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Hygroscopic growth of aerosol particles in the Po Valley

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ABSTRACT

A Tandem Differential Mobility Analyser (TDMA) was used to study the hygroscopic growth of individual ambient aerosol particles in the Po Valley, Italy. The measurements were made during the GCE fog experiment in November 1989. During fog, the interstitial aerosol (D_p(at ambient relative humidity) $< 5\ \mu$m) was sampled. Two modes of particles with different hygroscopic growth were found for $0.030\ \mu\text{m} < D_p(\text{dry}) < 0.20\ \mu$m. On average, the fraction of particles in the two modes were almost equal. The mean growth factor at 85% r.h. was 1.44 ± 0.14 for the more-hygroscopic mode and 1.1 ± 0.07 for the less-hygroscopic mode. The growth factors and the proportion of the particles that were less hygroscopic varied considerably from day to day, but no significant size dependence was seen. Comparison of growth factors for pure salt particles and the measured growth factors indicates that both hygroscopic modes contain a major insoluble part. The effect of the external mixing of hygroscopic properties on the activation of particles to fog droplets is discussed and the fraction of particles that were activated as a function of particle size is predicted. Comparison with the measured scavenging fraction as a function of particle size shows that the hygroscopic properties of the individual particle are as important as the particle size in determining if it will be activated in a fog.

1. Introduction

Most atmospheric aerosol particles grow by taking up water when the relative humidity increases. For a pure salt particle, very little happens until the partial pressure of the water vapour is equal to the partial pressure of the water vapour in the air around a droplet of a saturated salt solution. At this relative humidity, called the deliquescence point, the aerosol particle grows abruptly, and for increasing relative humidity the particle grows exponentially. However, the atmospheric aerosol particle rarely consists of one pure salt. In a mixture of salts the deliquescence point is lower than the lowest deliquescence point of the pure salts, and the growth curve is distorted with abrupt changes in the slope (Tang, 1976; Tang and Munkelwitz, 1986).

Winkler and Junge (1972) and Winkler (1973) have measured the aerosol mass as a function of relative humidity for bulk samples of atmospheric aerosol particles, pure salts and mixtures of salts. They found a higher growth for particles with diameters over 2 μm than for those in the range 0.2–2 μm. The growth curve of a continental aerosol is smooth and lower than for pure salts. The growth of the continental aerosol particles is lower due to insoluble material, hydrate water in dry particles and interaction between the ions in the complex mixture of soluble materials. Particles with diameter over 2 μm in a marine aerosol grow almost like sea salt. By using another integral parameter, the light scattering coefficient, to measure particle size, Charlson et al. (1978) obtained similar results.

Ahlberg et al. (1978) used two parallel impactors, one at ambient relative humidity and one at an increased relative humidity, to look at changes

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in mass mean aerodynamic diameter for different elements. They found that some elements, e.g., sulphur, have an increasing mass mean diameter with higher relative humidity, while others like vanadium do not show a changing size distribution with increasing relative humidity. These results gave evidence for a hygroscopically external mixture, i.e., an aerosol containing particles with strongly different hygroscopic properties. The technique with two parallel impactors at different relative humidities has also been used by Covert and Heintzenberg (1984) to measure the mixing of hygroscopic compounds and soot. They found a much smaller change in size distribution with relative humidity for soot than for hygroscopic materials like sulphur, implying that soot and the hygroscopic materials are present in different concentrations in different particles.

The studies discussed so far give clear evidence that the bulk of the atmospheric aerosol behaves hygroscopically. Some limited evidence was given that the aerosol could be externally mixed, even far from source areas. None of the techniques used so far could be used to calculate actual growth for single particles and thus reveal any inhomogeneities in the hygroscopic behaviour of the atmospheric aerosol.

