyethylene meshes or rods.

During 1982, concentrations of CCN were measured on the ground at a location remote from local anthropogenic sources, but in the vicinity of the aircraft flights. CCN concentrations active at 0.4% supersaturation with respect to water (S) were determined with a continuous flow thermal diffusion chamber (Hudson and Squires, 1976) and those active at between 0.03–0.15% S were measured with an isothermal haze chamber (Hudson, 1980).

Aerosol samples were collected on teflon filters at the same ground-level location as the CCN measurements. Both water and filter collections were analyzed by ion chromatography for the major water-soluble ions.

3. Microphysical observations

Air entrained into clouds will lower the LWC below the adiabatic value by changing the size and/or concentration of cloud droplets. Frequently, entrainment will act to reduce the number of droplets, but it can also lead to new cloud droplets and possibly an increase in the number concentration (e.g. Baker et al., 1980). In order to examine the consequences of increasing levels of pollutants on the number of cloud droplets without any such ambiguity, it is best to examine regions of cloud where mixing is unimportant.

Comparisons were made between the maximum LWC (1 second average; $\approx$ 70 m distance scale) observed during a cloud penetration and the adiabatic LWC calculated for the cloud under investigation. Although a 1 second average was used, the LWC of the surrounding cloud (i.e. over a path of several hundred metres) was generally similar to the maximum value. With the near adiabatic requirement in mind, 17 results from 1982, 12 from 1984a and 15 from 1984b were chosen. Data were also chosen to exclude the presence of the ice phase, so that droplet concentrations were not unduly influenced by evaporation resulting from the lower vapour pressure over ice surfaces relative to water surfaces. The measured and calculated adiabatic LWC's for these cases are plotted in Fig. 1. Much of the scatter in Fig. 1 can be attributed to uncertainties in the estimation of cloud-base parameters, and this accounts for the superadiabatic points. On average, the points are slightly subadiabatic, but within 20% of adiabatic.

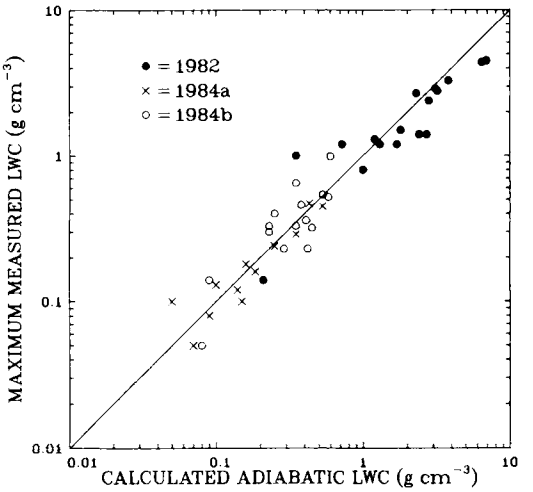

Fig. 1. Maximum liquid water content (LWC) measured during cloud penetrations compared with the adiabatic LWC calculated using observed cloud base temperature and pressure.

The LWC of these near adiabatic cloud parcels (Fig. 1) generally decreased from summer to autumn to winter. This happened because the measurement altitude, above cloud base, and cloud-base temperature tend to decrease from summer to winter. The lowering of the measurement altitude was the outcome of progressively weaker convective activity from summer to winter.

Fig. 2 shows a comparison of the combined particle plus droplet concentration (APC + CDC) measured in cloud with the cloud-base APC for the same 1 second points of Fig. 1. The droplet concentration at the point of the maximum LWC was not always the maximum concentration observed for a particular penetration. The mean of the ratio of the maximum CDC to the CDC at the maximum LWC was 1.11 with a standard deviation of 0.10. Therefore, the maximum observed CDC were only $\approx 11\%$ higher on average. The low standard deviation indicates, as is evident from the individual comparisons, that the discrepancies are not strongly weighted towards low or high concentrations. Because cloud droplets may be counted by the ASASP probe, some discrimination between aerosol and droplets is necessary to determine the in-cloud APC. This was accomplished by finding the minimum in the combined ASASP-FSSP size spectrum and defining all particles smaller than the diameter associated with the minimum to be interstitial aerosol. Such a procedure is valid as long as the mean size of the droplets is larger than ≈ 3–4 μm diameter, as is the case for these measurements.

The data of Fig. 2 suggest that for low particle concentrations, the CDC + in-cloud APC is greater than the cloud-base APC, presumably the result of particles smaller than the detection limit of the ASASP nucleating cloud droplets. For higher particle concentrations the CDC + in-cloud APC is similar to or slightly lower than the cloud-base APC. In Fig. 3, the CDC measured at the point of the maximum LWC is compared with the APC measured at or near cloud base. The observed range of the CDC is smaller than that of the APC. Below ≈ 750 cm^{-3} the CDC is greater than the APC, while above 750 cm^{-3} the CDC is lower than the APC. The slightly smaller droplet concentrations found in the winter study were probably the result of weaker convection during that period.

Measurements of CCN during 1982 coincided with 9 of the 17 chosen cloud penetrations. Although these observations were made on the ground, Hudson (1982) has shown that, for

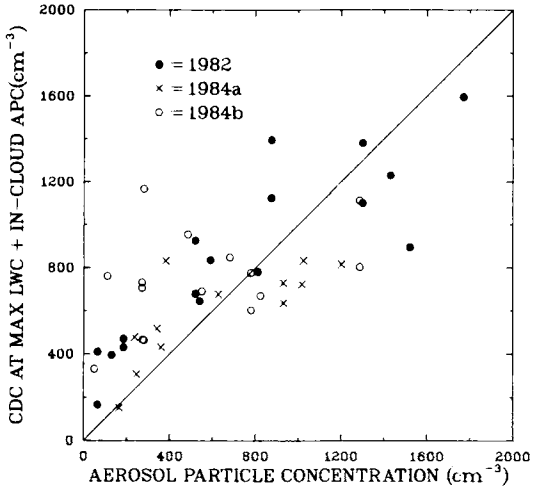

Fig. 2. The sum of the cloud droplet and in-cloud large aerosol particle (>0.17 μm) concentrations measured at point of maximum LWC (Fig. 1) as a function of the concentration of large particles measured at or near cloud base.

