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Nucleation scavenging of submicrometer aerosol particles

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ABSTRACT

The efficiency of nucleation scavenging of submicrometric aerosol particles with radii between 0.028–0.28 μm was measured at Tsukuba, Japan, during the summer and winter of 1987 by using two thermal gradient diffusion chambers, with and without a water vapor source. The efficiencies were measured as a function of the supersaturations (S). Although the efficiencies in winter tended to be lower than those in summer, mean efficiency by volume was evaluated to be 0.75 at $S = 0.25\%$, 0.81 at $S = 0.51\%$ and 0.93 at $S = 1.04\%$. On several occasions, individual aerosol particles were collected with a low-pressure impactor and were examined by the dialysis (extraction) of water-soluble material with water. It was suggested on the basis of these data that the efficiency of nucleation scavenging for submicrometer aerosol particles was closely related to the hygroscopic properties. Further, the reduction in the efficiencies at supersaturations less than 0.5% was mainly due to the presence of particles with small volume fractions of water-soluble material. Structural features of some cloud-inactive particles were also indicated.

1. Introduction

Submicrometer hygroscopic particles play an important role in the formation of cloud droplets in the atmosphere with supersaturations of less than 1%. Junge (1963) argued that in continental air, giant and most large particles act as cloud condensation nuclei and that cloud droplets will contain most of the aerosol mass present. In recent years, the incorporation of submicrometer aerosol particles into cloud droplets has been studied in natural clouds (Hegg et al., 1984; Sievering et al., 1984; Daum et al., 1987; ten Brink et al., 1987). Hegg et al. (1984) measured the number-size distribution of aerosols with range of 0.05–0.5 μm radius both in cloud-interstitial air in non-cloudy air. They obtained nucleation scavenging efficiencies for cumulus, stratus and strato-cumulus clouds, ranging from 0.2 to 0.9 with a mean of 0.76 ± 0.2 by volume. Sievering et al. (1984) observed the nucleation scavenging efficiency of particles in the "accumulation mode" by stratus clouds and showed high efficiencies of 0.76 to 0.91 by mass. High efficiency of about 0.9 was also measured by Daum et al. (1987) and ten Brink et al. (1987). Daum et al. (1987) measured the volume distributions of aerosol particles with radii in the range of 0.1–1.5 μm in the air below cloud and in the cloud air and implied that about 90% of the particles were activated to form cloud droplets in winter stratus clouds. Ten Brink et al. (1987) measured the light scattering coefficient of particles at a high resolution (2 s) in cloud-free air and cloud-interstitial air and obtained a high efficiency of 0.9 for nucleation. Recently, Heintzenberg et al. (1989) also obtained, on the basis of the measurements of clean air particles and droplet residues, that on the average, 80% of fine particulate mass was incorporated in stratocumulus cloud droplets.

Numerical studies of nucleation scavenging have also been carried out. Jensen and Charlson (1984) obtained the mass fraction of aerosol particles which form cloud droplets in a parcel of air moving upward in the area below the cloud base. The calculations were made for particles

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composed of pure ammonium bisulfate with a "clean continental background" and "urban average" distributions. They showed that the nucleation scavenging efficiency by mass for "clean continental background" aerosols was very near unity for all updraft speeds and the efficiency for "urban average" aerosols was close to unity for convective clouds. They also showed a large decrease in the efficiency for "urban average" with a decrease in the updraft velocity for stratiform clouds. Flossmann et al. (1985) calculated the reduction of aerosol particles removed by clouds and precipitation through nucleation scavenging and impaction scavenging. They found that through nucleation scavenging the total number concentration of aerosol particles was reduced by 48 to 94%, depending on the composition of particles. The above mentioned results obtained in natural clouds and numerical simulations showed a high efficiency for scavenging of submicrometer particles by nucleation.

However, some of the in cloud measurements showed a large variation in nucleation scavenging efficiency. This is likely to be mainly due to the inhomogeneous distribution of supersaturation and mixing (entrainment). The inhomogeneous distribution and fluctuation of supersaturation should be taken into account for the measurements in clouds. This is needed to assess whether aerosol particles in the cloud-interstitial air will nucleate at higher supersaturations than measured or hardly nucleate at any realistic atmospheric supersaturation. Hence, cloud condensation nuclei (CCN) spectra as measured by Hudson (1984) and hygroscopic properties of aerosol particles in cloud-interstitial air should also be measured to assess the variation of nucleation scavenging in clouds. In addition, the nucleation scavenging efficiency of atmospheric aerosol particles in non-cloudy air should be measured at various constant supersaturations in order to clarify the nucleation scavenging in clouds.

Some measurements on nucleation scavenging of atmospheric particles have been carried out at a supersaturation of near 1%. By using a thin film technique of barium chloride, Ono and Ohtani (1980) measured number concentrations of submicrometer sulfate-containing particles in air and in a sample that had passed through a cloud chamber-impactor system at a supersaturation range of 0.4–1.0%. They indicated that most of the atmospheric sulfate-containing particles with mass larger than 10^{-17} g were activated very efficiently as CCN at supersaturations less than 1%. Moreover, Ohtani and Ono (1981) measured the number concentration ratio of cloud-inactive particles to the total number by electron microscopy and showed that the ratio during the summertime in an urban atmosphere was 0.062 for particles on the collecting surface with apparent diameters of more than 0.07 μm. Their results indicated that most of the atmospheric submicrometer particles are not inactive as CCN even when the possible presence of organic material which might suppress the condensation of water vapor. Harrison (1985) measured the mass concentration of CCN and non-CCN of smaller than 2.5 μm in diameter by using a thermal diffusion cloud chamber in series with a dichotomous separator. The cloud chamber was operated with a temperature difference between the plates of 4°C. The results showed that the mean mass fraction of particles in an urban area which acted as CCN (the efficiencies of nucleation scavenging by mass) was a relatively low value of 0.43 and the scavenging efficiencies of sulfate and nitrate were 0.66 and 0.63, respectively. Moreover, Harrison (1985) measured the presence of soot in both the non-CCN and CCN fractions.

In order to study the nucleation scavenging of aerosol particles more clearly, the measurements of the efficiency should be carried out at various supersaturations less than 1% with knowledge of the hygroscopic properties of individual particles also being simultaneously obtained. The purpose of this paper is to determine the nucleation scavenging efficiency of submicrometer aerosol particles with radii between 0.028 and 0.28 μm and to discuss the efficiency with respect to the hygroscopic properties of individual particles. Structural features of some cloud-inactive particles are also shown in this paper.

2. Methods

2.1. Description of two thermal gradient diffusion chambers

In order to assess the nucleation scavenging of atmospheric aerosols under various super-

saturations clearly, the concentrations of both total particles and particles which form cloud droplets should be measured by using two thermal gradient chambers (continuous flow and horizontal types). The photograph of two chambers and temperature control unit was shown in Fig. 1. Two thermal gradient diffusion chambers, one without and the other with a water vapor source (A and B, respectively) were used for the measurements. Fig. 2 shows the schematic diagram of the instrument. Both chambers are enclosed in Plexiglas boxes and are placed upon the control unit. The circulators indicated by X and Y in Fig. 2, which contain both heater (maximum 1 kW output) and cooling tubes, supply the ethylene glycol to above and below the surface of the chambers, respectively, in order to realize constant temperatures at the top and bottom of both chambers. Note that other cooled ethylene glycol is supplied from a freezer (though not shown) to the cooling tubes in the circulators.

