Tellus (1998), 50B, 59–75
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TELLUS
ISSN 0280–6509

Aerosol particles and clouds: which particles form cloud droplets?

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(Manuscript received 10 June 1994; in final form 7 October 1997)

ABSTRACT

Measurements of cloud droplet residuals, which represent the cloud droplet nuclei (CDN) that formed cloud droplets, were made in ambient clouds with a 1-min time resolution. Only a weak relationship was found between the CDN number and volume concentrations, because the particles dominating the two concentrations resided in different size ranges. A comparison between the total particle size distribution and the size distribution of the CDN showed that only a small fraction of the total number of particles at a given size (smaller than 0.2 μm diameter) formed cloud droplets. Among the CDN, however, 75% of the number of particles were smaller than 0.2 μm diameter. Concurrent measurements showed that hygroscopic particles of the same size and larger remained in the interstitial air. The same feature was observed over longer time periods on a 1-min basis. Suggested hypotheses to explain why only a few of the smaller hygroscopic particles formed cloud droplets while larger particles remained in the interstitial air are that the growth of the droplet could have been influenced by the composition of individual particles and/or that entrainment introduced hygroscopic particles in the interstitial air.

1. Introduction

The indirect effect that aerosol particles may have on the radiation balance of the earth is one of the gaps that needs to be understood to quantify possible climate change. Studies of the number concentration of aerosol particles capable of nucleating cloud droplets (termed cloud condensation nuclei, CCN) at the supersaturations expected to be found in the atmosphere were originally done by Twomey (1959). In a series of measurements, a relationship was found where increased CCN number concentrations yielded higher number concentrations of cloud droplets (Squires and Twomey, 1960; Twomey and Warner, 1967; Twomey, 1980). If the number concentration of CCN forming cloud droplets at a given liquid water content (LWC) is increased, then the albedo of the cloud will increase because the cloud droplets are more numerous and smaller in size. Based on these arguments, the possibility that increased levels of aerosol particles could lead to an increased cloud albedo was suggested (Twomey, 1974; Twomey, 1977; Twomey et al., 1984). An increase of the global cloud albedo results in a larger fraction of the incoming solar radiation being reflected back to space. Thus, aerosol particles can have an indirect effect on the radiative balance of the earth.

Charlson et al. (1987) put forward a hypothesis that an increase in marine dimethylsulphide (DMS) production could result in an increase of the CCN concentration, thereby increasing the albedo of maritime clouds and hence affecting global climate. Several studies have been aimed at

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testing this hypothesis. A correlation between CCN and aerosol methanesulphonate (MSA) was found in clean marine air at Cape Grim, Tasmania (Ayers and Gras, 1991). At low MSA concentrations the number concentration of CCN active at 0.23% supersaturation varied linearly with MSA concentration, while at higher MSA concentrations the CCN concentration increased at a slower (non-linear) rate with respect to increases in MSA. A correlation between CCN and DMS has also been found in the boundary layer over the North-Eastern Pacific Ocean (Hegg et al., 1991). The correlation between DMS and CCN found by Hegg et al. (1991) agrees with the linear increase at low MSA found by Ayers and Gras (1991). A correlation between CCN and cloud water sulphate concentrations has also been found by Leaitch et al. (1992) in more polluted regions. They used the sulphate concentration in cloud water as an indication of increased pollution and found a slight increase of cloud droplet number concentration with increasing sulphate concentration.

The exact relationship between changes in the mass concentration of aerosol particles and changes in the number concentration of CCN is, however, not known and is likely to be non-linear. CCN are a subset of the aerosol particle population and whether a particle will act as a CCN at a certain supersaturation depends on its size and composition. If addition of mass on small particles allows them to grow large enough to be counted as CCN then an increase of CCN with increasing mass concentration would be expected. If, however, the mass increase is distributed among already existing CCN (which only would increase the size but not the number of CCN) then no relationship should be expected between changes in CCN and mass concentration.

The question of how CCN measurements relate to real cloud conditions is not well understood. Comparing measurements of the CCN concentration and the droplet population requires that the supersaturation time history of the instrument and the real cloud are equivalent. The comparison is further complicated by the potential confounding effects of processes other than condensational growth, such as entrainment and coalescence.

A discrepancy between predicted and observed concentrations of CCN was observed by Bigg (1986). The number of particles active as CCN was less than expected compared to measured particle size distributions with assumed compositions of ammonium sulphate or sodium chloride. A variation in time for the droplets to form in the CCN chamber was also observed. The above observations led Bigg (1986) to suggest that organic material might have been present and affected the growth of the particles. Novakov and Penner (1993) have shown that organic carbon (not only sulphate) is present in particles active as CCN in marine air.

To fully ascertain which aerosol particles form cloud droplets, measurements of the particles that actually formed cloud droplets in *real* cloud conditions have to be made. To distinguish these particles from the ones termed CCN, we designate them cloud droplet nuclei (CDN). Various parameters affect nucleation scavenging and characterisation of the unscavenged "interstitial" particles is needed to understand their influence. Processes that are important in altering the shape of the cloud droplet number distribution, such as entrainment and coalescence, will also affect this partitioning of aerosol particles between interstitial air and cloud droplets. Measurement of the partitioning of aerosol particles between interstitial air and cloud droplets as a function of time and at various locations in a cloud can help to discriminate between these various processes.

Anderson et al. (1994) made measurements of cloud droplet residual particles and could not find a sensitivity of the number of cloud droplets to the amount of aerosol present. They also found that the number population of cloud droplets was dominated by particles smaller than 0.1 μm diameter. We have used the same method to sample cloud droplet residues as Anderson et al. (1994), but have combined it with simultaneous measurements of the interstitial aerosol particles.

Partitioning can be described in terms of both physical and chemical differences between CDN and interstitial particles. We have addressed this issue from three different standpoints: chemical differences (Noone, et.al., 1992c; Martinsson et al., 1992; Hallberg et al., 1994a), partitioning based on total aerosol particle size distribution (Heintzenberg et al., 1989; Noone, et al., 1992b; Hallberg et al., 1994b) and the size distribution of residual particles (this study). Hallberg et al. (1994a) used single particle characterisation to determine if a difference in the compositon of two

equal-sized particles can be important in determining which of them can become a cloud droplet. It was found that at any given size, most of the residual particles were soluble while insoluble particles preferably remained in the interstitial air. Hallberg et al. (1994b) studied the fraction of the total number of particles incorporated in cloud droplets at a given size and found that the partitioning as a function of size and time had little variation within each cloud event studied.

However, the size-dependence of the partitioning fraction can be somewhat misleading when trying to determine the size of the particles that dominate the CDN number distribution. The fraction of the total number of particles at a given size that is scavenged, although of interest for other reasons (i.e. atmospheric residence time of aerosols), is dependent on the total number size distribution and can therefore give an incomplete picture of the partitioning issue. In this study, we will therefore concentrate on the partitioning from the cloud droplet's point of view; that is, focus on the actual number distribution of the CDN.