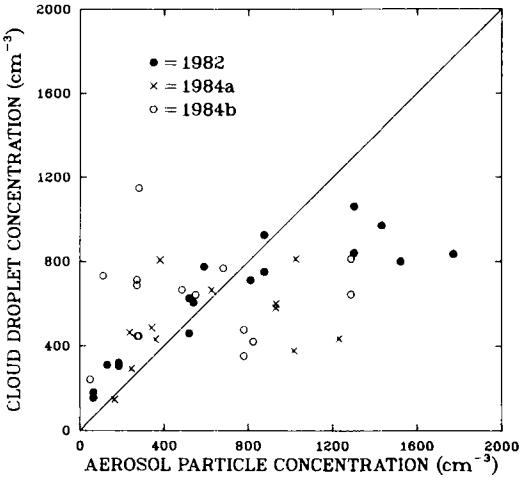

Fig. 3. Cloud droplet concentrations measured at points of maximum LWC (Fig. 1) as a function of the concentration of large aerosol particles (>0.17 μm) measured at or near cloud base.

summer convective situations, CCN spectra are generally conservative from ground to cloud base. Also, Isaac et al. (1986) show, from vertical profiles of APC, that the gradient in particle concentration from ground to cloud base was generally small and, on average, the cloud-base concentrations exceeded those near the ground. Because CCN concentrations during 1982 corresponded directly with particle concentrations (Fig. 4) it is expected that any vertical gradient in the CCN up to cloud base was generally small. The CCN concentrations spans a much larger range than the APC in Fig. 4 because, except for pure water insoluble particles, the particle size associated with 0.4% S is generally much smaller than that detectable with the ASASP: for pure $(NH_4)_2SO_4$ particles the size associated with 0.4% S is ≈ 0.05 μm. The concentration of cloud droplets at the maximum LWC versus that of CCN, active at 0.4% S, is plotted in Fig. 5. The bars in Fig. 5 are indicative of the range of concentrations measured during the period of the flight on which the CDC was measured. In Fig. 5, the droplet concentrations are apparently independent of the nucleus concentrations above a CCN concentration of ≈ 1000 cm^{-3}. The results in Fig. 3 and 5 are not incompatible with those of Twomey and Warner (1967). The latter study, if compared with measurements in Fig. 3 and 5 would probably occupy the region with particle or nuclei concentrations <500 and <1100 cm^{-3}, respectively, because of the relatively "clean" air in which their measurements were conducted.

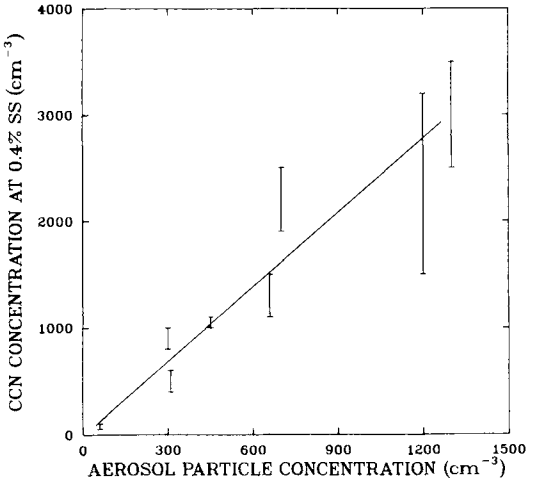

Fig. 4. Relation between the concentration of CCN active at 0.4% supersaturation and the concentration of large aerosol particles (>0.17 μm). Measurements are from 1982.

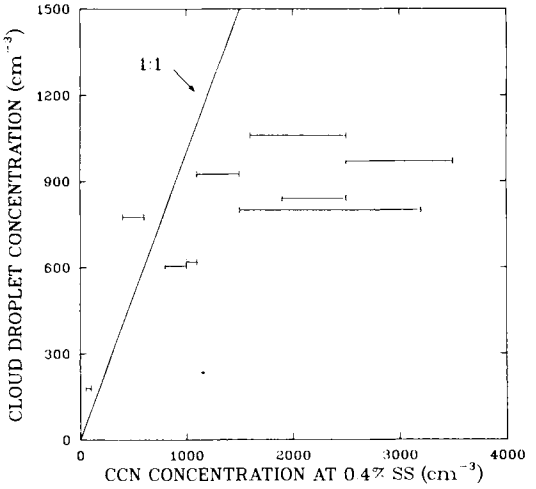

Fig. 5. Cloud droplet concentrations measured at points of maximum LWC (Fig. 1) as a function of the corresponding range (indicated by bars) of the concentration of cloud condensation nuclei active at 0.4% supersaturation and measured at ground level. Measurements are from 1982.

In order to examine whether or not the relationships between the CDC and APC/CCN (Fig. 3 and 5) could be explained by conventional nucleation theory, numerical simulations have been carried out. The model and simulations are described in the next section.

4. Model

The model is used to simulate the cloud droplet spectrum for a parcel of air ascending adiabatically for a specified updraft speed. The supersaturation is specified from the equation for the rate of change of the supersaturation taken from Pruppacher and Klett (1978) and written as

$$\frac{dS}{dt} = \left(\frac{\varepsilon L g}{R_a T^2 c_p} - \frac{g}{R_a T}\right) V - \left(\frac{p}{\varepsilon e_s} + \frac{\varepsilon L^2 [1+S]}{R_a T^2 c_p}\right) \frac{dW}{dt} \quad (1)$$

where

S = supersaturation
t = time
ε = 0.622 (molecular weight of water/molecular weight of air)
L = latent heat of evaporation
g = gravity
R_a = gas constant for dry air
T = temperature (K)
c_p = heat capacity of air
V = updraft velocity
p = pressure
e_s = saturation vapour pressure of water
W = liquid water content (LWC)

The microphysics of the condensation process is divided into two parts described below:

(a) For solution droplets with a salt mass concentration of $>1\%$: the rate of change of droplet growth is defined from Mason (1957), with i (van't Hoff factor) replaced by $\nu\cdot\Phi_s$ (Pruppacher and Klett, 1978), as

$$r\frac{dr}{dt} = \left\{S + 1 - \exp\left[\frac{2M_w\sigma_{s/a}}{R_g\rho_s Tr}\right] \times \left[1 + \frac{\nu\Phi_s M_w m}{M_s\left(\frac{4}{3}\pi r^3\rho_s - m\right)}\right]^{-\rho/\rho_s}\right\} \times \left\{\left[\frac{L^2\rho_s M_w}{K'R_g T^2}\right] - \left[\frac{L\rho_s}{K'T}\right] + \left[\frac{\rho_s R_g T}{M_s D' e_s}\right]\right\}^{-1} \quad (2)$$

(b) For dilute solution droplets: the rate of change of growth is defined from Pruppacher and Klett (1978) as

$$r\frac{dr}{dt} = \left\{S + 1 - \left[\frac{2M_w\sigma_{s/a}}{R_g\rho Tr}\right] + \left[\frac{\nu\Phi_s m M_w}{M_s\left(\frac{4}{3}\pi r^3\rho - m\right)}\right]\right\} \times \left\{\left[\frac{L^2\rho M_w}{K'R_g T^2}\right] - \left[\frac{L\rho}{K'T}\right] + \left[\frac{\rho R_g T}{M_s D' e_s}\right]\right\}^{-1} \quad (3)$$