The thermal gradient diffusion chamber B is shown in Fig. 3. The space in which cloud droplets were produced had a 10 mm height and

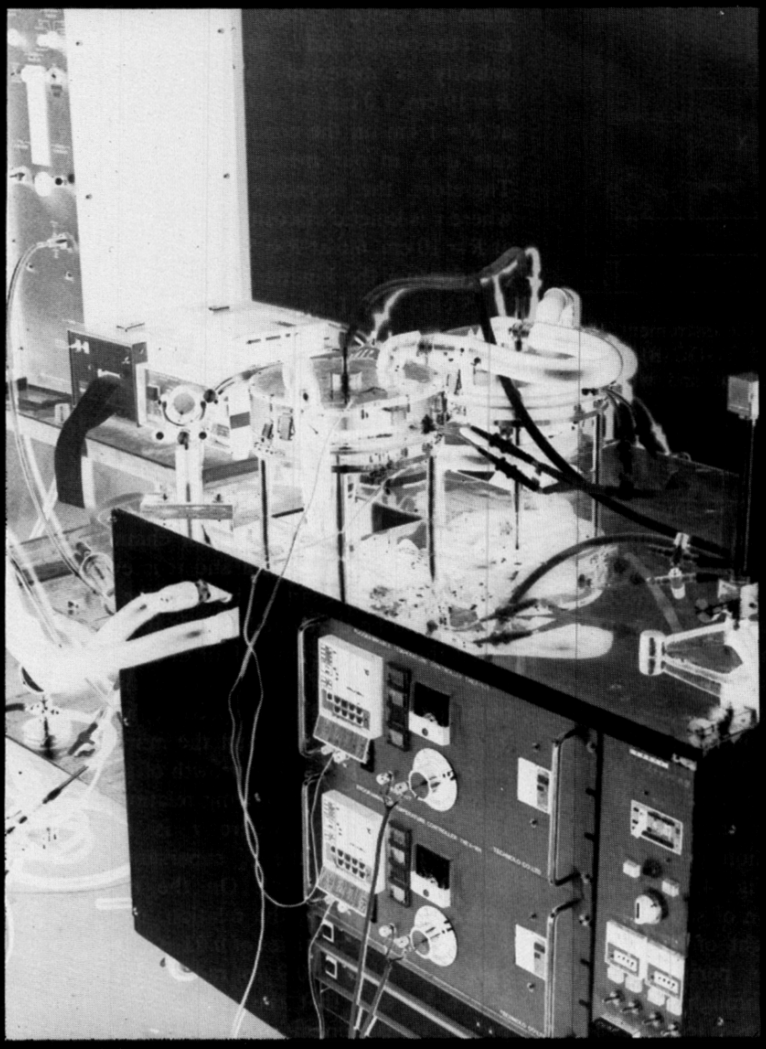

Fig. 1. Photograph of thermal gradient diffusion chambers and temperature control unit.

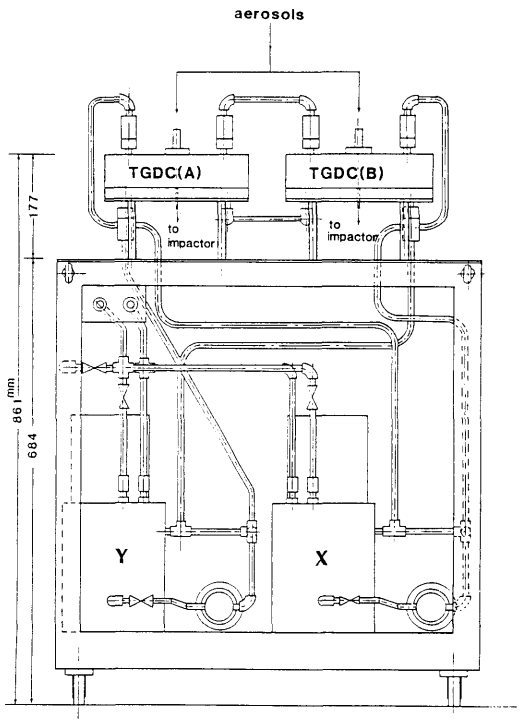

Fig. 2. A schematic diagram of the instrument. X and Y: Circulators, TGDC(A) and TGDC(B): thermal gradient diffusion chamber without and with water vapor sources, respectively.

200 mm diameter (volume 314 cm^{-3}). Water immersion filters were attached to the upper and lower surfaces of the space in order to create the supersaturation conditions. The thermocouples were located close to the centers of the bottom and top. By using the temperatures measured, the output of the heaters in the circulators was automatically controlled by using a Programmable Temperature Controller (Technolo Co. Ltd., Model TREX-100). The structure of the chamber A is identical to that of B with the exception of the water immersion filters. The calculated supersaturation profile for the chamber B is shown in Fig. 4, displaying a parabolic vertical distribution of supersaturation with a maximum at a height of 0.5 cm. The sample air enters from the periphery of the chamber and after passing through the chamber the air in high supersaturations is introduced into the sampling tube (indicated by E in Fig. 3) which is located at a height of 0.3 cm from the center of the lower surface. A water immersion filter was attached to the inner wall of the sampling tube so as to avoid the evaporation of cloud droplets before impaction. In order to draw off the air in low supersaturations close to the surface as much as possible, we used tubes J and K as shown in Fig. 3. The outer and inner diameters of tubes J and K, which are made of brass, are 0.30 and 0.27 cm, respectively.

Since the sample air enters from the entire diameter of the circle and moves toward the center, the air speed tends to increase toward the center as follows: $v_m = f/(2\pi Rh)$, where v_m is mean air speed, f flow rate of air, R distance from the center, and h chamber height. The mean velocity is expected to be 0.5 cm s^{-1} at $R = 10$ cm, 1.0 cm s^{-1} at $R = 5$ cm and 5.0 cm s^{-1} at $R = 1$ cm on the condition that total air flow rate used in our measurement is 1.9 l min^{-1}. Therefore, the Reynolds number Re ($= v_m h/\nu$, where ν is kinetic viscosity) is evaluated to be 3.3 at $R = 10$ cm, 6.6 at $R = 5$ cm and 33 at $R = 1$ cm by adopting the kinetic viscosity of air at 20°C (0.15 cm^2 s^{-1}). Low values of the Re show that the air flow is laminar and stable in the chamber. Since tubes J and K are parallel to the stable air flow and they occupy 1% of the surface area of the chamber plates, the effect of the tubes on the air flow would be quite small. Visual test by using smokes indicated the stable air flow and absence of vortex in the chamber.

Air speed at the midpoint of chamber height ($h/2$) should be maximum and it is evaluated to be 1.5× greater than v_m because the air flow is expected to be developed one. It is important to assess the residence time of air in the chamber. A minimum value of the residence time can be obtained by using the air speed at the midpoint. The estimation showed that the minimum value is approximately 7 s. The growth of particles can be evaluated by the following relation (Twomey, 1967); $r\,dr/dt = \beta S$, where r is the particle radius, t time, S the % supersaturation, and $\beta = 1.2 \times 10^{-8}$ cm^2 s^{-1}. On the basis of the calculation by using the relation, it would take less than 2 s for particles of 0.03–0.3 μm radius to grow to droplets of 0.9 μm radius. Consequently, it can be said that the residence time in the present measurement is available for the growth. The effect of droplet fallout on the measurement