A new technique was introduced by Liu et al. (1978), using Differential Mobility Analysers in a tandem arrangement, thus called Tandem DMA (TDMA), to facilitate measurements of the hygroscopic growth of individual particles in an aerosol. McMurry and Liu (1978) found that close to a freeway only nonhygroscopic particles appeared, except for short periods of time when one mode grew like H_2SO_4. In Tennessee haze, downwind of a steam plant, they found only particles which grew like a mixture of H_2SO_4 and $(NH_4)_2SO_4$. Other measurements of hygroscopic growth of ambient aerosol particles with the TDMA were made by Sekigawa (1983). He could not find any evidence of external mixing affecting the hygroscopic properties. However, an increase of the soluble fraction with particle size was observed for particles with diameters from 0.04 to 0.20 μm. McMurry and Stoltzenburg (1989) measured the hygroscopic growth of aerosol particles in Los Angeles. They observed an external mixing and an increase in growth with particle size. In the Grand Canyon, Zhang and McMurry (1991) observed a similar behaviour. Covert et al. (1991) report measurements from locations in northern Europe. In Hamburg two modes with different hygroscopic growth were observed. In Ny Ålesund, far from the source regions, the mode with low growth was rarely seen.

In conclusion, it is well-documented that the atmospheric aerosol particles have a clear hygroscopic behaviour, but what has been debated is the existence of hydrophobic particles, their lifetime, if they have any real influence on any atmospheric process, and how they are assimilated into the internally mixed hygroscopic aerosol. It is just in the most recent years that new techniques have made it possible to present strong new evidence of an external mixing concerning the hygroscopic properties of the atmospheric aerosol.

In addition to particle size, the amount of soluble material and the chemistry of the soluble fraction are, according to the theory, important in determining if the particle at a certain supersaturation will activate to a cloud droplet. In the case of an aerosol with external mixing, we can expect that different amounts of the various particles will act as cloud condensation nuclei (CCN). This implies that different chemical compounds have different lifetimes in the atmosphere and different deposition areas. Thus it is possible that different types of emission processes yield different deposition patterns. If cloud and fog droplets are formed on one specific type of particle, we can assume that an external mixing of the atmospheric aerosol will affect the heterogeneous chemical processes believed to act in the droplets.

The scattering and absorption of radiation in clouds willalso be affected by an external mixing, since they depend on the distribution of the insoluble material in the drops and that material's refractive index. It has been shown that the degree of external mixing and the distribution of elemental carbon in the cloud droplets are important for absorption of radiation (Heintzenberg, 1989). Another effect of external mixing that might be of climatic importance is its influence on the availability of cloud condensation nuclei (CCN). Anthropogenic sources increase the number of particles and, thus, probably the CCN. But with an external mixing that consistently prevents some part of the aerosol from becoming CCN, the total effect might be diminished.

Neither chemical data nor the hygroscopic properties of bulk samples will yield an evaluation

of an externally mixed aerosol. Studies of individual aerosol particles are necessary. One approach is to obtain chemical or elemental analysis of single particles that have been deposited. The method we have chosen is direct in-situ measurements of the size change, due to changing relative humidity, using highly accurate size fractionating aerosol instruments.

The aim of this work, which was done in the framework of the EUROTRAC project ground-based cloud experiments (GCE), was to study the uptake of water in individual aerosol particles at relative humidities below 100% before and during fog episodes. This information is important in understanding how the size distribution of aerosol particles is affected by the changing relative humidity immediately before the aerosol enters the fog. It is also needed to facilitate theoretical considerations concerning the microphysics of the fog and to complement the chemical measurements performed by other GCE groups on the actual fog. Another major objective of this study was to find evidence for the importance of hygroscopic properties of aerosol particles on the formation of fog droplets. This paper describes the hygroscopic properties of the atmospheric aerosol before fog formation and the interstitial aerosol during the fog episodes. We also extend our results theoretically into a prognosis about when particles will activate to droplets.

The measurements reported here were made during the field campaign in San Pietro Capofiume in the Po Valley in Italy during November 1989. The site and the main objectives and measurements are described by Fuzzi et al. (1992).