In this paper, we present measurements of the size distribution of residual particles from cloud droplets in ambient clouds. In the absence of chemical and physical processes changing the original particles that formed cloud droplets these residual particles represent the nuclei upon which the droplets formed. The measurements were performed under varying aerosol volume (mass) concentrations and hence the relationship between aerosol mass and cloud droplet number can also be studied.

The questions we address with this paper are: what are typical size distributions of CDN?; how can the observed CDN distributions be related to various cloud precesses?; how does the number concentration of CDN vary with increasing aerosol mass concentration?

2. Experimental description

The data presented in this paper were obtained during the second joint field campaign of the EUROTRAC sub-project "Ground-based Cloud Experiment" (GCE) that was held in October-November, 1990 on Mt. Kleiner Feldberg (825 m above sea level) in the Taunus Mountains near Frankfurt am Main, Germany. An overview description of the experiment and the site is given by Wobrock et al. (1994). Winkler et al. (1994) describe the meteorological conditions during the campaign in detail, so only a brief summary is given here. The campaign can be divided into two periods. In period I (27 October–2 November) the air masses originated mainly from the North Atlantic and travelled relatively quickly over northern France to the sampling site. In period II (10–13 November), air masses originated from a wide range of directions over the European continent and were transported with a significantly lower velocity than in the first period. The difference in air masses was also reflected in aerosol size distributions. Freezing temperatures between the two periods created unfavourable conditions for sampling. Cloud types observed in the 2 periods were mostly stratocumulus, or stratus in a few cases, and generally belonged to approaching frontal systems. But, since the field site is situated on a mountain, adiabatic lifting of moist air over the hill could also lead to cloud formation.

The approach of the study was to sample and characterise cloud droplets and interstitial particles, simultaneously and separately from each other. This was done by using two different inlets. The inlet used to sample cloud droplets was a counterflow virtual impactor (CVI, Ogren et al., 1985; Noone et al., 1988). Droplets and particles larger than the cut size of the CVI were impacted from abient air into a dry, particle-free carrier air stream. Once sampled, each droplet was evaporated, leaving behind a dry residual particle while water and other volatile species in the droplet were driven into the gas phase. The interstitial aerosol inlet used an annular slit impactor to remove droplets and particles above 5 μm diameter. Once separated, the interstitial particles were pulled through a 2.5 cm ID tube to a distribution plenum inside the field laboratory. Since the temperature in the laboratory generally was 10–20°C above ambient temperature, the particles were dried before reaching the plenum, Thus, the droplets and particles were separated and sampled at their ambient wet size, and characterised at their dry size.

Each inlet led to a distribution plenum with different instruments attached. The instruments used were condensation nucleus counters (CNC) and optical particle counters (OPC). More information on the details of the instruments is

given in Hallberg et al. (1994b). A DMPS (differential mobility particle sizer) was also attached to the interstitial inlet (Svenningsson et al., 1994). The liquid water content (LWC) of the droplets sampled by the CVI was determined by measuring the water vapour concentration in the CVI sample flow with a Lyman-α hygrometer (Zuber and Witt 1987). Ambient droplet distributions were measured during the campaign with forward scattering spectrometer probes (FSSP, Knollenberg, 1981). More information on the FSSPs and cloud microphysical results during the campaign are given in Arends et al. (1994).

3. Results

3.1. Data used

The field experiment involved simultaneous measurements of various gaseous and condensed phase species in two reservoirs: cloud droplets and interstitial air (Wobrock et al., 1994). An aerodynamic of 5 μm was chosen as the operational border between cloud droplets and interstitial particles, as the droplet spectra varied in shape between the two periods as well as within each period. The mode diameter of the droplet spectra in period I was smaller than in period II (Arends et al., 1994), and a variation in the fraction of droplets smaller than 5 μm diameter thus occurred. The likelihood that the CVI did not collect all cloud droplets was thus largest in period I. Since we want to get a representative picture of the CDN, as many as possible of the droplets have to be sampled. Below is a discussion of the criteria that were used to select data for subsequent analysis.

3.1.1. Data from the CVI. Two calibrations of the CVI's transfer function (i.e. collection efficiency vs. size) exist. The first calibration done by Noone et al. (1988) had a rather broad transfer function, in part due to the design of the CVI used and in part due to the "wet" calibration method used. The "wet" calibration method of Noone et al. (1988) was also not practical for droplet diameters below about 10 μm diameter due to the difficulty of preventing significant droplet evaporation prior to collection of the CVI. Anderson et al. (1993) used a "dry" calibration method that allowed a calibration for droplet diameters below 10 μm diameter. The design of the CVI deployed by Anderson et al. (1993) was also different from the one used by Noone et al. (1988). The CVI used in the present work had a blunt tip, similar to the CVI used by Anderson et al. (1993), and the calibration curves given in Anderson et al. (1993) are therefore a better description of the CVI used in this experiment than the results presented by Noone et al. (1988).

Sampling a representative population of the cloud droplets requires collection of as many cloud droplets as possible while excluding interstitial particles. Theoretically, a CVI should be able to eliminate particle contamination from interstitial particles, and Anderson et al. (1993) showed in their calibration that the CVI collection efficiency rapidly went to zero at diameters below the cut-size. The absence of small particle contamination was also predicted from fluid flow/particle trajectory calculations for the CVI presented in Lin and Heintzenberg (1995). Tests performed outside cloud during both periods of the experiment also established that no small particle contamination occurred.

The cut size of the CVI is dependent on the velocity achieved in the wind tunnel. During this experiment the cut sizes were about 7 μm diameter. (The calibration curve report by Anderson et al. (1993) also had a cut size of about 7 μm diameter). Since the cut size of the interstitial inlet was 5 μm, there was a gap between the size ranges covered by the interstitial inlet and the CVI and a fraction of droplets between 5 and 7 μm diameter was not sampled. Another fraction of the cloud droplets was not sampled due to losses in the CVI wind tunnel at high wind speeds (Noone et al., 1992b).

The fraction of droplets sampled by the CVI was estimated in Hallberg et al. (1994a, b). The total number of droplets larger than 5 μm diameter obtained from the FSSP was used as a reference for how many droplets the CVI shoud be able to sample, and the total number of droplets sampled by the CVI was given by the number concentration of residual particles measured with the CNC. The fraction of cloud droplets not sampled due to the gap between the sampling ranges and due to the loss at high speeds was also calculated. In the earlier calculations, all droplets in the size range between the cut sizes of the interstitial inlet and the CVI were estimated to be lost and the sampling collection efficiency by Anderson et al. (1993) was not applied. For the present work, the calculation

was repeated with the collection efficiency curve of Anderson et al. (1993) and the results are given in Table 1. Only time periods when the fraction of droplets sampled at least 70% compared to the FSSP were included in subsequent analyses using CVI data. Data from the two time intervals that met this criterion (both during period II) are shown in Table 2, where the CDN number concentration was obtained from the CNC and the CDN volume concentration in the diameter range 0.1–1 μm (accumulation mode) was obtained from the OPC.