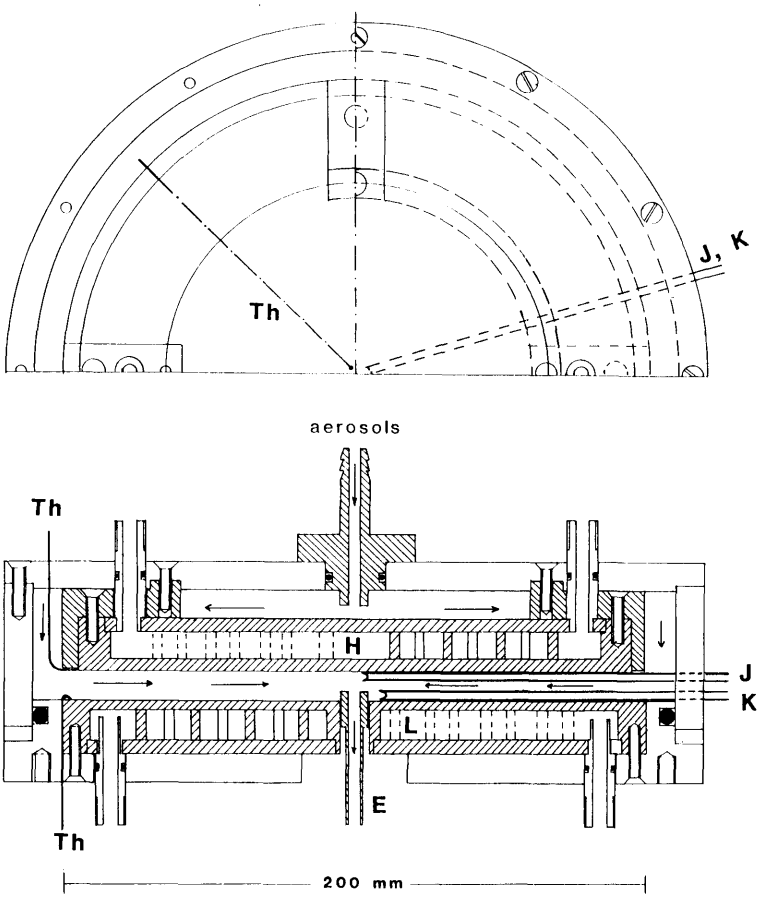

Fig. 3. A cross-section of the thermal gradient diffusion chamber B. The upper figure shows the top view of a half part of the chamber. Chamber A is identical to that of B, with the exception of the water source. Th: thermocouple, J and K: tubes for the subtraction of airs with relatively low supersaturations, E: tube for sampling, H and L: circulating ethylene glycol used for temperature control. The sample air enters from the entire periphery of the chamber and moves toward the center with increasing speed.

of nucleation scavenging is not a serious problem, since the measurement was carried out for cloud-inactive particles through the cloud chamber-impactor system.

2.2. *Procedures of measurement*

Measurements were carried out during the winter (from 16 to 26 December) and summer (from 8 June to 30 July) of 1987 at the Meteorological Research Institute which is located about 50 km north-northeast of Tokyo and 50 km west of the Pacific Ocean (Fig. 5). All measurements were carried out under the daytime conditions. The atmosphere over Tsukuba can be influenced by the transport of gaseous and particulate matter emitted from anthropogenic sources in Tokyo's Metropolitan area and by the invasion of maritime air over the Pacific Ocean.

Fig. 6 shows the system used for measurement in the present study. Air samples containing atmospheric aerosol particles were introduced into both chambers in an equal manner. Cloud droplets were formed in chamber B (with the water vapor source) and they were introduced into an impactor of a 1-mm diameter jet with a flow rate of 1.5 l min^{-1}. Air near the bottom and

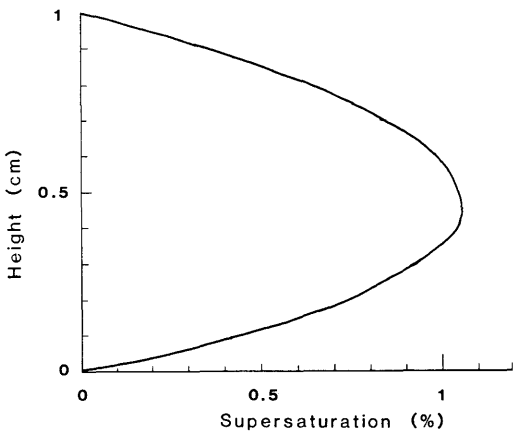

Fig. 4. Vertical distribution of the calculated supersaturation in the thermal gradient diffusion chamber B. The temperatures of the upper and lower boundaries are 23.0°C and 18.0°C, respectively.

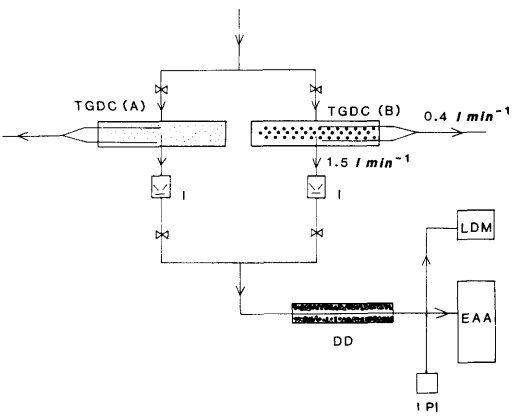

Fig. 6. A schematic diagram of the measurement system. TGDC(A) and (B): thermal gradient diffusion chamber without and with water vapor sources, respectively. I: impactor, DD: diffusion drier, EAA: electrical aerosol analyzer, LDM: laser dust monitor, LPI: low-pressure impactor for sampling.

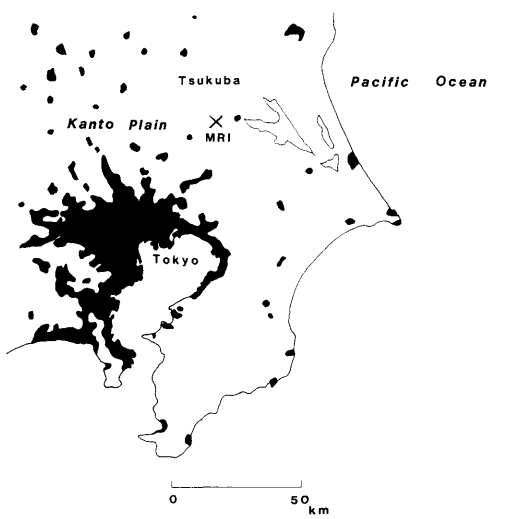

Fig. 5. Location of the site. The Meteorological Research Institute (X), urban area including the industrial area (black area).

top of the chamber was drawn off at a flow rate of 0.4 l min^{-1}. The collection efficiency of the impactor for particles with a density of 1 g m^{-3} was evaluated accordingly to the experimental results of Ranz and Wong (1952). On the basis of this calculation, the collection efficiency of particles with radii larger than 0.9 μm was 100%. Hence, cloud droplets were collected with this impactor. Particles which did not produce cloud droplets were also introduced into the impactor and were used for the measurement of number concentration $dN_B(r_i)$ in a size range. The r_i is midpoint radius of particles in the size range. Also, for the measurement of number concentration $dN_A(r_i)$, aerosol particles in chamber A (without water vapor source) were passed through the impactor. The number-size distribution of aerosol particles was measured with an electrical aerosol analyzer (EAA) (Thermo-systems Inc., Model 3030) and a laser dust monitor (LDM) (Hitachi Electronics Engineering Co. Ltd., Model TS-400). Number concentrations for radius range of 0.0089–0.05 μm and 0.05–0.25 μm were those measured with the EAA and the LDM, respectively. It should be noted that the air is dried with a diffusion drier before the measurements were taken. The relative humidity of the air after passing through the diffusion drier was 10–15%.

The value $dN_A(r_i) - dN_B(r_i)$ can be evaluated to be number concentration of particles in a size bin which formed cloud droplets and $[dN_A(r_i) - dN_B(r_i)]/dN_A(r_i)$ forms the efficiency of nucleation scavenging by number, $\Phi_N(r_i)$. By using the number-size distribution and $\Phi_N(r_i)$, the efficiency by volume (Φ_v) can be calculated in the

radius range of 0.028–0.28 μm as follows:

$$\Phi_v = \sum \Phi_N(r_i)\, dV(r_i) \Big/ \sum dV(r_i),$$

where $dV(r_i)$ is volume concentration of particles in a size bin. Note that uncertainties of the Φ_v were evaluated to be within ± 0.015 ($\pm 1.5\%$). The time required for the entire measurements is approximately 1 h.

2.3. *Testing of the thermal gradient diffusion chamber by using NaCl particles*

Nucleation scavenging efficiencies of artificial NaCl particles are shown in Fig. 7. Submicrometer NaCl particles were generated with a nebulizer which contained a 0.01 wt% NaCl solution. NaCl particles were introduced into the thermal gradient diffusion chambers after passing through a diffusion drier (not shown in Fig. 6). The efficiencies of nucleation scavenging as a function of dry radius were obtained at maximum supersaturations of 0.25, 0.50 and 1.04% and were found to increase with supersaturation. The results at a supersaturation of 1.04%, indicating by a dashed line (Fig. 7) show that high values of efficiencies greater than 0.9 are present for the case of particles with radii larger than 0.04 μm and tend to decrease with decreasing radius. The efficiencies for particles with radii of 0.009–0.016 μm (midpoint radius; 0.012 μm) and 0.016 to 0.028 μm (0.021 μm) were erratic because the currents measured with the EAA in these radius ranges had very low values at the flow rate of air (1.5 l min^{-1}) used in the present study.