2. Experimental

2.1. Aerosol sampling

During fog episodes, we wanted to separate non-activated interstitial aerosol particles from the activated fog droplets. As it is not currently possible to distinguish activated from non-activated particles, a separation based on particle size at ambient relative humidity was used. A minimum in the aerosol particle droplet mass distribution is found at 5 μm (Fuzzi et al., 1992). The aerosol particles with a diameter below 5 μm at ambient relative humidity were considered to belong to the interstitial aerosol. This limit was imposed by a slit impactor inlet, which had an upper particle size cut-off of 5 μm at ambient conditions. The inlet was ca. 6 m above the ground. The same inlet was used for measurements of interstitial particle concentrations and size distributions (Noone et al., 1992), for filter sampling (Hallberg et al., 1992) and for selective sampling of less-hygroscopic particles (Martinsson et al., 1992).

The relative humidity of the aerosol decreased to a maximum of 45% during transport from the inlet to the instrumentation, due to a temperature increase of 10–20°C. The final decrease in relative humidity for our experimental set-up was inside the first differential mobility analyser (DMA), where the aerosol was exposed to clean, dry air.

2.2. Instrumentation

The instrument used to study the hygroscopic growth of the aerosol particles is a Tandem Differential Mobility Analyser (TDMA). Fig. 1 shows the main aerosol, air and data flows through the TDMA. A short description of the instrumentation is as follows: Entering the instrument, the aerosol particles were given a well known charge in a bipolar charger. From this charged aerosol, a narrow size fraction was selected by a Differential Mobility Analyser (TSI 3071), named DMA1. When entering the DMA1 the aerosol met the dry sheath air, which dried the particles prior to their passage through the DMA. The triangular-shaped size distribution of the particles leaving the DMA had a total width of 20% of the mean size, which was determined with an precision better than 1%. This monodisperse aerosol entered a humidifier in which the relative humidity was controlled. A second DMA (TSI 3071 with the charger removed) in combination with a Condensation Nuclei Counter (TSI 3760) was used to determine the particle diameter after the humidification. The relative humidity of the sheath air in the second DMA was controlled in conjunction with the relative humidity in the aerosol flow. The first DMA was kept at one size while the second was scanned to determine the size distribution after the humidifier.

In the monodisperse aerosol from the first DMA some doubly charged particles with a larger size are present. Doubly charged particles can influence the measurements if hygroscopic growth varies

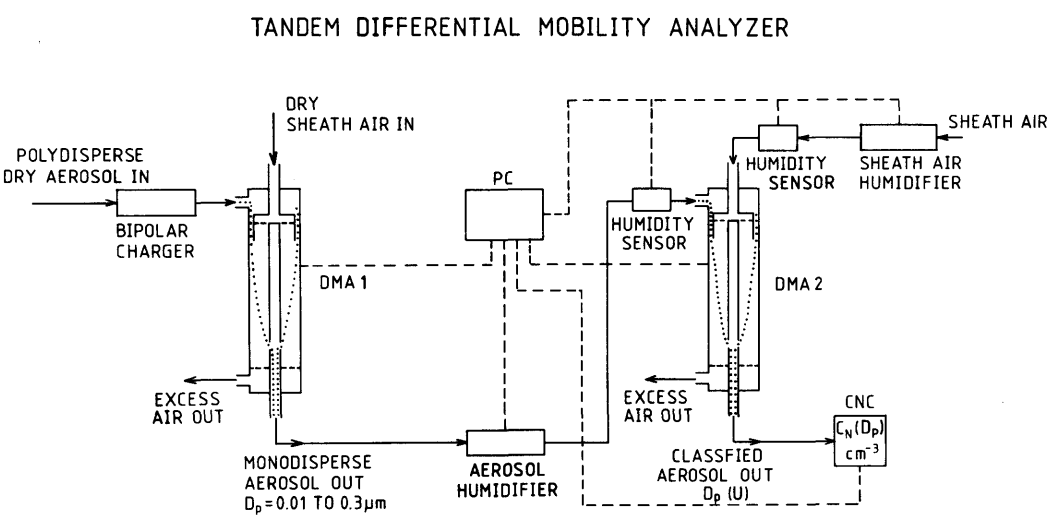

Fig. 1. Block diagram of the TDMA setup used in the Po Valley fog experiment. Air flows through the system (full line) and communication with the personal computer (dashed line) are indicated.