3.1.2. Data from the DMPS. The CVI could not provide information on the CDN during period I because the fraction of droplets sampled by the CVI was always below 70%, mainly due to the shape of the droplet spectra (Arends et al., 1994). Another approach for obtaining information about the CDN is to compare the pre-cloud particle distribution to the in-cloud interstitial particle distribution. Such a comparison is valid only when the total particle number distribution is the same in the clear air as in the cloud. The number concentration of particles from 0.017–0.05 μm diameter, as measured by the DMPS, was used as an indication of changes in total particle number distribution while sampling cloudy air. Particles in this size range are unlikely to activate and form cloud droplets. As will be discussed more in detail below, Svenningsson et el. (1994) made measurements of the hygroscopic growth of residual particles in the CVI shortly after the start of the cloud event on 1 November, and observed no particles smaller than 0.05 μm diameter. This strengthens the assumption that, for the clouds studied, the number concentration of particles in the size range 0.017–0.05 μm diameter was unaffected by cloud nucleation and, in the absence of air mass change, remained the same as before cloud formation.

A process that might affect interstitial particle number concentrations and residual particle size distributions in cloud is Brownian diffusion of interstitial particles followed by impaction and collection by cloud droplets. Noone et al. (1992b) calculated the turnover time for interstitial particles in a polluted fog and found that it was relatively long. The rate at which coagulation between interstitial particles and droplets takes place is dependent on the available droplet surface area and the difference in size among the particles and droplets. The surface area of the cloud droplets during the period of interest was $0.078 \pm 0.009\ \mu m^2\ m^{-3}$. This should be compared to a typical surface area of the droplet distribution during the Po Valley experiment which was $0.132\ \mu m^2\ m^{-3}$ (Arends, personal communication). Since the experiment at Kleiner Feldberg had a smaller surface area of the droplet population we would expect the half-life to be even longer and hence the number concentration of these

Table 1. *Comparison of CVI and FSSP measurements of droplet concentrations in different size intervals*

	10–11 November 23:00–3:00	12 November 3:22–5:00
N_{CVI}/N_{FSSP}	0.73 ± 0.09	0.89 ± 0.13
N_{gap}/N_{FSSP}	0.11 ± 0.03	0.11 ± 0.04
N_{wt}/N_{FSSP}	0.16 ± 0.03	0.11 ± 0.04
N_{sum}/N_{FSSP}	1.00 ± 0.10	1.10 ± 0.15
N-conc. 4–5 μm (0.9%)	0.04 ± 0.02	0.05 ± 0.02
N-conc. 5–6 μm (5%)	0.57 ± 0.20	0.58 ± 0.19
N-conc. 6–7 μm (12%)	2.6 ± 0.87	2.1 ± 0.73
N-conc. 7–8 μm (77%)	21.1 ± 6.2	15.8 ± 4.8
N-conc. 8–9 μm (100%)	28.5 ± 9.0	18.4 ± 4.8

FSSP measurements of the droplet number concentration larger than 5 μm diameter are denoted by N_{FSSP}, the FSSP-derived number concentration of particles in the gap not sampled by either the interstitial or CVI inlets is denoted by N_{gap}, and the number concentration of particles not sampled by the CVI wind tunnel is denoted by N_{wt}. The number concentration of droplets measured by the CVI, with the inclusion of the CVI collection efficiency curve from Anderson et al. (1993), is denoted by N_{CVI}. The sum of N_{CVI}, N_{gap}, and N_{wt} is denoted by N_{sum}. The lower part of the table gives the calculated number concentration of cloud droplets (cm^{-3}) sampled by the CVI, when applying the collection efficiency curve, for different size ranges of the FSSP. %s in the parentheses are the collection efficiencies.

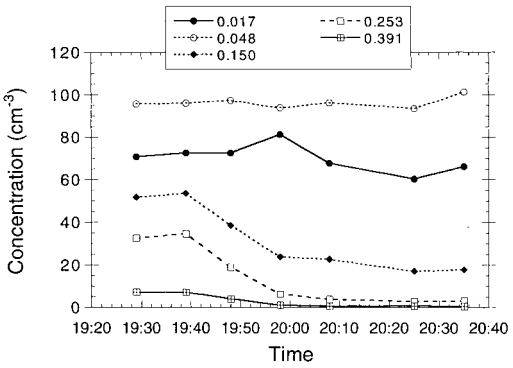

Fig. 1. Time series of the number concentrations of particles in size ranges unaffected and affected by the cloud. Particle sizes are in μm. Cloud was present from ca. 20:00.

particles in cloud will not change much over the time period studied. Additionally, Noone et al. (1992b) calculated that this process would not substantially influence the residual particle size distribution.

The integral difference between the DMPS distributions before the cloud arrived to when the cloud was present should also agree with the FSSP cloud droplet number concentration. One cloud event in period I (starting 1 November) allowed us to use this approach, and Fig. 1 shows a time series of the number concentrations of particles in the size range unaffected and affected by the cloud. The number concentrations of 0.017–0.05 μm diameter particles remain stable while larger particles that form cloud droplets decrease in concentration as the cloud forms. The integral number concentration obtained from the DMPS data for the first hour in cloud is given in Table 2 along with the average number concentration of droplets larger than 5 μm diameter obtained from the FSSP. There is good agreement between the DMPS and the FSSP number concentrations. During period II, the number concentration in the 0.017–0.05 μm diameter size range showed excessive variability to justify a similar comparison.

3.2. *Processes and artifacts affecting the CDN*

The residual particles can be assumed to represent the CDN in the absence of chemical and physical processes changing the original particles that formed cloud droplets. Differentiation between processes that actually affect the size of the CDN and processes that only change the partitioning of aerosol particles as a CDN or as an interstitial particle is, however, important in this respect. The former processes will affect the CDN directly and hence the residual particles will not be representative of CDN. The latter processes will not affect the original CDN, only their distribution between the cloud droplet and interstitial reservoirs, and hence the residual particles can be assumed to represent the CDN. In this section only processes and artifacts affecting the size of the original CDN will be discussed.

3.2.1. Loss of volatile residual particles. One hypothesised artifact that could influence the residual particles is loss of volatile material in the CVI, which would reduce their original size. We believe that this was not a problem for the measurements reported here because there was insufficient time for the volatile compounds to evaporate before

Table 2. *Data for the periods of the campaign chosen for analysis*

Date and time	Cloud droplet N-conc., $D>5$ μm (cm^{-3})	CDN N-conc. (cm^{-3})	CDN V-conc. ($\mu m^3\ cm^{-3}$)	D_{75} of CDN number distribution (μm)	D_{25} of CDN volume distribution (μm)
1 November 1st hour of cloud	326 ± 31	334 ± 53	2.0 ± 0.1	0.22 ± 0.005	0.22 ± 0.003
10–11 November 23:00–03:00	327 ± 47	238 ± 37	2.4 ± 0.9	0.25 ± 0.02	0.31 ± 0.03
12 November 03:22–05:00	289 ± 21	258 ± 37	3.6 ± 0.7	0.29 ± 0.02	0.37 ± 0.02

Cloud droplet number concentration was obtained from the FSSP. The residual number and volume concentrations for the 1st of November were obtained from the DMPS and for the remaining periods from the CNC and OPC connected to the CVI.

the particles reached the analyzers. Loss of NH_4NO_3 from aerosol particles has been observed by several authors (see e.g. Appel et al., 1980), but these studies dealt with losses from particles collected on filters sampled for periods of hours. In contrast, the time from when a droplet was impacted into the CVI to when it reached the instruments was on the order of seconds. Major ions were analysed on extracted impactor samples of the interstitial particles and the whole aerosol population when no cloud was present (Fuzzi et al., 1994). These results suggest that the major inorganic salt composition of the aerosol particles was a mixture of $(NH_4)_2SO_4$ and NH_4NO_3. Forrest et al. (1982) studied the nitrate loss from ammonium nitrate particles as they passed through a diffusion denuder, with residence times similar to those encountered in the CVI, and found that the loss of nitrate from the particles was negligible. Given the average chemical composition of the aerosol and the short residence times in the CVI, we do not believe that volatilisation of aerosol material was a significant problem.