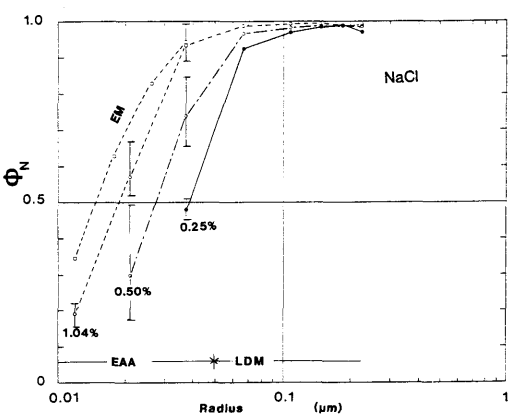

Fig. 7. Efficiencies of nucleation scavenging of artificial NaCl particles by number (Φ_N) at maximum supersaturations of 0.25%, 0.50% and 1.04%. Dashed line (marked by EM) is the efficiency at 1.04% supersaturation evaluated by electron microscopy.

In order to assess the efficiency values at a supersaturation of 1.04% more clearly, NaCl particles were collected by a low-pressure impactor (Okada, 1983) having an air pressure drop of 65 cm Hg. The efficiency indicated by EM (Fig. 7) was obtained on the basis of electron micrographs of NaCl particles collected from air passing through the impactors having a 1-mm diameter jet attached below A and B chambers and the diffusion drier. The efficiency indicated that approximately 35% of the NaCl particles of 0.012 μm radius are activated at supersaturation of 1.04%. The results of present measurements are nearly consistent with previous findings (Gerber et al., 1977; Aloft et al., 1979). It should be noted that number concentrations of NaCl particles which were activated at an applied maximum supersaturation of 1.04% are from 5×10^3 to 10^4 cm^{-3}. The concentration range of NaCl particles corresponds to that of atmospheric aerosol particles measured in this study.

The growing droplets should reduce the supersaturation due to the consumption of water vapor and the addition of latent heat in a thermal gradient diffusion cloud chamber. By using the consideration presented by Hudson and Squires (1973), approxiamtely 10^3 nuclei cm^{-3} would be acceptable for 10% decrease of supersaturation in the case that the droplets grow to 1 μm radius. However, the radius of droplets should be much smaller in the region where they are activated. In the continuous flow-type chamber used in this study, air containing aerosol particles enters from the entire diameter of the circle and particles can be activated in the first stage of the invasion. As shown in the relation by EM in Fig. 7, NaCl particles in the radius range of 0.01–0.014 μm (midpont radii; 0.012 μm) began to form cloud droplets at an applied maximum supersaturation of 1.04%. On the basis of the results reported by Aloft et al. (1979), a critical supersaturaation for activating NaCl particles of 0.012 μm radius is 0.95%. Although we could not assess the degree of the reduction of supersaturation in the activation region clearly, the reduction is considered to be approximately 10% even if the

concentrations of activated nuclei are approximately 10^4 cm^{-3} at a supersaturation of 1.04%.

2.4. *Examination of the hygroscopic properties of individual particles*

Together with the measurement of nucleation scavenging, individual aerosol particles of 0.03–0.35 μm radius were collected on a carbon-covered nitrocellulose film using the low-pressure impactor and then hygroscopic properties were examined by use of an electron microscope (Hitachi, H-600). Collected aerosol particles on the film were coated with a vapor-deposited thin film of Pt/Pd alloy with a shadowing angle of arctan 0.5 in order to investigate the shape and volume. The dialysis (extraction) of water-soluble material was applied to the sample by floating the electron microscopic grid on distilled water, with collecting surface upward as stated by Mossop (1963). A dialysis time was 3 h in the present study. The residues after the dialysis were also coated with Pt/Pd alloy with shadowing angle of arctan 0.5 in order to estimate the volume of water-insoluble material. Mixture state of particles with regard to the hygroscopicity and the volume fraction of water-soluble material (ε) were estimated by the method indicated in Okada (1983). Error of the ε estimated by electron microscopy is assumed to be due to the error of size measured on the photographs ($\times$14,000 magnitude). If the error of measured sizes for both total part and inclusions is 0.1 mm, the error of ε is considered to be within ± 0.1 for particles of 0.05–0.13 μm with $\varepsilon < 0.8$, within ± 0.05 for those with $0.8 < \varepsilon < 0.9$ and within ± 0.02 for those with $\varepsilon > 0.9$. However, the values of ε for hygroscopic particles with irregular shaped inclusions are more erratic.

The meteorological data used in the present study were those obtained at the Tateno Aerological Observatory, which is about 0.5 km north of the Meteorological Research Institute.

3. Results

3.1. *Features of nucleation scavenging efficiency*

Fig. 8 gives an example of measurements obtained for atmospheric particles during the period from 11:01 to 12:00 LST on 23 December 1987. Although the nucleation scavenging efficiencies

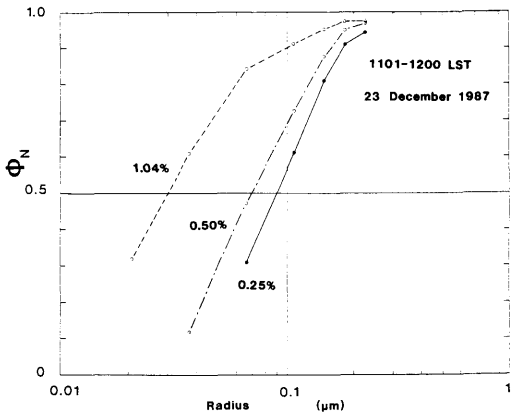

Fig. 8. Efficiencies of nucleation scavenging of atmospheric aerosol particles by number (Φ_N) at maximum supersaturations of 0.25%, 0.50% and 1.04%. The measurement was carried out during the period from 11:01 to 12:00 LST on 23 December 1987.

tend to increase with supersaturation, they are lower than those of NaCl particles (Fig. 7) for each supersaturation. In order to show the features of nucleation scavenging efficiency (Φ_N) of atmospheric aerosols as a function of supersaturation, the efficiencies for particles with radius range of 0.05–0.09 μm and 0.13–0.165 μm are indicated in Figs. 9a and b, respectively. It should be noted that these particles in the "accumulation mode" contribute largely to the volume concentration. In these figures the efficiencies for NaCl particles are also indicated by dotted lines and are found to be larger than those of atmospheric aerosols.

For the case of particles with radii of 0.05–0.09 μm, the efficiencies found during June–July 1987 have values of more than 0.6 at a supersaturation of about 0.2% and increase gradually with supersaturation. The efficiencies at a supersaturation of 1.04% have values greater than 0.9 during the summertime. On the other hand, the efficiencies during December 1987 range form 0.2 to 0.5 at a supersaturation of 0.25% and increases strongly with supersaturation. The wintertime efficiencies at a supersaturation of 1.04% range from 0.7 to 0.9. The results for particles with radius range of 0.13–0.165 μm also show similar tendencies