with particle size. From the size distribution and the known charge distribution for different particle sizes, the relative amount of doubly charged particles can be calculated. We estimate that less than 10% of the analysed particles were doubly charged.

A PC with analog-to-digital and digital-to-analog converters and pulse-counting cards was used for humidity control, DMA voltage settings and data acquisition. The stability of the relative humidity was monitored. Tests with pure salts like $(NH_4)_2 SO_4$ and NaCl were made, and the deliquescence points and the growth curves were reproduced.

The change in particle diameter, i.e., the growth factor, when exposed to 85% r.h. compared to <30% r.h. was investigated for particles with diameters 0.030, 0.050, 0.10, 0.15 and 0.20 μm. At the time it was not possible to work with larger particles, due to technical limitations.

2.3. *Data evaluation*

The growth factor spectrum, i.e., the number of particles as a function of growth factor for a certain particle size (see Fig. 2), was evaluated with the program TDMAfit (Stolzenburg and McMurry, 1988), which applies a least squares fitting of the transfer function through two DMA's and assumes that the growth factor distribution can be described as two normal distributions. The mean growth factors, the standard deviation and the total number of particles in each distribution are free parameters that are fitted in the program. An example of data and fitting is presented in Fig. 2. Further in the text we will refer to the 2 normal distributions as 2 modes with different growth factors, growth factor 1 and 2 respectively. Growth factor 1 refers to the mode with the smallest growth factor, i.e., the less-hygroscopic mode, and growth

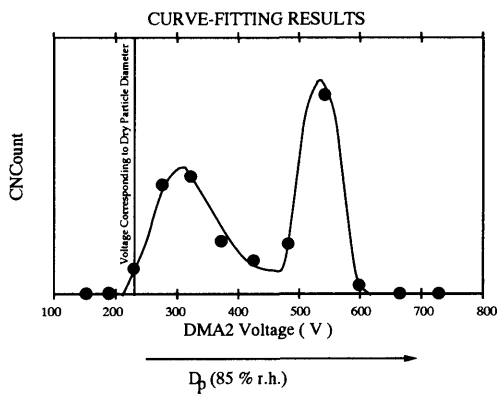

Fig. 2. An example of data (full circles) from a TDMA scan at 85% RH and a fitting (full line) made by the program TDMAFIT (Stolzenburg and McMurry, 1988).