3.2.2. Aqueous phase production. It is well established that in-cloud oxidation of sulphite to sulphate can occur and thus add more mass to the original particles that formed cloud droplets. The possibility for such a mass increase due to in-cloud oxidation therefore has to be evaluated. The question of sulphate production during this field experiment was addressed by Fuzzi et al. (1994). Due to low pH of the cloud water the rate of O_3 oxidation was calculated to be very slow. Oxidation with H_2O_2 was also thought to be negligible since no appreciable amounts of H_2O_2 were detected in either the aqueous or gaseous phases. They concluded that the sulphate found in the cloud water originated from the aerosol particles and not from in-cloud chemical reactions.

Colville et al. (1994) present model calculations for the Kleiner Feldberg experiment which show that little sulfate mass would have been produced in the cloud under the conditions found during the experiment. These calculations are consistent with the measurements of Fuzzi et al. (1994), indicating that little non-volatile mass should have been produced in the aqueous phase. Lin and Noone (1996) describe a sensitivity study of the sampling characteristics of the CVI using the conditions encountered during the Kleiner Feldberg experiment as a case study. They concluded that if aqueous phase chemical reactions had been occurring in the cloud to the maximum extent possible, then the influence on the residual particle size distributions should have been observable. Taken together, these three studies show that aqueous phase production of non-volatile aerosol mass should not have had a substantial influence on residual particle size distributions.

3.2.3. Coalescence. The onset of coalescence, based on theoretical calculations, would require that some droplets grew to sizes larger than 40 μm diameter. The observed droplet spectra for the periods discussed here did not, however, have any droplets larger than 30 μm diameter (Arends et al., 1994). If coalescence was active, one would expect to find an evolution of the droplet spectra with time, leading to a bimodal distribution. This was not observed for the periods examined here, so it is unlikely that coalescence could have influenced the observed residual distribution.

3.3. Size distribution of CDN compared to the total particle size distribution

Fig. 2 shows the interstitial and total (interstitial plus residual) number size distributions for the time periods given in Table 2. The solid lines depict the total number distribution and the dashed lines show the interstitial number distribution. The difference between the solid and dashed lines corresponds to the particles that formed cloud droplets. The distributions from period I are obtained from the DMPS and are one-hour averages of pre-cloud and in-cloud air. The distri-

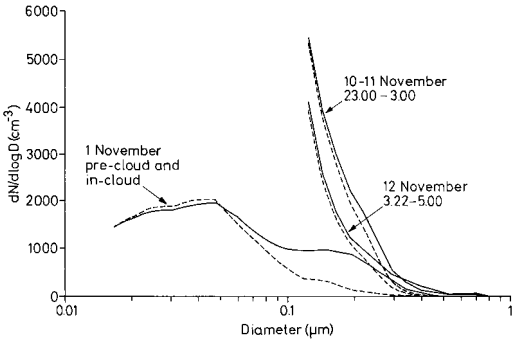

Fig. 2. Total and interstitial number size distributions for the periods given in Table 2. Solid lines depict the total number distribution and the dashed lines show the interstitial number distribution.

butions from period II are obtained from the OPCs in the inerstitial inlet and the CVI system, which only determine the size distribution in the accumulation range. The distributions from the OPCs are based on data with one minute time resolution and averaged over the time periods of interest. Fig. 3b presents 5 consecutive, 1-min averages of the OPC-derived particle size distributions to illustrate that both the one-minute and several-hour averages reveal the simultaneous presence of interstitial and residual particles of the same size.

The averaged total size distribution, obtained with the DMPS during period II, is shown in Hallberg et al. (1994b, Fig. 2). During period II, only a small fraction of the total number of particles of a given size smaller than 0.2 μm diameter formed cloud droplets (Hallberg et al., 1994b). For comparison, the average CDN number size distributions in the accumulation mode, as obtained by the OPC for the periods in period II, are shown in Fig. 4. The distributions in Fig. 4 never approach zero at smaller sizes, indicating that many of the CDN were smaller than the range covered by the OPC. The number of these particles was estimated by taking the difference of the CNC number concentration and the integral OPC number concentration. As shown in Table 2, 75% of the number of CDN were smaller than 0.2–0.3 μm diameter. So, even though a small fraction of the particles of a given size smaller than 0.2 μm diameter formed cloud droplets, these particles dominate the total number of CDN. Anderson et al. (1994) also found that the droplet number population was dominated by smaller particles, in their case smaller than 0.1 μm diameter.

One hypothesis concerning the size distribution of CDN is that all particles above a certain size would form cloud droplets if they all have the same composition and are all exposed to the same supersaturation, which is how nucleation scavenging is treated in many cloud models. This hypothesis is now tested against the observations from 12 November (Fig. 5). The interstitial particle number distribution, indicated by the solid line, was measured over 10 min (4:41–4:51) with the DMPS. The total (interstitial plus residual) distribution obtained from the OPCs is indicated by a heavy dashed line. The interstitial size distribution obtained by the OPC is also shown (squares) to demonstrate that the DMPS and OPC agree very well. Both the interstitial and total distributions obtained by the OPCs are 10-min averages of the one-minute time resolution data.

Hallberg et al. (1994b) report studies of the effects of particle size distribution and updraft velocity on the maximum supersaturation. A model run was also done (although not presented in Hallberg et al., 1994b) using the aerosol spectra observed at 4:41 on 12 November, assuming that the particles were composed of pure ammonium sulphate and that the updraft speed was 0.5 m s^{-1}. The maximum supersaturation achieved in the parcel for this case was 0.154%, which corresponds to a dry critical diameter of 0.10 μm. The dashed line in Fig. 5 represents this critical diameter and indicates the size of the smallest particle capable of activating under the assumed conditions. All particles larger than this size would have formed cloud droplets. The particles that actually formed cloud droplets are given by the difference between the interstitial distribution (solid line) and the total distribution (heavy dashed line). As can be seen, the observations are very different from the hypothetical case.