The terms in eqs. (2) and (3) are defined as follows:

r = radius of droplet
$\sigma_{s/a}$ = surface tension at solution/air interface (function of temperature and solute concentration)
ρ_s = density of solution droplet
m = mass of dry nucleus
ν = number of ions into which the salt dissolves
Φ = osmotic coefficient of solution droplet
ρ = density of water
T = temperature
R_g = universal gas constant
M_w = molecular weight of water
M_s = molecular weight of nucleus material
L = latent heat of evaporation (function of temperature)
e_s = saturation vapour pressure at temperature T
S = supersaturation

D' and K' are defined as follows:

$$D' = \frac{D}{\left[\frac{r}{r+\lambda} + \frac{D}{r\alpha_c}\left(\frac{2\pi M_w}{R_g T}\right)^{1/2}\right]}$$

$$K' = \frac{k}{\left[\frac{r}{r+\lambda} + \frac{k}{r\alpha_t\rho c_{pa}}\left(\frac{2\pi M_a}{R_g T}\right)^{1/2}\right]}$$

where

D = diffusivity of water vapour in air
k = thermal conductivity of air
c_{pa} = specific heat of air
M_a = molecular weight of air
λ = 1.2×10^{-5} cm
α_c = accommodation coefficient for the condensation of water vapour
α_t = thermal accommodation coefficient

If the aerosol particles were to be considered as only partially water soluble then the $\nu\Phi_s$ term in eqs. (2) and (3) would be replaced by

$$\frac{\nu\Phi_s\varepsilon M_w\rho_n r_n^3}{M_s(r^3 - r_n^3)}$$

where

ε_m = mass fraction of the water soluble material
ρ_n = density of the combined dry nucleus
r_n = radius of the combined dry nucleus

Computations were initiated with the composite aerosol size distribution illustrated in Fig. 6. The three modes of the distribution are the results obtained from gamma functions which approximate an average of measurements made with the diffusion battery—CN counter, ASASP and FSSP. The distribution was subdivided into 51 discrete size classes for computational pur-

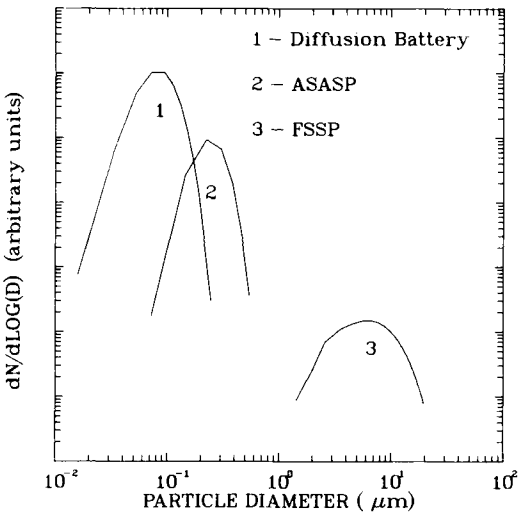

Fig. 6. Dry particle size distributions used in the calculations of cloud droplet concentrations. The curves are derived from gamma functions which have been approximated to the measurements made using the diffusion battery, the ASASP and the FSSP.

poses. The presence of two modes or a double peaked size distribution between ≈ 0.01 and 1.0 μm has been previously reported by Hoppel et al. (1985). In the latter study, the two modes were attributed to the partitioning of the size distribution by successive processing of the aerosol by cloud with a high fraction of the larger particles acting as cloud condensation nuclei. Since most of the size distributions used in the average for Fig. 6 were collected in the vicinity of cloud, this explanation is not inconsistent with this study.

Three sets of assumptions concerned with the initial aerosol spectrum were considered as follows:

(*Case 1*)—Submicron particles (modes 1 and 2, Fig. 6) were composed of pure $(NH_4)_2SO_4$ and the supermicron (mode 3) particles were composed of pure $Ca(NO_3)_2$ (a possibility suggested, for the North Bay study area, by Leaitch et al., 1986: there was no evidence for the presence of significant concentrations of NaCl in the aerosol). Concentrations were varied between 0 and 2000 cm^{-3} for mode 2 particles, with the mode 1 particle concentrations assumed to be a factor 5 greater than the mode 2 values. The latter factor is based on the measurements of condensation nuclei made during 1984a. The concentration of particles in mode 3 was chosen as a constant 0.12 cm^{-3}, according to the average of our measurements with the FSSP. The concentration of particles in this size range has been shown to be nearly independent of the concentration of the submicron aerosol (Isaac et al., 1986), for moderate to heavily polluted situations.

(*Case 2*)—The submicron aerosol was specified as for case 1, but the concentration of supermicron particles was chosen to be zero. This was done in order to study the potential effect of the supermicron aerosol on the nucleation of cloud droplets and because of much uncertainty as to the composition of the supermicron aerosol.

(*Case 3*)—The particle concentrations were specified as for case 1, but the submicron particles were composed of 50% $(NH_4)_2SO_4$ and 50% SiO_2 (an inorganic water-insoluble substance). Similarly the supermicron particles were composed of 50% $Ca(NO_3)_2$ and 50% SiO_2. Partially water soluble fractions were chosen because aerosol measurements, in general, indicate that the aerosol is seldom purely water soluble. This was found to be the case for the 1982 study with estimates of the water soluble fraction ranging between 40% and 80% (Isaac et al., 1986). Evidence presented in section 6 of this paper indicates that the average water soluble fraction of the aerosol was even less during 1984a than during 1982.

A CCN spectrum was derived from equilibrium considerations (described by the numerator in eq. (3)) for particles in modes 1 and 2 in Fig. 6. In doing so, the particles were assumed to be composed of pure $(NH_4)_2SO_4$. The result is shown in Fig. 7 as spectrum B (note that spectra compiled assuming a pure NH_4HSO_4 or H_2SO_4 aerosol will not differ significantly from the result in Fig. 7). Curve B has been scaled to a concentration of 1200 cm^{-3} at 1% S for purposes of comparison only. The average CCN spectrum, compiled from the measurements with the thermal diffusion chamber and the isothermal haze chamber, is also shown in Fig. 7 and labelled spectrum A. The characteristic shape of spectra A and B are generally similar, indicating that the initial aerosol size distribution together with the appropriate assumptions of composition is a reasonable description of the nucleation characteristics of the aerosol. A further comparison with the average of ten months of CCN