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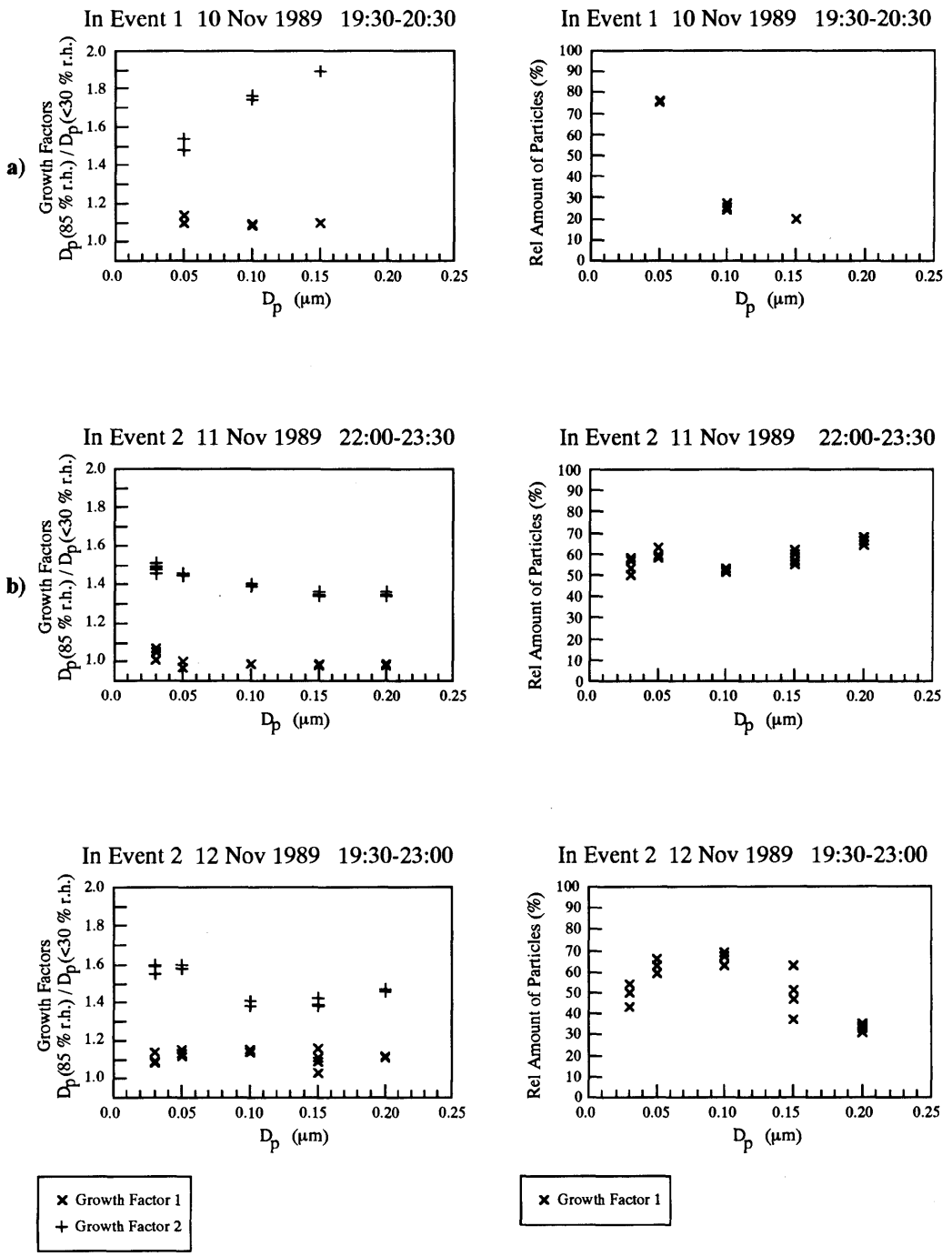
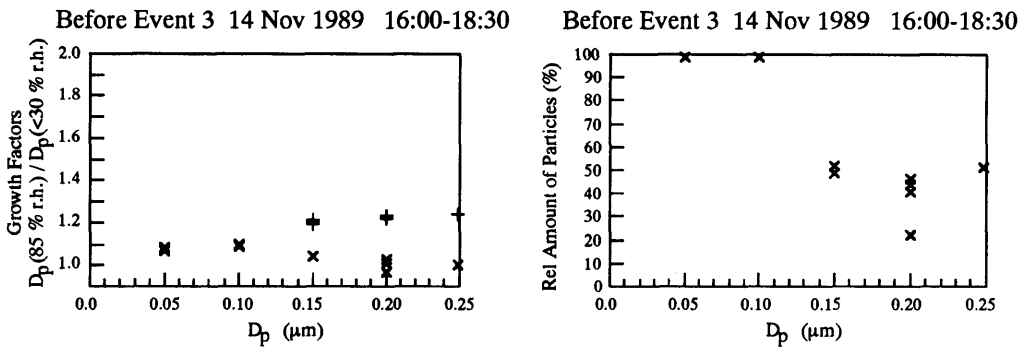
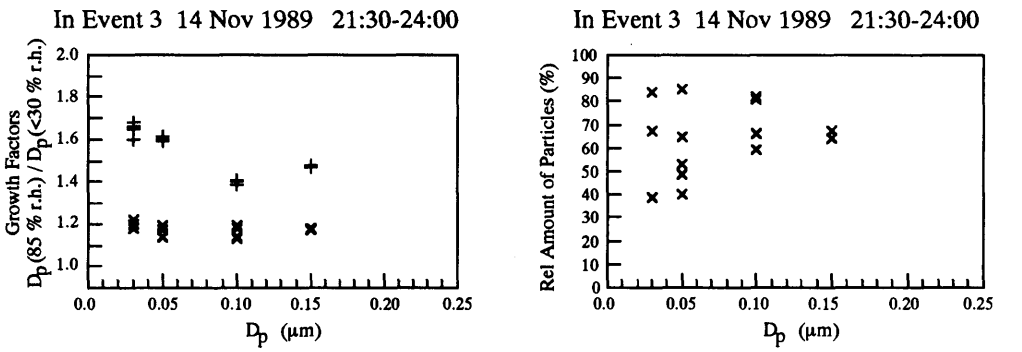