As discussed above, the assumption that all particles have the same composition does not apply to the cases studied here. One could then hypothesise that all particles of a given size with a high growth factor formed cloud droplets while the particles that remained in the interstitial air belonged to the group of particles with a low growth factor. However, Svenningsson et al. (1994) reported that a substantial fraction of particles with a high growth factor remained among the interstitial particles at diameters of 0.15 and 0.3 μm. The hatched areas of the interstitial particle size distribution in Fig. 5 represent the relative abundance of particles with high and low growth factors, based on the observations of Svenningsson et al. (1994). The conclusion from the growth factor data is that there were many hygroscopic particles in the interstitial air that were larger than the smallest observed CDN. Why would only a few hygroscopic particles form cloud droplets, while many others of the same size and larger did not? Hypotheses to explain this are discussed in the next section.

3.4. Hypotheses to explain the presence of large hygroscopic particles in interstitial air

The explanation for the existence of many hygroscopic particles, larger than the smallest

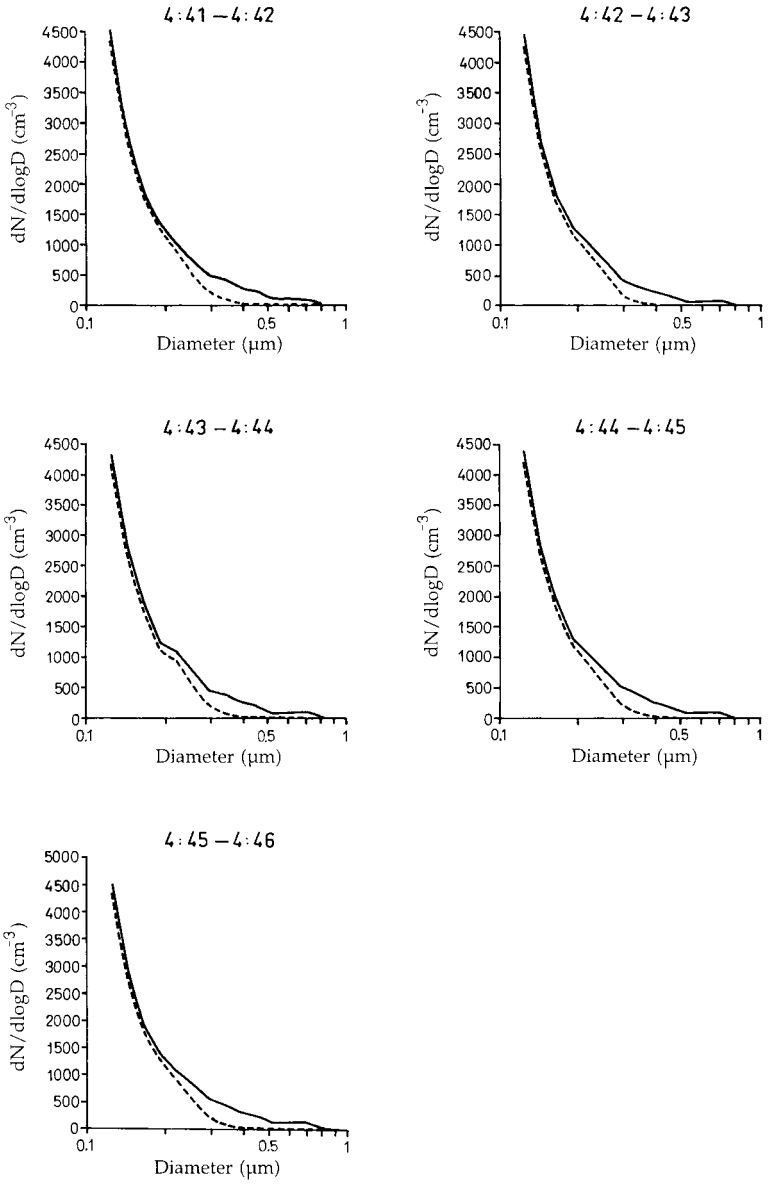

Fig. 3. Total and interstitial number size distributions on a one-minute basis. The solid lines depict the total number distribution and the dashed lines show the interstitial number distribution. Interstitial and residual particles of the same size were found to have been present in cloudy air even on a 1-min time basis.

CDN, needs to be sought in the processes governing the partitioning of aerosol particles between cloud droplets and interstitial air.

3.4.1. Varying updraft. A variation in updraft velocity can lead to a variation in the maximum supersaturation achieved when clouds form. A subsequent variation of the size of the smallest particle that forms a cloud droplet can therefore be expected. One can then hypothesise that the observations result from changes in updraft velocity during the 1-min averaging interval of the OPC data, and that the few particles that formed

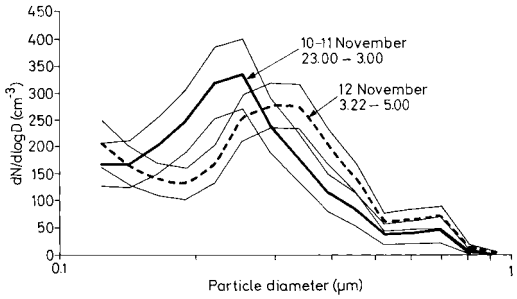

Fig. 4. Average CDN number size distributions from cloud events in period II. One standard deviation is indicated by hatched areas.

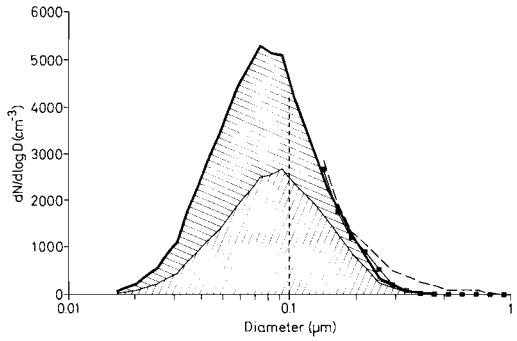

Fig. 5. Comparison of hypothetical nucleation scavenging and observations. The heavy solid line is the interstitial distribution obtained by DMPS. The hatched areas under this distribution indicate two types of particles with different hygroscopic growth, constructed from the measurements of Svenningsson et al. (1994). The dashed vertical line indicates the smallest particle that activated in a cloud parcel model (see text), assuming that all particles had the same composition. The heavy dashed line is the total (interstitial plus residual) distribution obtained from the OPCs. The line with squares indicates the interstitial distribution measured with the OPC. The difference between the heavy dashed line and the squared line represents the particles that formed cloud droplets.

cloud droplets had been subjected to a higher supersaturation compared to parts of the cloud with lower updraft velocities. This hypothesis was tested in Hallberg et al. (1994b) using a cloud parcel model to vary the updraft velocity. The variation of the updraft velocity needed to achieve the requisite variation of supersaturation was much larger than the observed variation of updraft velocity (Arends et al., 1994). Another factor opposing the hypothesis of varying updraft velocity is that the variation must have been the same minute-to-minute, since the observations were made with a one-minute time resolution. This large minute-to-minute variation is highly unlikely, and a variation in updraft velocity is therefore rejected as the explanation for the observations.

3.4.2. Entrainment. Entrainment of non-clody air followed by subsequent mixing could affect the cloud droplet population and also yield more hygroscopic particles in the interstitial air that are larger than the smallest CDN. Different theories exist to explain how this entrainment can occur.