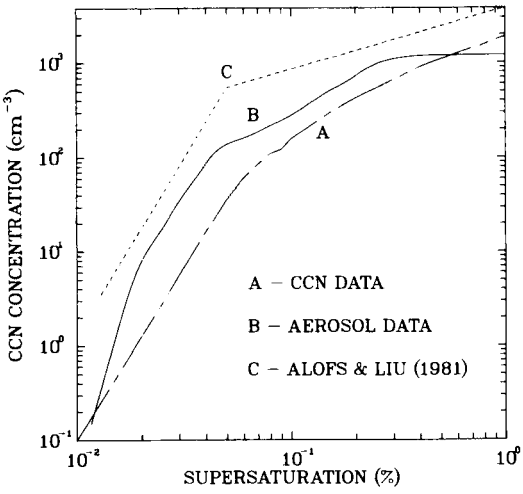

Fig. 7. Cloud condensation nucleus spectra; curve A—average of measurements, curve B—adapted from aerosol particle measurements, curve C—the average of long-term urban measurements by Alofs and Lui (1981).

measurements made at Rolla, Missouri (Alofs and Lui, 1981) is shown in Fig. 7 (Spectrum C). Alofs and Lui suggest that their result was most typical of a polluted urban situation. Spectrum A represents more average conditions and therefore is much lower in concentration; however, the behaviour of both spectra A and B are quite similar to the result of Alofs and Lui.

In computing the particle or droplet radius from eqs. (2) or (3), the dry particle radius is initially increased by a factor of 1.5 in order to overcome the initial phase of salt dissolution, which eqs. (2) and (3) do not treat. The starting relative humidity was constrained by the value of the updraft speed. For updraft speeds of 1, 0.5 and 0.1 m s^{-1} the starting relative humidity was set to 95%, 99% and 99.9%, respectively. This allows sufficient time for the submicron particles to equilibrate, before saturation is reached. Computations were performed using a four point Runge-Kutta forward differencing scheme, as used by Fitzgerald (1972). The initial time step of 0.002 seconds was increased to 0.01 for dilute solutions (i.e. solute concentration $<1\%$). The thermal accommodation coefficient, used in parameter K', was chosen to be 1.0 and the condensation coefficient, used in parameter D', was initially chosen to be 0.032 according to the discussion of Pruppacher and Klett (1978). Except where otherwise indicated, the updraft velocity was held constant throughout each computation and computations were performed for a cloud-base pressure and temperature of 800 mb and 10°C, respectively. The results are described in the following section.

Cloud droplets are defined in the model calculations as any particle >2 μm diameter at a LWC $= 0.2$ g m^{-3}, except where the updraft speed was specified as a constant 0.1 m s^{-1}. In the latter case, the CDC was specified at a LWC of 0.1 g m^{-3}. The 2 μm cutoff was chosen because it is approximately the size of particles counted in the lowest size range of the FSSP. In the model, the vertical profile of S goes through a maximum very near cloud base, while the LWC increases continually with height. The choice of 0.2 g m^{-3} was made because this LWC occurs at a height which is well past the height of the maximum S. Also, 0.2 g m^{-3} represents approximately the lower end of the near adiabatic LWC for 1982 and 1984b observations (Fig. 1). As a result of the S vertical profile, the effect of specifying the CDC at some higher LWC, for a constant updraft speed, will be to lower the CDC by some amount. Thus, from this point of view, the model results can be considered as upper limits when comparing with observations. The choice of 0.1 g m^{-3} for an updraft speed of 0.1 m s^{-1} is more consistent with the observations made in mostly stratiform cloud (1984a, Fig. 1) and is still beyond the point of the maximum supersaturation.

5. Model results and discussion

Number concentrations of cloud droplets were computed according to the above specifications. The concentrations have been tested for sensitivity to several items. These are:

(i) the constant updraft speed (V),
(ii) the concentration of mode 3 particles (i.e. case 2),
(iii) the water soluble fraction of the aerosol (i.e. case 3),
(iv) different cloud-base temperature and pressures,
(v) the accommodation coefficient for water,
(vi) the concentration of mode 1 particles and
(vii) a variable updraft speed.

The effects of these variables are discussed below.

(i) Some computed cloud droplet concentrations are plotted in Fig. 8 as a function of the concentration of aerosol particles in mode 2: the latter is approximately equal to the concentrations measured with the ASASP. Results with the mode 3 concentration = 0.12 cm^{-3} (case 1) are shown in Fig. 8, for updraft speeds of 0.1, 0.5 and 1.0 m s^{-1}. The modelled droplet concentrations depend very strongly upon the updraft speed. Measured droplet concentrations from Fig. 3 are also shown. These concentrations are much less than predicted unless the updraft speed is very small, ≈ 0.1 m s^{-1}.

(ii) The resulting cloud droplet concentrations determined when no giant particles were present (case 2) and for an updraft speed of 0.5 m s^{-1} are also included in Fig. 8 and are no different, based upon the method of calculation described here, than those calculated for the case 1 assumptions. While the exclusion of the giant aerosol removes one of the water vapour sinks, this leads to only marginally higher values of the supersaturation, which are not significant enough to affect these results. Still, there must remain some uncertainty regarding the effect of this mode because: (a) the assumed chemical composition is questionable, (b) the particles were treated as acting homogeneously within the cloud, (c) a change in the composition of the aerosol in the smaller size ranges might induce a noticeable effect and (d) smaller updraft speeds might also enhance any effect through the lowering of the supersaturation.

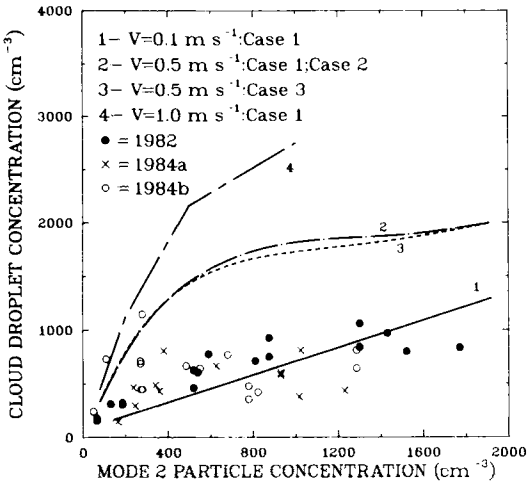

Fig. 8. Calculated cloud droplet concentrations as a function of updraft speed and the concentration of mode 2 particles. The data points from Fig. 3 are also included.

(iii) The droplet concentrations determined for a reduction of the amount of water soluble material in the aerosol (i.e. case 3) are also illustrated in Fig. 8, for $V = 0.5$ m s^{-1}. The concentrations are smaller than those determined for case 1 and $V = 0.5$ m s^{-1}, which indicates that the increase in supersaturation due to a smaller initial water uptake by the aerosol with the smaller soluble component is not large enough to offset the increase in the supersaturation necessary for these particles to activate as cloud droplets. The reduction in cloud droplet concentration accompanying a reduction in water soluble content has been previously reported by Fitzgerald (1974).