Fig. 3. Growth factors (left) and the relative amount of particles in the less-hygroscopic mode (right) as a function of particle size, for each fog event. (a) Event 1, (b) event 2, (c) event 3, (d) event 4.

c)





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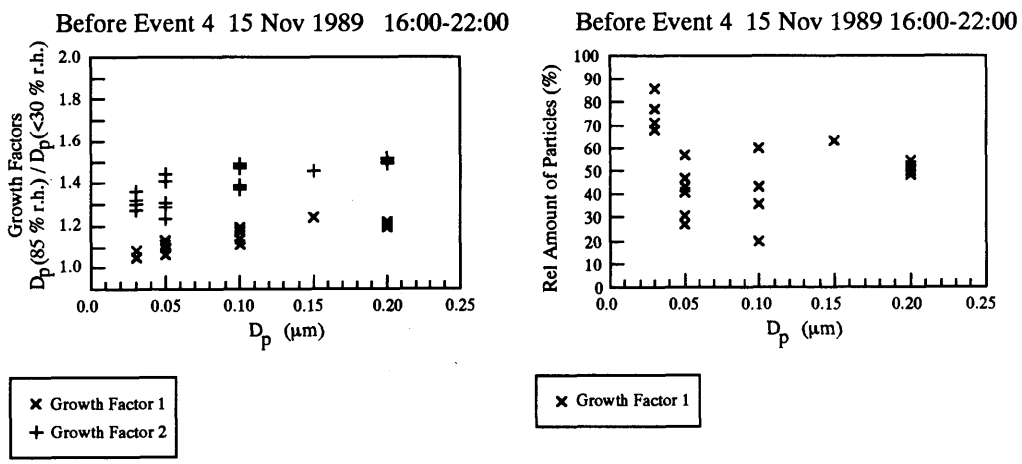

Fig. 3. (cont'd).

factor 2 to the one having the higher growth factor, i.e., the more-hygroscopic mode. TDMAfit also gives an estimate of the standard deviation of the distributions of the two modes, which will be discussed below. Since the assumption that the growth factor distribution can be described as two normal distributions does not have any direct support in theory, estimates of the fraction not fitting into the two normal distributions were made for each spectrum.

3. Results

3.1. Observed growth factors

The results will be presented in two parts. First, general results will be shown, and thereafter, the results from each of the fog events will be presented.