Most of the studies and theories dealing with entrainment have been concerned with cumulus clouds where turbulence and hence entrainment are most likely. Continuous, homogeneous entrainment considers that entrained air is brought in from the sides of a rising cloudy air parcel. The entrained air is mixed instantaneously and thoroughly across the cloud element. As a result, all droplets are subjected to the same decrease in saturation ratio and they will all shrink by evaporation. Comparison between measurements and theoretical calculations (Warner, 1973) has pointed out that this theory of entrainment cannot explain the observed features of clouds. Another theory for entrainment was suggested by Baker et al. (1980), where the entrainment occurred in pulses that are intermittent in both time and space. This theory is called discontinuous, inhomogeneous entrainment. The effect of inhomogeneous entrainment is that evaporation occurs in the regions first exposed to the entrained air, creating volumes that are droplet-free but saturated. These volumes then mix with the cloudy air, reducing the concentration of droplets by dilution without changing their size. The cloud will then be inhomogeneous with respect to cloud droplet number concentration and cloud liquid water content (LWC) on a larger scale, and a strong correlation would be expected between the LWC and the droplet number concentration.

Some studies have also been concerned with stratiform clouds. Observations of nocturnal stratocumulus (Caughey et al., 1982; Slingo et al., 1982a) revealed a very sharp and intermittently turbulent interfacial entrainment layer. The observed microphysical properties indicated that inhomogeneous mixing occurred at the cloud top. Slingo et el. (1982b) also showed a strong correla-

tion between LWC and droplet number concentration, as would be expected from inhomogeneous mixing. Nicholls and Turton (1986) studied the structure near the top of stratocumulus clouds, and found a larger variation in parameters likely to be affected by entrainment (i.e., droplet number and LWC) close to cloud top than further below cloud top. These studies suggest mixing initially occurs in a shallow layer near the top of the stratocumulus clouds, and that air from that shallow layer is then mixed downwards into the rest of the cloud.

The clouds observed on Kleiner Feldberg were either formed in an approaching frontal system or by orographic uplift of moist air (Winkler et al., 1994). Orographic clouds were more frequent in period I, while the clouds observed in period II more often formed elsewhere before reaching the site. During period I the measurement site was close to cloud base, while in period II it was well above cloud base. The calculated cloud base, assuming an adiabatic updraft, agreed well with observations for period I but not for period II (Winkler et al., 1994). A decrease in LWC at the summit would result in a calculated cloud base higher than what was observed. The discrepancy during period II between the observed and calculated cloud base could be due to entrainment that reduced the LWC, or to the possibility that the temperature, pressure and LWC observed at the summit were not representative of the conditions prevailing where the cloud formed (since the cloud was formed elsewhere), or to a combination of the two.

According to theory, inhomogeneous entrainment of non-cloudy air would result in spatial variations of the microphysical properties of the cloud. The variability in cloud droplet number and LWC during period II was less than during period I, as was the turbulent kinetic energy (Arends et al., 1994). Arends, et al. (1994) found that while there were variations in the amount of liquid water on time scales of minutes to hours, the number of cloud droplets in the clouds during period II remained relatively constant. The partitioning curve presented in Hallberg et al. (1994b, Fig. 5a) shows a relatively constant shape, and Fig. 3 in this paper shows little change in the interstitial and total particle size distributions on a one-minute time scale. If entrainment was responsible for the presence of large hygroscopic particles in the interstitial air, it was occurring on a spatial scale smaller than our measurements could resolve (300 m for a wind speed of 5 m s^{-1}). It also had to have been a steady process in time to yield the constant shape of the residual size distributions that was observed over the extended time period studied. Within these constraints, however, the measurements cannot reject the possibility of entrainment as the cause of the presence of large hygroscopic particles in the interstitial air.

3.4.3. Enhanced or suppressed growth of some particles. Köhler theory (Köhler, 1923) gives the equilibrium relationship between water vapor saturation ratio and droplet size for a given CDN mass and composition. The relationship has a single maximum, where the critical diameter and the critical supersaturation are the values of droplet diameter and supersaturation at the maximum. Below its critical diameter, a droplet will grow or shrink according to the condensational growth law until it reaches the equilibrium size given by the surrounding conditions. If the supersaturation remains above the droplet's critical supersaturation for a sufficiently long period of time, the droplet will grow to and beyond its critical diameter. A droplet larger than its critical diameter is said to be activated, and will continue to grow as long as the ambient supersaturation is higher than the equilibrium saturation ratio of the droplet.

One factor that can influence nucleation scavenging is the time required for a particle to grow to its critical diameter. If this is longer than the time that the droplet is exposed to supersaturations higher than its equilibrium saturation ratio, then the particle will remain as an interstitial particle. To test his scenario, the growth of droplets originating on different sized particles has been studied. Hallberg et al. (1994b) used a simple adiabatic air parcel model (Flossmann et al., 1985) to study how the supersaturation varied for different particle number distributions observed during the campaign. We have used the time history of supersaturation from one of those model runs (case 2, 22:30 on 10 November) as an input for our growth calculations. The model used a moist adiabatic temperature profile between cloud base (550 m, 960 hPa, 6°C) and top (850 m, 930 hPa, 4.3°C), and a constant updraft velocity of 0.5 m s^{-1}. The variation of supersaturation with time is shown in Fig. 6.

Table 3. *Characteristics of particles used in growth calculations*

Particle	Dry diameter (μm)	Critical diameter (μm)	Critical supersaturation (%)
A	0.11	1.1	0.14
B	0.15	1.8	0.089

Both particles consist of ammonium sulphate (T = 5°C).

The growth of droplets was caculated according to the equations given in the Appendix. Two different sizes of dry particles, both assumed to consist of ammonium sulphate, were used. Information on the dry sizes, critical diameters and supersaturations of the two particles is given in Table 3. The maximum supersaturation achieved in the model run was 0.153% (Fig. 6), sufficient to activate both particle groups according to the Köhler equation (Table 3). The growth of the particles is also depicted in Fig. 6, which shows that only one of the particles reached its critical diameter and was activated. So, even though the maximum supersaturation achieved when a cloud forms may be high enough to activate a particle according to the Köhler equation, the time may not be sufficient for it to grow to its critical size and activate.

The possibility that droplets may not have enough time to activate in real clouds should therefore be taken into consideration when measuring the cloud droplet nucleating properties of aerosol particles, but CCN are often measured at a constant supersaturation. To study droplet activation under such conditions, the supersaturation was assumed to be constant with time in the growth calculations and with a value equal to the maximum supersaturation in Fig. 6. The times needed for the particles to grow to their critical sizes under these conditions were 29.4 and 18.7 seconds for particle A and B, respectively. Thus, both particles would be counted as CCN if allowed to grow for 30 s or more. This implies that even though a particle is able to activate during a CCN measurement, it may not necessarily activate in real clouds.

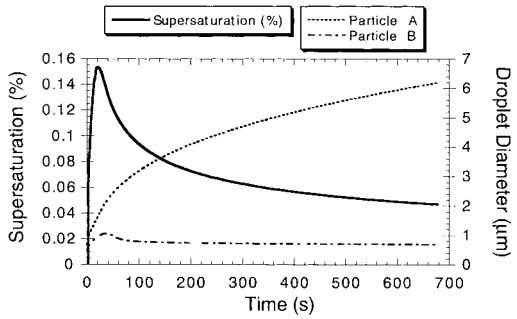

Fig. 6. Supersaturation as a function of time used in the growth calculations and growth of particle A and B.