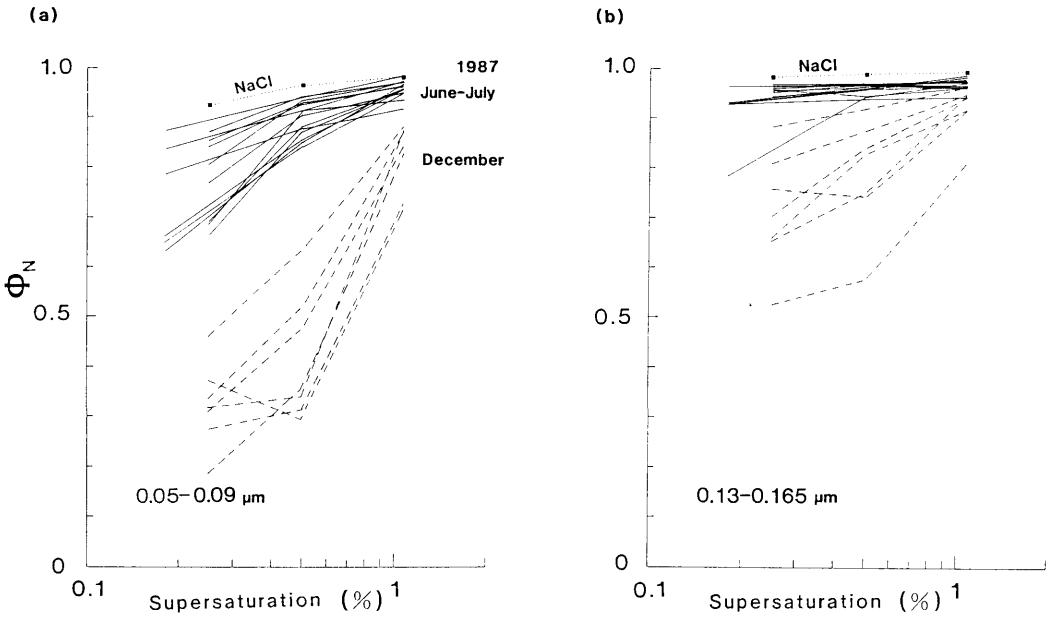

Fig. 9. Efficiencies of nucleation scavenging (Φ_N) of aerosol particles having radii between 0.05 and 0.09 μm (a) and between 0.13 and 0.165 μm (b) as a function of supersaturation. Values in summer (June–July) and winter (December) are indicated by solid and chain lines, respectively. Values of NaCl particles are indicated by the dotted line.

although the efficiencies are greater than those from aerosols in the range of 0.05–0.09 μm.

Fig. 10 shows the relation between the efficiencies (Φ_N) for particles of 0.05–0.09 μm radius and total number concentrations of cloud droplets formed on particles in the cloud chamber (N_d). These relations were obtained at supersaturations of 0.50% (Fig. 10a) and 1.09% (Fig. 10b). The number concentration of the droplets was estimated by aerosol number concentrations and efficiencies (Φ_N). Data indicated by open and closed circles are those measured in the summer and winter, respectively. The efficiencies indicated by cross marks were obtained from the measurements for NaCl particles. As found in Fig. 10, the number concentrations of droplets formed on atmospheric aerosol particles in the cloud chamber mainly range from 10^3 to 1.5×10^4 cm^{-3}. In the summer, the efficiencies at 0.50% and 1.04% supersaturations are greater than 0.8 and 0.9, respectively, regardless of the droplet concentration. The efficiencies in the winter are lower than those in the summer in the whole range of droplet concentration. This suggests that the difference in the efficiencies between summer and winter are closely related to the physico-chemical properties of aerosol particles.

It is important to assess the efficiency of nucleation scavenging by volume, Φ_v, in order to obtain basic knowledge on the incorporation of aerosol mass into cloud droplets by condensation and on cloud and precipitation chemistry. Fig. 11 shows the nucleation scavenging efficiencies of aerosol particles by volume in the radius range of 0.028–0.28 μm. The efficiencies of NaCl particles (dotted line) are also shown in Fig. 11. In the summertime (June–July), the efficiencies range from 0.7 to 0.95 at a supersaturation of 0.25% and tended to increase gradually with supersaturation. On the other hand, the winter efficiencies (December) are found to be lower than those in summer at each supersaturation, having values from 0.4 to 0.7 at a supersaturation of 0.25%. The winter efficiencies exhibit a stronger increase with supersaturation, with

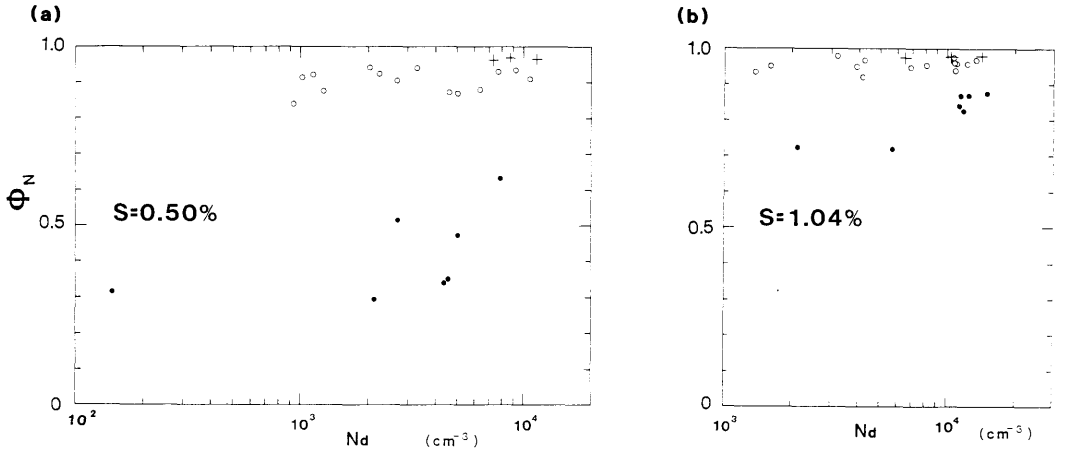

Fig. 10. Relation between the efficiency (Φ_N) for particles of 0.05–0.09 μm radius and total number concentration of cloud droplets in the cloud chamber (N_d). The relation was obtained at a supersaturation of 0.50% (a) and that of 1.04% (b). Data indicated by open and closed circles are those measured in the summer and winter, respectively. The data indicated by cross marks are obtained from the measurement for NaCl particles.

values reaching 0.75–0.87 at a supersaturation of 1.04%.

As can be seen in Fig. 11, the efficiencies of NaCl particles by volume are found to be 0.94–0.98, although the efficiencies should be unity at supersaturations of 0.25–1.04%. This tendency is probably closely related to the nonuniform distribution of supersaturation in the air sample. Hence, the observed efficiencies of aerosol particles are divided by the efficiencies of NaCl particles. Table 1 shows mean values of the normalized efficiencies of aerosol particles by volume during summer (21–30 July) and winter (16–25 December). The difference in the efficiencies between summer and winter is large at supersaturations lower than 0.5%. The mean values of the efficiencies obtained from the summer and winter data are also indicated in Table 1. From Table 1, the mean efficinecy is found to be 0.75 at a supersaturation of 0.25%, 0.81 at 0.50% and 0.93 at 1.04%.

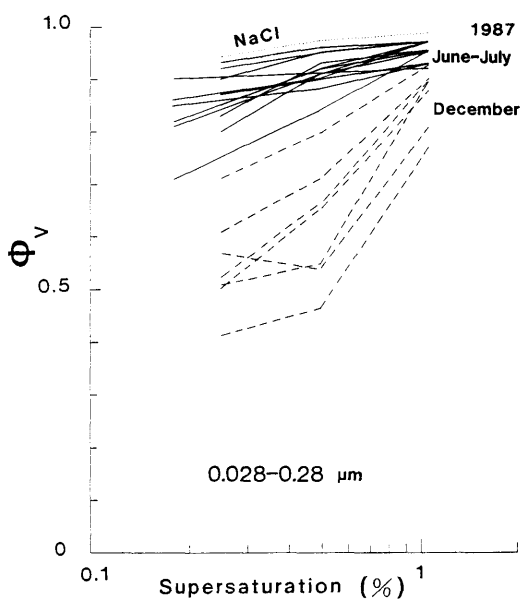

Fig. 11. Efficiency of nucleation scavenging (Φ_v) of aerosol particles with radii between 0.028 and 0.28 μm as a function of supersaturation.