Almost always we can see two modes of particles with different growth factors. In 36 of the 120 spectra evaluated, 14 (± 6)% of the particles did not fit this bimodal pattern. (This is to be compared with less than 5% not fitting the bimodal pattern in the other 84 spectra.) In all spectra from the first 4 fog events, the mean growth factor of the more-hygroscopic mode was 1.44 with a standard deviation of 0.14 (see Table 1). The less-hygroscopic mode had a mean growth factor of 1.10 with a standard deviation of 0.07. The relative amount of particles in the two modes varied significantly from time to time with a mean for the less-hygroscopic mode of 57% $\pm$ 19%. Table 1 shows as well that no significant size dependence in the average growth factors was found. Even though on some occasions a clear size dependence was seen (e.g., event 1), on most of the occasions no clear dependence was seen. The average relative number of particles in the two modes did not show any significant particle size dependence either.

The measured growth factor, 1.10, for the less-hygroscopic particles means that they contained some soluble material. They were not totally insoluble. The more-hygroscopic particles must have had some insoluble material as well, because the important salts in the atmosphere grow more than a factor of 1.44 in diameter at 85% relative humidity. The expected growth factors for NH_4NO_3 and for $(NH_4)_2SO_4$ are about 1.8 and for NaCl it is even higher. So, we see two modes of particles with different hygroscopic properties, but not a total separation of hygroscopic and nonhygroscopic material.

By assuming that the particles consist of a core of insoluble material surrounded by a salt mixture of 50% NH_4NO_3 and 50% $(NH_4)_2SO_4$, the relative amount of soluble material can be calculated for the two different modes. The Kelvin and Raoults equations (see eq. (1)) give 7% and 43% for the less-hygroscopic and the more-hygroscopic modes respectively. The assumption of the composition of the salt mixture is based on measurements of the major ions in the aerosol during the field campaign (Hallberg et al., 1992).

Fog Event 1. In the beginning of fog event 1, see Fig. 3a, there are two well defined modes of particles. Growth factor 2 increases with diameter, and so does the relative amount of particles in this mode. 80% of the particles with a diameter of 0.15 μm belonged to the more-hygroscopic mode. The more-hygroscopic particles with dry diameters of 0.10–0.15 μm showed a growth factor

Table 1. *Mean values and standard deviations for the growth factors and the relative number of particles in the less-hygroscopic mode*

D_p (μm)	Growth factor of the less hygroscopic mode	Growth factor of the more hygroscopic mode	Relative number in the less-hygroscopic mode (%)	N
0.030	1.10 $\pm$ 0.06	1.49 $\pm$ 0.13	61 $\pm$ 14	14
0.050	1.10 $\pm$ 0.05	1.49 $\pm$ 0.12	63 $\pm$ 21	24
0.10	1.11 $\pm$ 0.06	1.46 $\pm$ 0.12	59 $\pm$ 24	25
0.15	1.07 $\pm$ 0.08	1.43 $\pm$ 0.15	53 $\pm$ 11	16
0.20	1.09 $\pm$ 0.09	1.44 $\pm$ 0.07	47 $\pm$ 13	17
average	1.10 $\pm$ 0.07	1.44 $\pm$ 0.14	57 $\pm$ 19	96

N is the total number of scans for each size. The table contains averages over fog events 1 to 4.

of ca. 1.8, which indicates that they are composed of almost 100% soluble material (calculated as in Subsection 3.2 with eq. (1) and 50% NH_4NO_3 and 50% $(NH_4)_2SO_4$). Thus the total concentration of soluble material increases strongly with size for diameters between 0.050 and 0.15 μm, and was over 80% for particles with a diameter of 0.15 μm.

Fog Event 2. Two modes of particles can be seen in the beginning of fog event 2, see Fig. 3b, but the standard deviations of both modes are relatively high. No difference between particle size can be seen in the growth factors, the relative amount of particles in each mode or in the standard deviation within each mode. The next TDMA measurements were made 1 day later but in the same fog event. For particles with diameters larger than 0.10 μm the main difference from the day before is a decrease in the relative amount of particles in the less-hygroscopic mode with a dry diameter of 0.20 μm. However, particles with diameters of 0.030 and 0.050 μm show a different pattern. The mean growth factors are just a little bit higher, but the standard deviation is very low compared with the day before.