The above analysis was for different sizes of particles and cannot explain the nucleation of only a few particles of any single size. One hypothesis to explain the observation of many large, hygroscopic particles in interstitial air is that compositional differences generated differences in the time needed for particles of the same dry size to grow beyond their critical diameter. Organic compounds can affect the evaporation and absorption of water vapour by changing the surface tension and condensation coefficient of the droplets, and have been utilised in trying to suppress fog formation (Bigg et al., 1969). The effect of organic films on droplet growth has also been studied theoretically (Warner and Warne, 1970; Podzimek and Saad, 1975). Gill et al. (1983) argued that the hydrometers most likely to be affected by organic films in the atmosphere were aerosol particles, fog droplets and cloud droplets.

Dissolved organic componds could decrease the surface tension of Particle A enough to allow it to activate under the conditions simulated above. Fig. 7 shows that reducing the surface tension of Particle A from 0.075 to 0.061 N m^{-1} allows it to activate. The few particles that activated could thus be particles that had lower surface tension compared to other particles of the same size.

The fraction of water vapour molecules that are adsorbed when they strike a growing water droplet is termed the condensation coefficient and is designated β in the growth equations in the Appendix. A layer of organic molecules on the surface of a

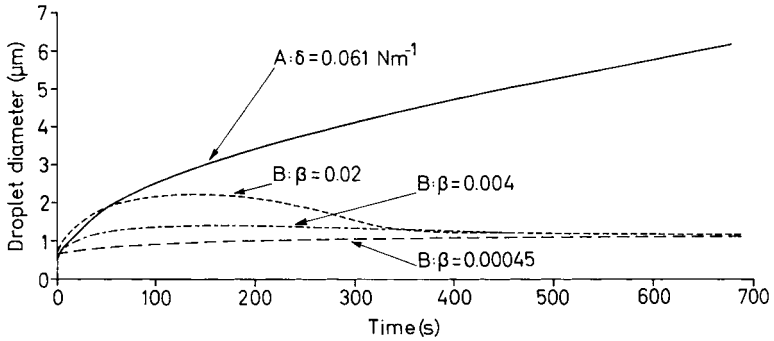

Fig. 7. Growth of particle A with a lower surface tension and the growth of particle B with different condensation coefficients.

droplet can decrease this condensation coefficient and hence retard the growth of the droplet. However, information on condensation coefficients due to layers of various organic compounds is sparse. The value of 0.04 used for the condensation coefficient of a water droplet in the Appendix was obtained from Fukuta and Walter (1970). Rubel and Gentry (1985) made measurements of ß on droplets covered with hexadecanol and observed a value of 0.00045. The corresponding growth of particle B with different values of β is shown in Fig. 7. A value half of that for a pure water droplet is sufficient to maintain particle B as an interstitial particle. The large hygroscopic particles in interstitial air could then be ones that had lower condensation coefficients and hence did not activate.

Even though the above analysis is a very simple sensitivity study, it indicates that organic compounds can affect droplet growth in either direction. Testing these hypotheses of the role of organic compounds in controlling droplet growth would require characterisation of the organic molecular composition of both residual and interstitial particles of the same size, which was not done for the present work.

3.5. *Relationship between CDN number and volume concentrations*

The relationship between changes in the number concentration of cloud droplets and the volume (mass) concentration of the aerosol particles can also be studied with this data set. Fig. 8a shows the number and volume concentrations of CDN, measured with the CVI, for the time intervals of period II (Table 2). The CDN number concentration was obtained from the CNC and the volume concentration from the OPC. Each dot repsents a one-minute average. The coefficient of determination (r^2) using a linear relationship is 0.461 (Fig. 8a). A polynomial function (second order) gives only a slight improved relation ($r^2 = 0.504$). The correlation between the number and volume concentrations of the CDN was thus not very strong.

A correlation between the number and volume of CDN can be artificial, because both quantities were sampled by the CVI. A co-variation in the number of CDN and the volume of the CDN one minute to the next can be achieved simply by a variation in the number of droplets sampled. The fraction of droplets not sampled, due either to the gap between the two sampling ranges or to losses in the CVI wind tunnel, can vary from one minute to the next, giving rise to an artificial relationship between the number and volume. The LWC will co-vary with the number and volume concentrations of CDN as the number of cloud droplets sampled varies. To avoid this artifact the number and volume concentrations were divided by the LWC measured by the Lyman-α hygrometer. The linear r^2 achieved after division with LWC was 0.5, and thus the slight relationship does not seem to be a sampling artifact.

A relationship between CDN number and volume concentrations can also be artificially achieved if the air sample contained varying amounts of entrained air one minute to the next. To avoid this potential artifact, the CDN number and volume concentrations were divided by an independent observation of LWC from a Particle Volume Monitor (Arends et al., 1994). The linear r^2 obtabined with this normalization was 0.48,

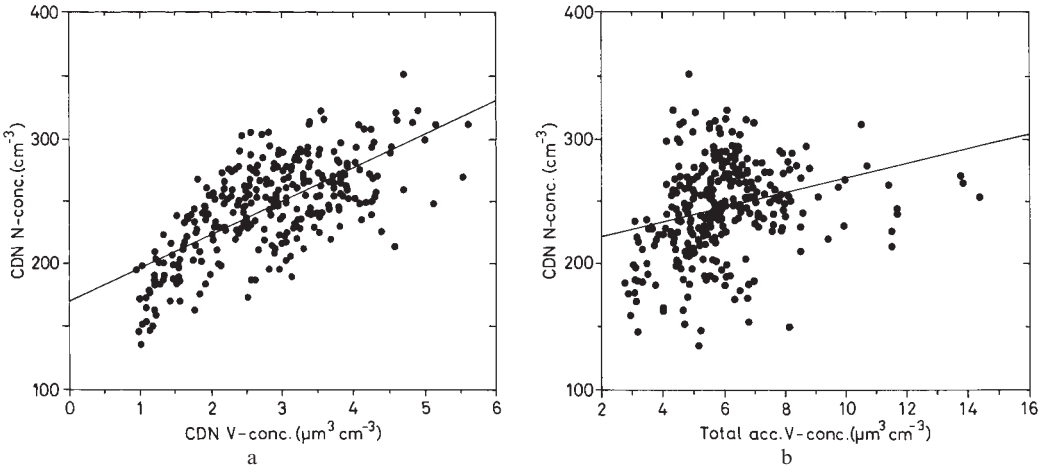

Fig. 8. (a) CDN number concentration versus CDN volume concentration from cloud events in period II (Table 2). Each dot represents a one minute average. (b) CDN number concentration versus total accumulation mode volume concentration from cloud events in period II. Each dot represents a one minute average.

suggesting that the slight relationship does not seem to be due to entrainment.