(iv) In order to investigate the influence of cloud-base pressure and temperature on the CDC, the calculations of cloud droplet concentrations were performed, using the assumptions of case 1, for a constant updraft speed of 0.5 m s^{-1}, cloud-base temperatures of -10, 0, 10 and 20°C and cloud-base pressures of 800 and 900 mb. These ranges are typical of the variations encountered during the 1982 and 1984 studies. The difference in the CDC resulting from the above variation in cloud-base pressure was found to be negligible. Temperature, particularly low values, was found to be of some consequence, as demonstrated in Fig. 9. In this figure, the droplet concentrations are plotted as a function of aerosol particle concentration for different cloud-base temperatures. Some of the variance in the CDC shown in Figs. 3 and 4 might be explained by systematic temperature differences. Indeed, for the region of study, high pollutant concentrations are observed with warmer temperatures (e.g. Isaac et al., 1986).

(v) A major uncertainty in modelling the condensational growth of cloud droplets is the value of the condensation coefficient (α_c) to be used in the computations. Pruppacher and Klett (1986) have suggested a value of ≈ 0.032 for atmospheric clouds and, as indicated in section 4, this value has been used in the computations to this

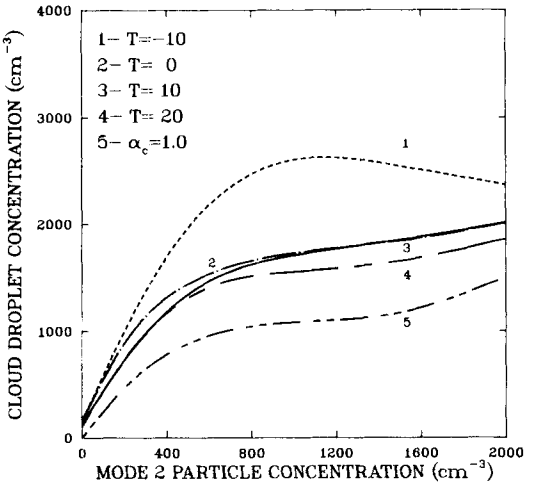

Fig. 9. Calculated cloud droplet concentrations as a function of the mode 2 particle concentration for different cloud-base temperatures. Curves 1–4 are calculated with $\alpha_c = 0.032$. Curve 5 is for $\alpha_c = 1.0$ and encompasses all temperature variations. The assumptions described by case 1 were used.

point. However, recent experimental studies (Wagner, 1982; Tang et al., 1985, pers. comm.) and theoretical arguments (Mozurkewich, 1986) have pointed to a value much closer to unity. The calculations of cloud droplet concentrations were repeated for $\alpha_c = 1.0$ and the four cloud-base temperatures discussed above. The assumptions of case 1 were used with a constant updraft speed of 0.5 m s^{-1}. The effects of temperature on the droplet concentrations, noted for $\alpha_c = 0.032$, were not evident in this case and all four cloud base temperatures are represented by one curve (5) in Fig. 9 for α_c. Apparently, the effects of temperature are overshadowed by a large increase in the growth rate due to the increase in α_c. Increasing α_c to unity not only reduces the effect of temperature, but also lowers the predicted droplet concentrations to where, for a constant updraft speed of 0.5 m s^{-1}, they agree quantitatively with the measurements. The lack of high variability in the data points which is predicted for data collected over a wide temperature range and the relatively low absolute concentrations argue strongly that $\alpha_c = 1.0$ is a more appropriate choice for the modelling of the condensational growth of cloud droplets.

(vi) The assumption of the concentrations of mode 1 particles varying linearly with mode 2 particles will, of course, not always hold. Measurements (Whitby, 1978), free of local source influence, have shown that the ratio of particle number concentrations between what Whitby defines as the nuclei and accumulation aerosol modes may typically vary between ≈ 1 and ≈ 6. Although the modes defined here are not identical with Whitby's, in terms of particle size, there is considerable size overlap and the apportionment used here (5:1) is not inconsistent with Whitby's results. However, Fig. 5 shows that during 1982 the concentration of CCN active at 0.4% S was ≈ 2.3 times as large as the concentration of aerosol particles >0.17 μm. Since 0.4% S is equivalent to pure $(NH_4)_2SO_4$ particles of ≈ 0.05 μm diameter, the number of nucleating particles in mode 1, relative to the concentraton in mode 2, might have been as low as ≈ 2. With this in mind, the consequence of reducing the ratio of the mode 1 concentration of particles to the mode 2 concentration from 5 to 2 was examined for a constant updraft speed of 0.5 m s^{-1}. In Fig. 10 the effect of this reduction is shown for values of $\alpha_c = 0.032$ and 1.0. The upper

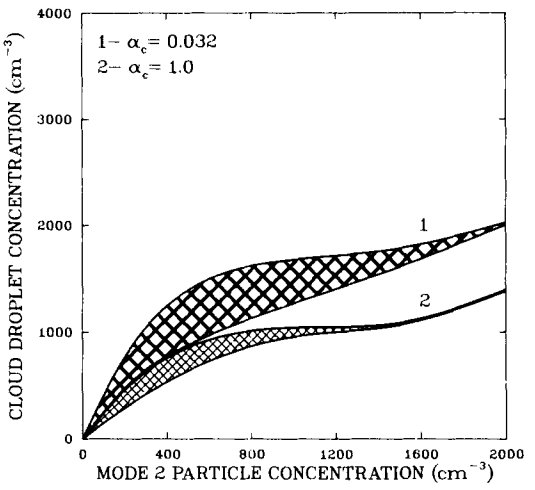

Fig. 10. Result of varying the concentration of particles in mode 1 for $\alpha_c = 0.032$ (curve 1) and 1.0 (curve 2). Upper boundaries on the envelopes were obtained for the mode 1 concentrations equal to five times those in mode 2 (i.e. case 1). The lower boundaries were obtained for the mode 1 concentrations equal to two times the mode 2 concentrations.

boundaries on the envelopes of droplet concentrations in Fig. 10 represent the results for the above ratio set to 5, while the lower boundaries were determined for the above ratio set to 2. There are noticeable reductions in the droplet concentrations for the less polluted situations when the concentration of mode 1 particles was reduced. However, for increasing particle concentrations, the change in the droplet concentrations is reduced to insignificant owing to the dominance of the mode 2 aerosol on the excess water vapour concentration. The particles of mode 1 have a negligible effect on vapour depletion as long as they remain small enough not to be considered as cloud droplets.