3.2. *Hygroscopic properties of individual aerosol particles*

Fig. 12 shows nucleation scavenging efficiencies (Φ_N) as a function of supersaturation measured during the periods of 14:16–15:25 LST on 8 June, 15:38–16:40 LST on 11 June and 10:38–11:42 LST on 25 December 1987. The efficiencies were those measured for the radius ranges of 0.05–0.09 μm (Fig. 12a) and 0.09–0.13 μm (Fig. 12b). Efficiencies on 8 June and 11 June correspond to minimum and maximum values, respectively for the summertime measurements, while efficiencies shown for 25 December

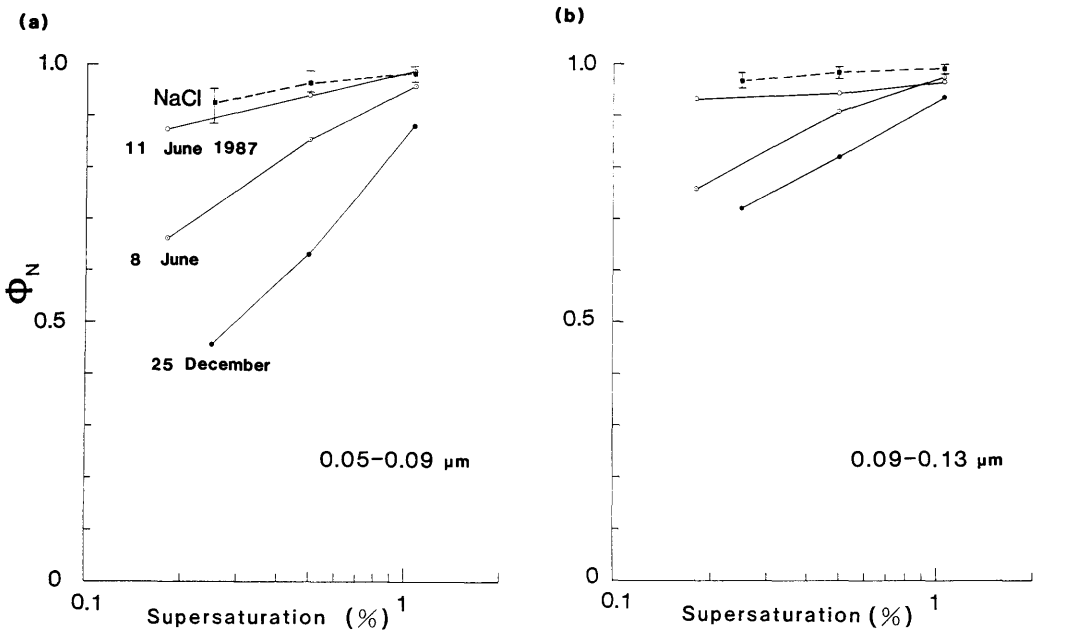

Fig. 12. Efficiencies of nucleation scavenging (Φ_N) of aerosol particles with radii of 0.05–0.09 μm (a) and 0.09–0.13 μm (b). Wind conditions during the measurements were southerly wind of 7 m s^{-1} on 8 June, northeast wind of 6 m s^{-1} on 11 June and southerly wind of 0.9 m s^{-1} on 25 December 1987.

Table 1. *Mean efficiency of nucleation scavenging (Φ_v) of aerosol particles with radii between 0.028 and 0.28 μm in summer (21–30 July 1987) and in winter (16–25 December 1987); the efficiency has been divided by the efficiency of NaCl particles; the range of calculated values is indicated in parenthesis*

	Supersaturation		
Period	0.25%	0.50%	1.04%
summer (7)* (21–30 July 1987)	0.92 (0.85–0.99)	0.96 (0.93–0.99)	0.98 (0.95–0.99)
winter (7)* (16–25 Dec. 1987)	0.58 (0.44–0.75)	0.65 (0.48–0.82)	0.88 (0.78–0.95)
mean†	0.75	0.81	0.93

* Number of measurements.
† Mean value of the data in summer and winter.

are the maximum values for the wintertime measurements. On 11 June, a northeast wind of 6 m s^{-1} was observed. While on 8 June a southerly wind of 7 m s^{-1} was observed. The air moving from the south on 8 June should be influenced by the emissions from anthropogenic sources in the Tokyo Metropolitan area. It should also be noted that relatively low efficiencies at a supersaturation of about 0.2% were observed under the southerly winds in June–July. No systematic change in the relation between wind direction and nucleation scavenging was detected during December.

Hygroscopic properties of submicrometer particles were investigated by electron microscopic examinations applied to the samples collected during the measurements of nucleation scavenging. The collections were carried out with the low-pressure impactor with an air pressure drop of 30 cm Hg. Fig. 13 shows example of the electron micrographs of particles collected during the period from 15:43 to 15:53 LST on 8 June, before and after the dialysis with water. From a close comparison of these electron micrographs, most particles were found to be hygroscopic particles which contain water-soluble material. Hygroscopic particles which contain water-insoluble parts (inclusions) were also found and they were termed mixed particles. Moreover, particles also existed which hardly changed their

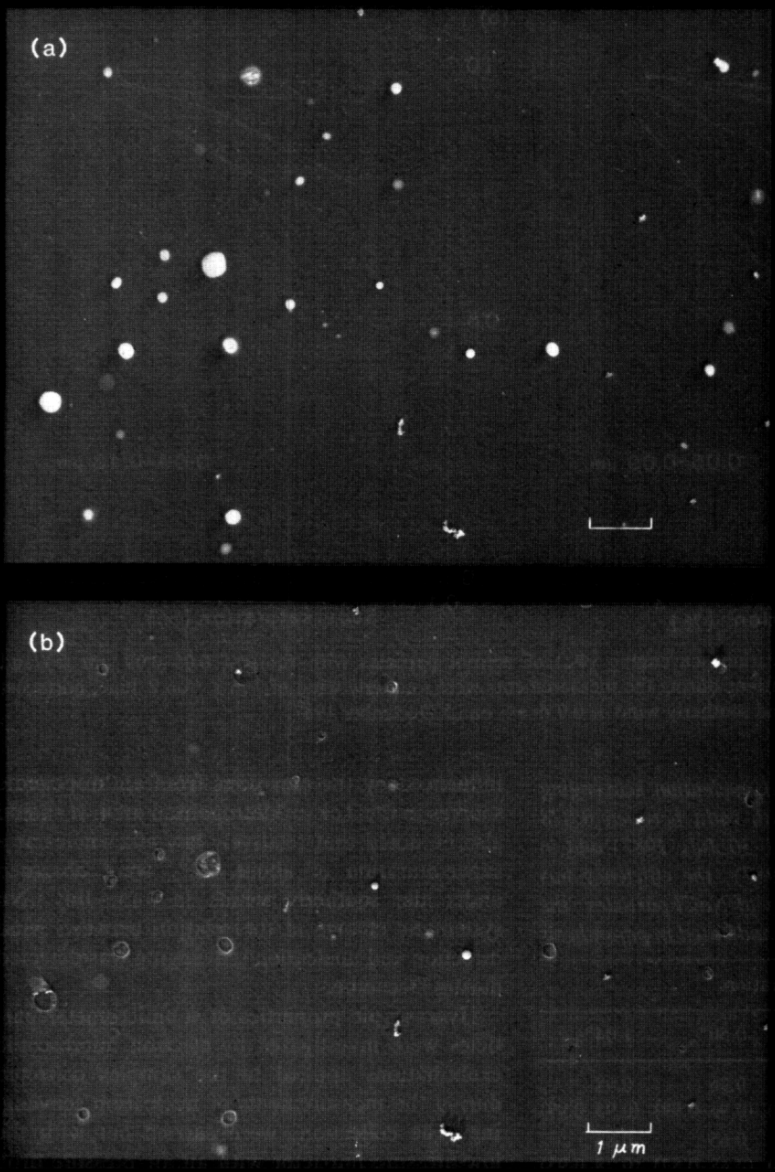

Fig. 13. Electron micrographs of aerosol particles before (a) and after the dialysis of water-soluble material (b). These particles were collected with the low-pressure impactor during the period from 15:43 to 15:53 LST on 8 June 1987. Both scale bars are 1 μm.

morphological features before and after the dialysis and they were termined water-insoluble particles.