The reason for the weak correlation can be sought in the shape of the CDN number and volume distributions. The quartiles of the number and volume size distributions are useful parameters for identifying the size ranges of particles that control the number and volume (mass) concentrations. The particle sized denoted D_{25} and D_{75} are the diameters where 25 and 75% of the total number or volume of the particles comes from particles smaller than these sizes. The diameter below which 75% of the number of CDN were found given in Table 2. As can be seen, most of the cloud droplets originated on particles that were smaller than 0.2–0.3 μm diameter. In contrast, the value of D25 given in Table 2 for the CDN volume distribution shows that the CDN volume (mass) distribution is dominated by particles larger than ca. 0.2 μm diameter. This comparison illustrates how weak the relationship between the number concentration of cloud droplets and the mass concentration of the CDN can be, because in our experiment the particles dominating the two concentrations resided in different size ranges.

So far, we have only discussed the relationship between the number of cloud droplets and the mass concentration associated with the CDN. Hallberg et al. (1994b) showed that the partitioning fractions for the accumulation mode volume were 0.42 and 0.64, respectively, for the two events studied in period II. A substantial fraction of the aerosol volume was thus not incorporated in the cloud droplets, as also has been discussed above. This low scavenging efficiency affects the relationship between CDN number and total accumulation mode volume concentration, depicted in Fig. 8b for each one-minute average. In Fig. 8b, the CDN number and total accumulation mode volume concentrations are plotted for each one-minute average. The corresponding linear r^2 for the data in Fig. 8b is 0.077, which has important implications for studies of relationships between CDN number and volume concentrations using cloud models. Since particle composition is important in determining if it will be a CDN, the relative distribution of particles with different composition needs to be considered.

Leaitch et al. (1992) made measurements in polluted stratiform and found a weak correlation between cloud droplet number concentration and cloud water sulphate, based on several cloud passages. Our data, with a higher spatial resolution, indicate that large variations can occur between number and mass concentrations even within one cloud. The use of a mass concentration to yield a typical cloud droplet number concentration for a cloud and thereby calculating the effect

on cloud albedo is thus associated with large uncertainties.

4. Conclusions

Measurements of cloud droplet residuals, which represent the cloud droplet nuclei (CDN), were made in ambient clouds with a one-minute time resolution. The CDN number distribution showed no substantial variations from minute to minute. A comparison of the total particle distribution (CDN plus interstitial) showed that only a small fraction of the total number of particles at a given size, smaller than 0.2 μm diameter, was found as CDN. Among the CDN, however, approx. 75% of the particles were smaller than this size. This feature was consistent from minute to minute over several hours.

From other simultaneous measurements it was observed that hygroscopic particles of the same size or larger than the CDN remained in the interstitial air. Hypotheses to explain why only a few of the smaller hygroscopic particles formed cloud droplets while larger hygroscopic particles remained in the interstitial air were (a) that the growth of some droplets was chemically enhanced or suppressed and (b) that entrainment introduced hygroscopic particles in the insterstitial air. The spatial variation of the entrainment process must, however, have been on a smaller scale than the ca. 300 m the measurements could resolve.

A weak relationship was found between the CDN number and volume concentrations during this study, because the particles that dominated the two concentrations resided in different size ranges. The number concentration of CDN was dominated by particles smaller than 0.2 μm diameter, while the CDN volume concentration was dominated by particles larger than 0.2 μm diameter.

5. Acknowledgements

The group at the Department of Nuclear Physics, Lund University is acknowledged for providing the DMPS data. Beate Arends is acknowledged for providing FSSP data. K. Holmén and I. Wrangel are acknowledged for their help with the computer programming. L. Bäcklin, S-Å. Odh and S. Moritz helped prepare the CVI equipment. Funding for the experiment was provided by the Swedish Environmental Protection Board. The Kleiner Feldberg Cloud Experiment 1990 was carried out within the project EUROTRAC, subproject GCE (Ground-based Cloud Experiment).

6. Appendix

The equations used were obtained from Pruppacher and Klett (1980). The growth of a droplet with radius a with time is given by

$$a\frac{\mathrm{d}a}{\mathrm{d}t}=\frac{s-1-y}{F_{\mathrm{D}}+F_{\mathrm{K}}},$$

where s is the saturation and

$$y=\frac{2\sigma_{\mathrm{s/a}}M_{\mathrm{w}}}{\mathscr{R}\,\mathrm{T}_{\infty}\rho_{\mathrm{w}}a}-\frac{v\Phi_{\mathrm{s}}M_{\mathrm{w}}\rho_{\mathrm{s}}r_{\mathrm{s}}^{3}}{M_{\mathrm{s}}\rho_{\mathrm{w}}a^{3}},$$

$$F_{\mathrm{D}}=\frac{\rho_{\mathrm{w}}\mathscr{R}T_{\infty}}{e_{\mathrm{sat,w}}(T_{\infty})D'_{\mathrm{v}}M_{\mathrm{w}}},$$

$$D'_{\mathrm{v}}=\frac{D_{\mathrm{v}}}{\left[1+\frac{D_{\mathrm{v}}}{a\beta}\sqrt{\frac{2\pi M_{\mathrm{w}}}{\mathscr{R}T_{\mathrm{a}}}}\right]},$$

$$F_{\mathrm{K}}=\frac{L\rho_{\mathrm{w}}}{k'_{\mathrm{a}}T_{\infty}}\left(\frac{LM_{\mathrm{w}}}{\mathrm{T}_{\infty}\mathscr{R}}-1\right),$$

$$k'_{\mathrm{a}}=\frac{k_{\mathrm{a}}}{\left[1+\frac{k_{\mathrm{a}}}{a\alpha\rho_{\mathrm{a}}c_{\mathrm{pa}}}\sqrt{\frac{2\pi M_{\mathrm{a}}}{\mathscr{R}T_{\mathrm{a}}}}\right]}.$$

Below, are the symbols defined and values used in the calculations.

r_{s} = radius of dry salt particle (see Table 2)
M_{w} = molecular weight of water = 18 g/mol
M_{s} = molecular weight of salt = 132.1 g/mol
M_{a} = molecular weight of air = 28.97 g/mol
ρ_{w} = density of water = 1 g/cm^3
ρ_{s} = density of salt = 1.77 g/cm^3
ρ_{a} = density of air = 1.184 kg/m^3
$\sigma_{\mathrm{s,a}}$ = surface tension of water against air = $7.49\cdot10^{-2}$ N/m
v = number of ions into which a salt molecule dissociates in water = 3
Φ_{s} = osmotic coefficient for aqueous solution = 1
T_{∞} = temperature of environment = 5°C = 278 K

T_a = temperature of drop surface = T_∞
$\mathscr{R}$ = universal gas constant = 8.3143J/mol·K
$e_{sat,w}(T_\infty)$ = saturation vapour pressure over plane water surface at T_∞ = 872.47 N/m^2
D_v = diffusivity of water vapour in air = $2.42 \cdot 10^{-5}$ m^2/s
k_a = heat conductivity of air = $2.44 \cdot 10^{-2}$ J/m·s·K
c_{pa} = specific heat of air = 1 kJ/kg·K
L = latent heat of phase change per unit mass = 2489 J/g
α = thermal accomodation coefficient = 1
β = condensation coefficient = 0.04

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