(vii) Absolute agreement between the observed data points and the computed results is good only for relatively low updraft speeds (i.e. $\leqslant 0.5$ m s^{-1}), even with $\alpha_c = 1.0$. Such low updraft speeds may be reasonable for the winter data, which were collected mostly in stratiform cloud, but it is questionable for the summer measurements. Gust measurements form the 1982 and 1984b studies (values of a few m s^{-1} were not uncommon), a study by MacPherson and Isaac (1977) and more general considerations of cumulus clouds (e.g. Mason, 1957) lead us to believe that, for the summer data and, to a lesser degree, the autumn data, the updraft speeds should be much greater than 0.5 m s^{-1}. MacPherson and Isaac determined a modal RMS gust velocity of ≈ 1.7 m s^{-1} for Canadian cumulus clouds, with a corresponding peak vertical velocity of 5 m s^{-1}. Similar theoretical results were obtained from a study by Tremblay and Leighton (1986). They modelled in three dimensions the formation of a cumulus cloud using environmental data from one of the more polluted days (July 15, 1982) for which data are included in this paper. The purpose of their model was to investigate how the spatial and chemical structure of the $SO_4^=$ concentration was affected by the development of the cloud. Although the model did not delineate the cloud droplet spectrum, the LWC and wind velocities were computed. The computed updraft speed at cloud base, in this model, was ≈ 0.5 m s^{-1}, and it increased to a maximum value of ≈ 5.0 m s^{-1} at ≈ 1200 m above base, representing a linear rate increase of ≈ 0.6 (m s^{-1}) min^{-1}. In order to assess some consequences of a variable updraft speed, the cloud droplet calculations described here have been repeated for initial updraft speeds of 0.1 m s^{-1} (beginning at 99.9% relative humidity) and 0.5 m s^{-1} (beginning at 99.0% relative humidity) both of which were increased linearly at a rate of 0.6 (m s^{-1}) minute^{-1} to a maximum of 5.0 m s^{-1}. The condensation coefficient was set to 1.0. It was found for the case 1 assumptions that the calculated cloud droplet concentration at the point of the maximum updraft speed (LWC ≈ 2.0 g m^{-3}, ≈ 1300 m above cloud base) was the same as it was at a LWC of 0.2 g m^{-3}. In this case, the supersaturation peaked near the base, declined thereafter for a short time and then gradually increased, finally reaching a supersaturation very close to the peak value near cloud base. For the assumptions of case 3, the cloud droplet concentrations for low particle concentrations were found to increase slightly in going from 0.2 to 2.0 g m^{-3}, and therefore the values at 2.0 g m^{-3} were used for graphical presentation. The results of the computations using the assumptions of case 1 with a variable updraft speed are shown in Fig. 11 as curves 1 and 2. Curve 1 more closely approximates the observed data than curve 2, but the concentrations are yet too high for the largest particle concentrations. The results of compu-

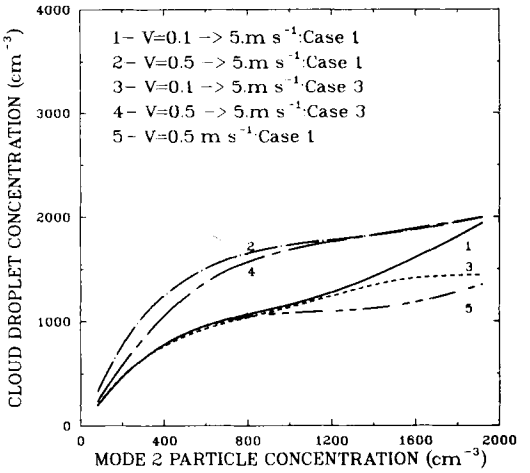

Fig. 11. Computed cloud droplet concentrations as a function of the mode 2 particle concentrations for $\alpha_c = 1.0$ and a linearly increasing updraft speed. Also shown, for comparison, is the previous result for constant $V = 0.5$ m s^{-1} and $\alpha_c = 1.0$ (curve 5).

tations performed for the assumption of a 50% water soluble fraction (i.e. case 3) are shown in Fig. 11 as curves 3 and 4. All four curves exhibit the tendency for droplet concentrations to increase sharply at low concentrations, followed by a reduction in the rate of increase. Observing the large differences between curves with different updraft speeds, it is clear that the updraft speed near cloud base is important to the determination of the cloud droplet concentration. In an absolute sense, curve 3 best approximates the measured data (Fig. 3), but the droplet concentrations are still slightly high compared with the measurements.

The results of adiabatic computations of cloud droplet concentrations for varying aerosol particle concentrations have been described in this section. The model was able to predict the relative variation of the CDC with increasing APC (i.e. CDC > APC for lower APC and CDC < APC for higher APC) observed in the measurements (Fig. 3); nevertheless, the CDC obtained from the model were generally higher in absolute terms. Certain factors, such as a reduction in the water soluble fraction of the aerosol and a reduction in the number of particles $<0.2\ \mu m$ led to improved absolute agreement. A more important factor which improved the absolute agreement was adopting a value of unity for the value of the accommodation coefficient for the condensation of water. This not only lowered the predicted CDC, it also dampened temperature variations which were evident in the calculations performed for $\alpha_c = 0.032$, but not so apparent in the measurements. By employing a linearly varying updraft speed it was found that the updraft speed near cloud base is most important to the determination of the CDC. Having considered cloud droplet measurements in near adiabatic parcels (Section 2) and adiabatic computations of cloud droplets, Section 6 deals with more bulk cloud properties.

6. Mean cloud droplet and cloudwater sulphate observations

Up to this point, only the adiabatic or near adiabatic situation has been considered. Fast-frequency continuous measurements make this feasible for cloud droplet measurements, but the bulk measurements necessary for measuring CW $SO_4^=$ concentrations force the inclusion of cloudwater from many different regions of cloud. Accordingly, to make a proper comparison with $SO_4^=$ concentratons, the average cloud droplet concentration for a particular cloud penetration should be considered. In this section, the mean droplet and CW $SO_4^=$ concentrations are examined as a function of their respective below-cloud aerosol variables. But first, the relationship between aerosol $SO_4^=$ and particle number concentrations is considered.