Number frequencies of these three types of particles and the volume fraction of water-soluble material in individual particles were evaluated on the basis of electron micrographs. Fig. 14 shows the frequencies of occurrence of the three types of particles with radii between 0.028 and 0.158 μm collected on 8 June, 11 June and 25 December 1987, indicating large frequencies of hygroscopic particles of more than about 80% of the total

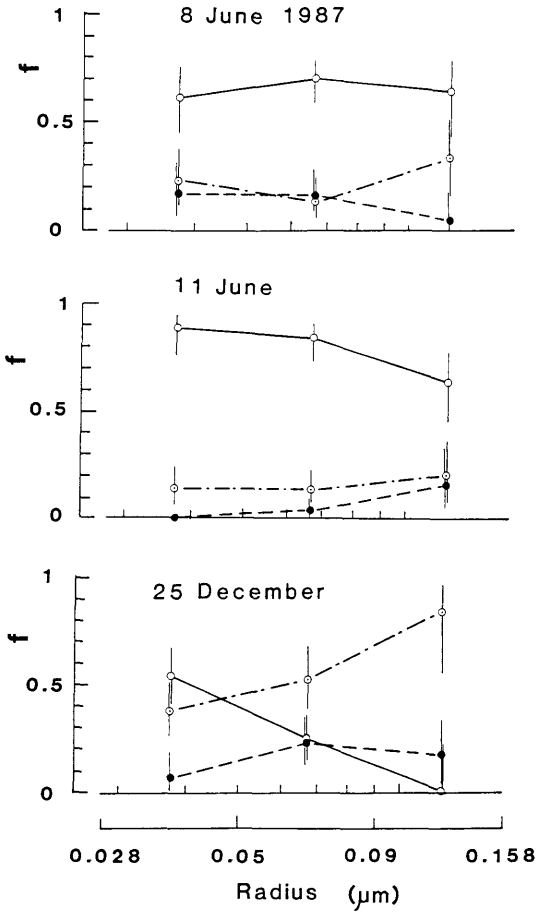

Fig. 14. Frequencies of three types of particles with radii between 0.028 and 0.158 μm collected on 8 June, 11 June and 25 December 1987. Hygroscopic particles without water-insoluble inclusion (——○——), hygroscopic particles with water-insoluble inclusions (mixed particles) (-·-⊙-·-), water-insoluble particles (---●---). Bar indicates the range of ±90% confidence limits.

particles. The difference in the properties of the particles between 8 June and 11 June was that number fraction of Aitken water-insoluble particles on 8 June (16%) was greater than that for 11 June (<5%). However, 60–90% of the total particles were hygroscopic particles without water-insoluble material on both of these days. On the other hand, 40–80% of the total particles were mixed particles on 25 December and the frequencies of mixed particles increase with radius.

The volume fraction (ε) of water-soluble material in individual particles is important for assessing the nucleation scavenging as indicated by Junge and McLaren (1971) and Fitzgerald (1973). Fig. 15 shows the frequency of ε for individual particles with radii in the ranges of 0.05–0.09 μm and 0.09–0.158 μm collected on 8 June, 11 June and 25 December. Number of particles examined is indicated in parenthesis. Note that water-insoluble particles and hygroscopic particles without water-insoluble inclusions have a ε of 0 and 1, respectively. Fig. 15 indicates that the ε distributions for particles observed on 25 December exhibited features quite different from those on 8 and 11 June. Particles with ε smaller than 0.5 are found in high frequencies of 60–83% in the radius range of 0.05–0.158 μm on 25 December, whereas particles with $\varepsilon \leqslant 0.5$ on 8 and 11 June have relatively small frequencies of less than 25%. The mean values of ε for particles with radii between 0.05 and 0.158 μm are evaluated as shown in Table 2. The mean values of ε on 8 and 11 June were found with high values of 0.78–0.94 which were consistent with the results for a summertime urban atmosphere investigated by Okada (1983). The values on 25 December were 0.3–0.5 and tended to decrease with radius. The decrease in ε was due to the presence of mixed particles having a small ε in larger radius range. The difference in nucleation scavenging with respect to the hygroscopic properties of particles is discussed in the next section.

Table 2. *Mean values of ε in the radius ranges of 0.05–0.09 μm and 0.09–0.158 μm*

	Radius range (μm)	
Period	0.05–0.09	0.09–0.158
8 June 1987 15:43–15:53 LST	0.78	0.80
11 June 1987 17:08–17:18 LST	0.94	0.83
25 December 1987 10:29–10:34 LST	0.46	0.28

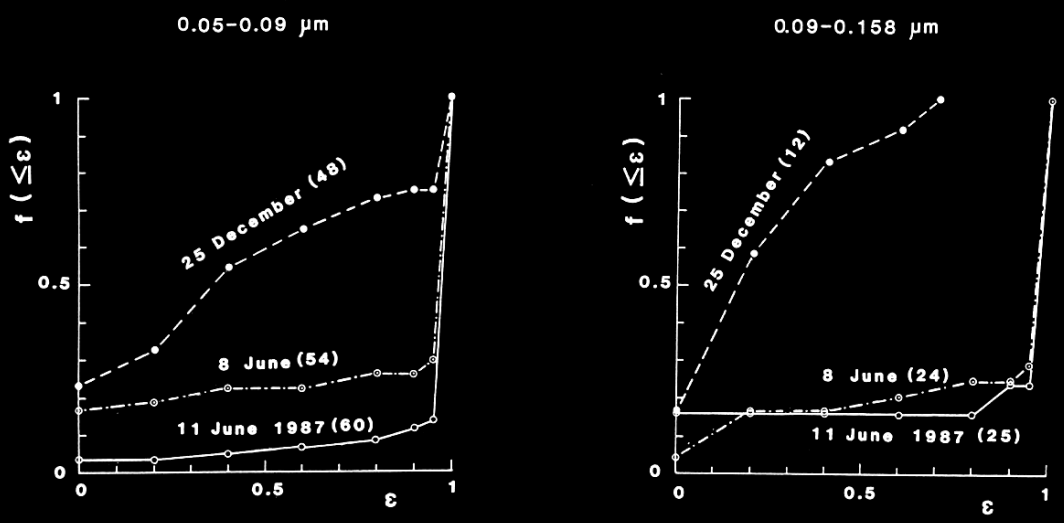

Fig. 15. Frequencies of volume fraction of water-soluble material (ε) in individual particles with radii between 0.05 and 0.158 μm collected on 8 June, 11 June and 25 December 1987. The ordinate indicates frequency smaller than ε. The number of analyzed particles is shown in parenthesis.

3.3. *Features of cloud-inactive particles*

As shown previously in Fig. 9, more than 70% of the total particles in the "accumulation mode" act as efficient cloud condensation nuclei at a supersaturation of 1%. Particles which passed through the impactor below the cloud chamber were collected with the low-pressure impactor in order to obtain information of the particles which did not form cloud droplets. The collection was carried out during a case of a supersaturation of 1.04% in chamber B. Fig. 16 shows the electron micrographs of cloud-inactive particles at a supersaturation of 1.04%. Particles in Fig. 16a are formed by aggregations of electron-dense spherules, which have structural features similar to carbon particles. No change in morphology of these particles was found before and after the dialysis with water. Particles in Fig. 16b were

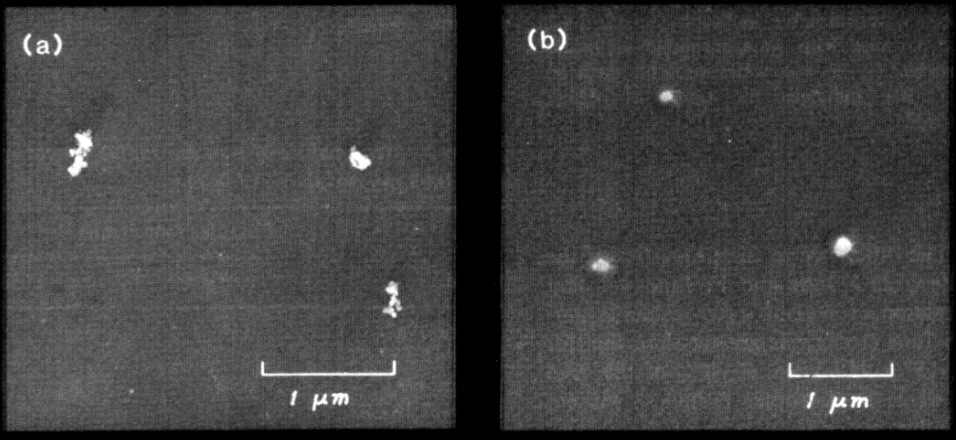

Fig. 16. Cloud-inactive particles at 1.04% supersaturation. These particles were collected during the periods from 15:31–15:41 LST on 8 June (a) and from 16:44–17:04 LST on 11 June 1987 (b).

also classified as cloud-inactive particles. It was found on the basis of the examination with the dialysis that the particles were composed of a central soluble material surrounded by a semi-transparent insoluble material displaying some wrinkles. The semi-transparent material has structural features similar to the organic material suggested by Husar and Shu (1975).