A variety of observations (e.g. Whitby, 1978) have shown that aerosol $SO_4^=$ is usually found in the aerosol size range between ≈ 0.2 and $2.0\ \mu m$ diameter. Also, a linear relationship between the mass of aerosol $SO_4^=$ and the light scattering coefficient (usually dominated by submicron particles) have been demonstrated (e.g. Pierson et al., 1980; Barrie et al., 1981; tenBrink et al., 1984). Evidence is presented here for a near linear relationship between the number concentration of aerosol particles and the mass concentration of aerosol $SO_4^=$. In Fig. 12, the concentration of aerosol particles $>0.17\ \mu m$ at >950 mb (as measured from the aircraft) has been compared with the concentrations of aerosol $SO_4^=$ measured during the same time periods, but

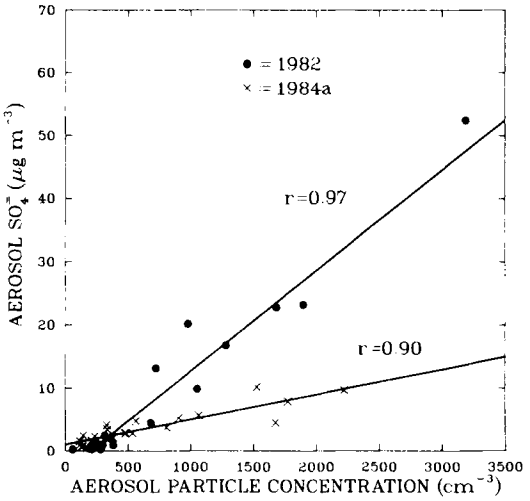

Fig. 12. Relationship between ground-level aerosol $SO_4^=$ and the number concentration of large particles ($>0.17\ \mu m$), measured at 950 mb. Correlation coefficients are indicated for the summer and for the winter data.

at ground level. Only summer (1982) and winter (1984a) data have been described and both data sets yield high linear regression coefficients (0.97 and 0.90 for the summer and winter, respectively) indicating strong correlations between the mass of aerosol $SO_4^=$ and the number concentration of particles >0.17 μm. A similar plot of aerosol number and volume concentrations is shown in Fig. 13. The foundation for the strong near linear relationship between number and volume is a low value of the measured geometric dispersion for the aerosol particles in the 0.2–2.0 μm size range (≈ 1.36 for mode 2 in Fig. 6), which brings the mean-number and mean-volume diameters close together. Although the correlation coefficients are strong for both summer and winter, the slopes of the regression lines are considerably different in Fig. 12. Since the number-volume relationship of the submicron aerosol spectra in the summer and winter are quite similar (Fig. 13), the different slopes for the regression lines suggest for particle concentrations >300 cm^{-3}, that $SO_4^=$ composed a much smaller fraction of the submicron aerosol during the winter study than during the summer study. Correspondingly, the ratio of SO_2 to $SO_4^=$ was much higher during the winter (mean of ≈ 4.1) than during the summer (mean of ≈ 0.36), suggestive of a lowering of the photochemical production of oxidants during the winter. Having demonstrated a near linear relation between aerosol $SO_4^=$ and aerosol number concentrations, the relationship between CW $SO_4^=$ and aerosol $SO_4^=$ mass concentrations is compared to that between the mean cloud droplet and aerosol particle number concentrations.

In Fig. 14 the mean CW $SO_4^=$ concentrations (referenced to a standard cubic metre of air using the LWC measurement) are plotted against ground-level concentrations of aerosol $SO_4^=$. The two different scales (one for the summer $SO_4^=$ data, one for the winter $SO_4^=$ data) are employed because of the differences between summer and winter shown in Fig. 12. Although cloud-base concentrations of aerosol $SO_4^=$ are preferable (reliable aircraft measurements of aerosol $SO_4^=$ are unavailable), vertical profiles of the aerosol size distribution (Isaac et al., 1986) for the 1982 study, indicate that aerosol concentrations were similar or even slightly higher at cloud base than on the ground. The same is assumed to have been true for the winter conditions. Mean cloud droplet concentrations (i.e. averaged over one or more cloud penetrations at one altitude) have also been plotted in Fig. 14 as a function of cloud-base aerosol particle concentrations.

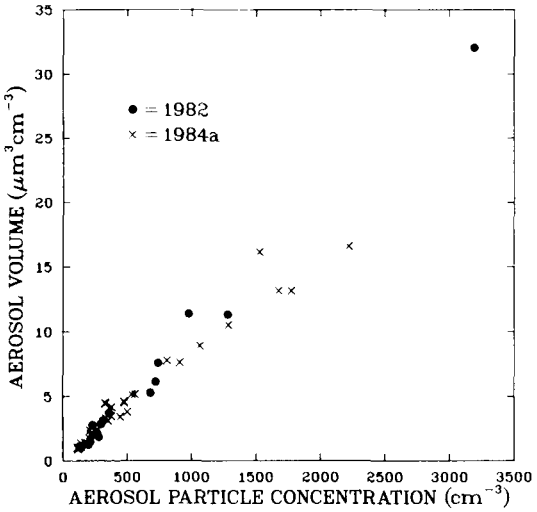

Fig. 13. Relationship between the volume concentrations and the number concentrations of the aerosol as determined from the measurements made with the ASASP. Spherical particles were assumed in computing the aerosol volume.

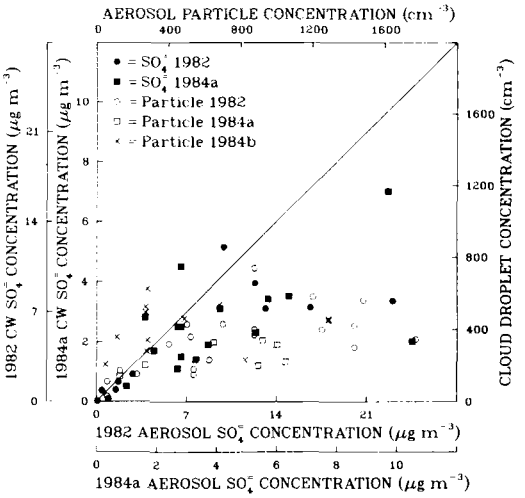

Fig. 14. Cloudwater $SO_4^=$ concentration as a function of the aerosol $SO_4^=$ concentration (summer and winter) measured at the ground and the mean cloud droplet concentration (right ordinate) as a function of the cloud base large aerosol particle concentration (top abscissa).

The particle/droplet measurements illustrated in Fig. 14 show a behaviour very similar to the near adiabatic measurements (Fig. 3). That is, as the aerosol loading is increased, the average concentration of cloud droplets decreases, relative to the cloud-base aerosol concentrations. These general droplet concentrations are, however, considerably lower than the maximum concentrations shown in Fig. 3. The average of the individual ratios of the CDC in Fig. 14 to the maximum CDC (Fig. 3) was $\approx 57\%$. This is an indicator of the degree to which mixing processes influenced these results. The variation in the mass concentrations of CW $SO_4^=$ with those of aerosol $SO_4^=$ contains more scatter than the droplet versus particle data. The $SO_4^=$ data points in Fig. 14 are slightly higher relative to the particle data points for high concentrations, while at low concentrations the separation between $SO_4^=$ and particle data is much less. Even in the absence of in-cloud SO_2 oxidation, this result is expected because, for low concentrations, particles of a size represented by mode 1 in Fig. 6 will contribute to the number concentration of droplets, but not significantly to the mass concentration of $SO_4^=$. For high concentrations, the particles nucleating the cloud droplets are also those contributing most to the mass concentration of $SO_4^=$.

It is conceivable that the variation of the $SO_4^=$ data points in Fig. 14 is similar to that of the particle data points, but the uncertainty is very large. The average cloud scavenging ratio for $SO_4^=$ is $\approx 73\%$ (75% for the summer data and 72% for the winter data) and this value agrees reasonably well with the mean nucleation scavenging ratio for $SO_4^=$ of 63% derived by Hegg and Hobbs (1983). The latter study attempted to correct their data for the influence of SO_2 in-cloud oxidation; however the result presented here represents a complete cloud scavenging ratio, and this may increase the average. It is also interesting to note that the measurements of Hegg and Hobbs also give some indication of a decrease in the fraction of aerosol $SO_4^=$ scavenged by nucleation with increasing cloud-base aerosol $SO_4^=$ concentration, although they do not discuss this point. Another factor which might result in a larger scavenging ratio for the data presented here is that some aerosol $SO_4^=$ concentrations may have been higher near cloud base than on the ground (where the aerosol $SO_4^=$ values were obtained), as suggested by Isaac et al. (1986).

The efficiency with which cloudwater is collected as a function of cloud droplet size is important to the description of the $SO_4^=$ data of Fig. 14. For the collectors used during 1982, the theoretical collection efficiency, as a function of cloud droplet radius, has been described by Mohnen (1980). Mohnen indicates that for aircraft speeds such as for this study (≈ 60 m s^{-1}), the efficiency of collection is $\approx 80\%$ for droplet radii > 10 μm and $< \approx 10\%$ for droplet radii < 5 μm. In practice, the collection efficiency is seldom as high as 80%, and this must indicate a limitation in application of the theory. Still, it is useful to consider how potential variations in collection efficiency with droplet size affect the collection of cloudwater $SO_4^=$ concentrations. Combining Mohnen's result with model calculations it was determined that, for the assumptions described by case 1 and with $V = 0.5$ m s^{-1} and $\alpha_c = 1.0$ (see Fig. 9, curve 5), the total CW $SO_4^=$ and theoretical "collected" CW $SO_4^=$ concentrations at 0.2 g m^{-3} are virtually identical for small aerosol concentrations. For the maximum aerosol concentration considered here (i.e. 2000 cm^{-3} in mode 2), the "collected" CW $SO_4^=$ was $\approx 12\%$ less than the total $SO_4^=$ concentration in the cloud water. This occurred because for larger droplet number concentrations the droplets are smaller and the collection efficiency is smaller than for lower droplet concentrations. As a result, this could lead to an artifactual fall-off in the $SO_4^=$ nucleation scavenging ratio with increasing aerosol $SO_4^=$ concentration. Increasing the LWC, hence droplet size, will reduce this effect, while evaporation of droplets by mixing processes will enhance it.

A near linear relationship between the number concentration of particles > 0.17 μm diameter and the mass concentration of aerosol $SO_4^=$ has been introduced. It has been shown that for certain conditions the ratio of cloud droplet concentrations to cloud-base aerosol particle concentrations will decline with increasing aerosol loading. This may also lead to a decline in the fraction of aerosol $SO_4^=$ scavenged by the cloudwater. A decline in the CW $SO_4^=$ concentration with increasing aerosol $SO_4^=$ concentration might also be induced by variations in the efficiency with which the cloudwater is collected.

All of these discussions have been based upon the continuity of assumptions, and while the assumptions may be generally valid, real variability in important parameters (aerosol soluble fractions, cloudwater absorption of HNO_3, SO_2 concentration, concentrations of oxidants, etc.) will lead to a large random element in the data and therefore some uncertainty in the conclusions.

7. Summary and conclusions

During the summer of 1982, the winter of early 1984 and the autumn of 1984, cloud droplet concentrations were measured in a variety of polluted situations, as characterized by concentration measurements of aerosol particles and CCN. Both cumuliform and stratiform cloud were studied, although the convective activity was at best moderate and generally light. The concentration of cloud droplets observed in near adiabatic parcels was not continuously linear with respect to the concentration of aerosol particles >0.17 μm or with the concentration of CCN active at 0.4% supersaturation. Droplet concentrations in near adiabatic conditions never exceeded 1200 cm^{-3}, in spite of much larger concentrations of aerosol particles (≈ 1800 cm^{-3}) and CCN (≈ 3000 cm^{-3}). When the observed concentration of cloud-base particles >0.17 μm was <750 cm^{-3}, the concentration of these cloud droplets was nearly equal to or exceeded the concentration of particles. For cloud-base particle concentrations >750 cm^{-3}, the cloud droplet concentration was less than the cloud-base particle concentraiton in 15 of 16 cases.

Adiabatic computations of the condensational growth of cloud droplets indicated that the concentration of cloud droplets could be expected to vary with the concentration of particles in a non-linear manner similar to that of the observations. Quantitative agreement between the model predictions and the observations was obtained for the low constant updraft speeds, which is reasonable for the stratiform cloud in the winter. However, for the summer and autumn data, the droplet concentrations predicted by seemingly reasonable higher updraft speeds were much larger than the observed values. It cannot be ruled out that the measurements were not truly representative of adiabatic concentrations. Nevertheless, other factors were found which led to improved agreement between the model and the summer and autumn observations. These factors were:

(1) Increasing the value of the condensation coefficient from 0.032 to 1.0.

(2) A reduction in the inorganic water soluble fraction of the nucleating aerosol.

(3) The use of a linearly varying updraft speed. This reconciled higher updraft speeds with cloud droplet concentrations specified by low updraft speeds (i.e. near cloud base).

Mean concentrations of cloud droplets were found to vary with respect to the concentration of cloud base aerosol particles in a manner similar to that of the adiabatic results (i.e. the proportion of scavenged particles decreased with increasing aerosol concentrations). However, cloud mixing processes lowered the mean concentrations to about 0.6 of the adiabatic values. The mean ratio of CW $SO_4^=$ to ground-level aerosol concentrations was $\approx 73\%$. There was some indication that measured CW $SO_4^=$ concentrations decreased with increasing ground-level aerosol $SO_4^=$ concentrations, but it was shown that this might be, in part, an artifact of the cloudwater collection process.

The results reported here support the conclusions of Twomey et al. (1984) as they apply to relatively pristine regions such as remote ocean areas. That is, for low concentrations, the number of cloud droplets will increase proportionately with the number of available CCN and, therefore, cloud albedo will increase with pollutant loading. However, if the pollutant loading is heavy and convection is weak (i.e. the cloud may be semi-transparent and the albedo relatively low) then the peak supersaturation is low and only the nuclei active at very low supersaturations nucleate cloud droplets. Hence, the CDC are predicted only from the concentrations of these relatively large soluble particles and can be limited. It follows therefore, that the cloud albedo also will not continue to increase proportionately.

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