Bigg (1986a, b) suggested that particles coated with surface-active organic material were often present in high proportion which could delay or suppress cloud droplet formation. Although the particles shown in Fig. 16b were found in the present study, the proportion was evaluated to be quite small values of less than 0.03 by number for particles with radii between 0.028 and 0.13 μm.

Table 3. *Comparison between observed and calculated nucleation scavenging efficiencies (Φ_N) of aerosol particles of 0.05–0.09 μm radius at 0.25% supersaturation; the error of ε was also considered in the estimated value shown in parenthesis*

Date	Observed value	Estimated value
8 June 1987	(0.73)*	0.78–0.83 (0.78–0.83)†
11 June 1987	(0.91)	0.95–0.97 (0.94–0.97)
25 December 1987	0.46	0.44–0.76 (0.39–0.79)

* Evaluated from the data at supersaturations of 0.18% and 0.50%.
† Error of ε was considered.

4. Discussion

The nucleation scavenging efficiency of submicrometer aerosol particles was studied with respect to the hygroscopic properties of particles. As was shown in the previous section, efficient scavenging of submicrometer particles by nucleation scavenging was found especially at supersaturation of 1%. However, a great difference in the efficiencies was noted at supersaturations lower than 0.5%.

First, we shall discuss the particles in the range of 0.05–0.09 μm radius for a case of 0.25%. Nucleation scavenging efficiencies for particles of 0.05–0.09 μm radius measured on 8 June, 11 June and 25 December 1987 were obtained by using the hygroscopic properties in Fig. 15 on the assumption that the water-soluble material was ammonium sulfate. The characteristic features of individual sulfuric-acid particles are satellite droplet rings on the collecting surface (Frank and Lodge, 1967). These particles could not be found in the electron micrographs used for analysis. Moreover, sulfate-containing particles are expected to be dominant in the radius range of <0.3 μm (e.g., Okada et al., 1983; Okada, 1985). Consequently, the assumption would be valid. On the basis of numerical results (Fitzgerald, 1973), for ammonium sulfate-containing particles of 0.05 μm and 0.09 μm radius, the minimum values of ε required for nucleation are 0.43 and 0.06 at 0.25% supersaturation, respectively. Table 3 indicates the comparisons between observed and estimated efficiencies at a supersaturation of 0.25% on 8 June, 11 June and 25 December 1987. The normalization by the value for NaCl particles was not applied to the observed value. The upper and lower efficiencies for the range of estimated values corresponded to those of aerosol particles of 0.09 μm and 0.05 μm radius, respectively. The estimated efficiencies nearly agree with the observed values. It is necessary to obtain the distribution of ε in the range of less than 0.1 in order to make comparisons at supersaturations of more than 0.5%. Since the distribution of such a low value of ε is hard to assess by electron microscopic examinations, the comparisons at a supersaturation of 0.5% could not be performed. However, the comparison in Table 3 suggests that hygroscopic particles with small ε contribute largely to the reduction of nucleation scavenging efficiencies at supersaturations less than 0.5%.

Secondly, it is of interest to compare the measured and estimated efficiencies at 1.04% supersaturation on the assumption that all water-insoluble particles of 0.05–0.09 μm radius, determined by electron microscopy, cannot be activated at 1.04% supersaturation (Table 4). As found in Table 4, measured efficiencies on 8 June and 25 December are 0.10 greater than the estiamted efficiencies. This means that some of the water-insoluble particles were activated, suggesting the presence of insoluble particles with a wetting angle close to 0°. Although the comparisons as shown in Tables 3 and 4 were not carried

Table 4. *Measured efficiency for nucleation scavenging of aerosol particles of 0.05–0.09 μm radius at 1.04% supersaturation and the estimated efficiency, on the assumption that all water-insoluble particles in the radius range are not activated*

Date	Observed value*	Estimated value
11 June 1987	0.98	0.97
8 June 1987	0.96	0.83
25 December 1987	0.89	0.77

* Divided by the efficiency of NaCl particles.

out for the large size range, relatively high efficiencies of large particles are consistent with the results that more than 80% of the large particles were hygroscopic.

During summertime (June–July), the efficiencies when the wind was southerly showed relatively low values at supersaturations smaller than 0.5%. This would be mainly due to the transport of particles with small ε, originating from anthropogenic sources in the Tokyo Metropolitan area and its surrounding suburbs. On the other hand, dependence of the efficiencies on wind direction was not detected in December. Wind speeds in December were usually less than 2 m s^{-1} and lower efficiencies than those in summer were measured, especially at supersaturations smaller than 0.5%. As found in Fig. 9a, the wintertime efficiencies for particles with radii between 0.05 and 0.09 μm were less than 0.5 by number at a supersaturation of 0.25%. This suggests a high frequency of appearance of particles with ε smaller than about 0.5 during winter. The presence of these particles in weak winds during December would also be closely related to the emission of particles from the combustion of straw and chaff at the farms on the Kanto Plain, including Tsukuba.

It is suggested on the basis of morphological examination that some of the water-insoluble inclusions in mixed particles are thought to be made up of carbonaceous material. Nucleation scavenging of these mixed particles would lead to the presence of carbon in cloud droplets. Since carbon in cloud droplets should contribute to an increase of the absorption of solar radiation in clouds (e.g., Heintzenberg, 1989), nucleation scavenging of carbon should be measured, together with the mixture state of carbon in individual particles by electron microscopy.

5. Conclusions

Measurements of the efficiency for nucleation scavenging of submicrometer aerosol particles with radii between 0.028 and 0.28 μm were carried out at Tsukuba, Japan, during the summer and winter of 1987 by using two thermal gradient diffusion chambers, one with and one without a water vapor source. The measurements were made at supersaturations of approximately 0.2–1%. Aerosol particles were sampled on several occasions during the measurement of nucleation scavenging by using a low-pressure impactor. Features of the efficiencies by number and volume were obtained. Nucleation scavenging efficiencies were studied with respect to the hygroscopic properties of individual aerosol particles.

(1) Mean efficiency by volume, obtained from the data during summer and winter, showed efficient scavenging of submicrometer aerosols of 0.028–0.28 μm radius being 0.75 at 0.25%, 0.81 at 0.50% and 0.93 at 1.04% supersaturation. The values in winter tended to be lower than those in summer with the difference being larger at supersaturations less than 0.5%.

(2) The measured efficiencies of nucleation scavenging for particles with radii between 0.05 and 0.09 μm were discussed with respect to the hygroscopic properties of the individual particles and were found to be in good agreement with the efficiency estimated from the hygroscopic properties at a supersaturation of 0.25%. It was also suggested that the low efficiencies at supersaturations less than 0.5%, which were usually found in winter, were mainly due to the presence of hygroscopic particles having a small volume fraction of water-soluble material. Moreover, efficient scavenging of particles having radii more than 0.05 μm was usually measured at 1.04% supersaturation and was consistent with the result that more than 80% of the particles were hygroscopic.

(3) Particles which did not form cloud droplets at a supersaturation of 1.04% were found to be water-insoluble particles which are similar in structural features to carbon particles and those

made up of a central soluble material surrounded by a semi-transparent insoluble material displaying some wrinkles. The latter particles were thought to be covered with an organic material which suppresses the condensation of water vapor. However, the proportion of these particles collected was quite small values of less than 0.03 by number for particles with radii of 0.028–0.13 μm.

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