Fog Event 3. Before fog event 3, see Fig. 3c, there is very little soluble material in the particles in the size range 0.050 to 0.25 μm. Particles with diameters of 0.050–0.10 μm show only one mode with the mean growth factor of 1.05. However, for particles between 0.15 and 0.25 μm there are two modes, but growth factor 2 is just 1.25. Making the same assumptions as above, this indicates a soluble fraction in the more-hygroscopic mode of only ca. 20%. In the fog just a few hours later, the picture is very different. In all sizes there is a narrow mode with a high growth factor. In the fog there is as well a strong variation in the distribution of particles between the two modes. This might be due to entrainment of a different aerosol. It can also be an effect of a variation of the total number concentration, as the number of particles in the 2 modes are not measured at exactly the same time.

Fog Event 4. Before fog event 4, see Fig. 3d, the difference between growth factor 1 and 2 is small. Both growth factors increase with diameter. Growth factor 2 is low (ca. 1.3) for small particles (0.030–0.050 μm) and growth factor 1 is high (ca. 1.2) for large particles (0.20 μm). We can see a short time variation, due to either entrainment of a different aerosol or an instrument effect as above.

Fog Event 5. Before fog event 5, see Fig. 4, the measurements were limited to particles with a diameter of 0.10 μm. We can see how the hygroscopic properties change. Growth factor 2 decreases with time as well as the relative amount of particles in the more-hygroscopic mode.

3.2. *Fog droplet formation*

One of the major objectives of our investigation, besides to accurately characterise the hygroscopic behaviour of the aerosol, is to use this information

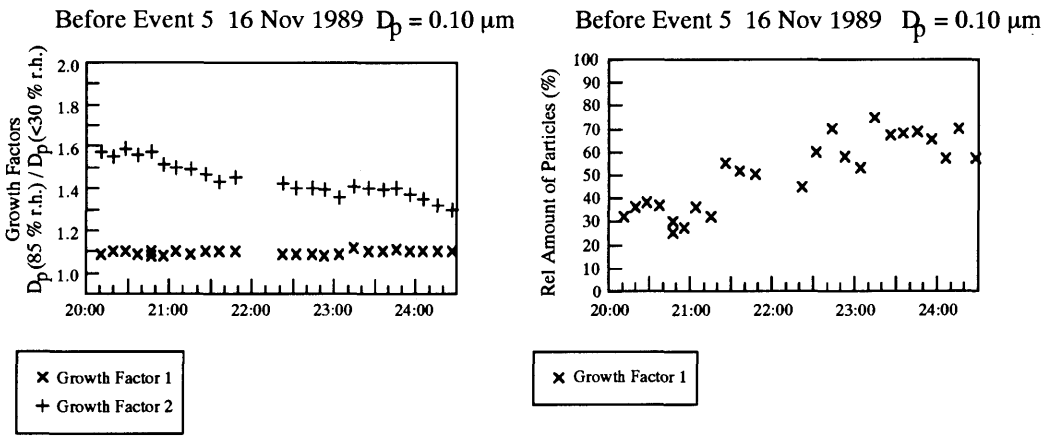

Fig. 4. A time series of the growth factors (left) and the relative amount of particles in the less-hygroscopic mode (right) for 0.10 μm particles before fog event 5.

to predict how the aerosol particles will act as condensation nuclei in fog droplet formation. The measurements of the droplet residue size distribution with the Counter-flow Virtual Impactor and of the interstitial dry size distribution (Noone et al., 1992) allow us to test the prediction.

We have used a simple model of the particles, which are assumed to be spheres and consist of insoluble cores surrounded by salt solutions. In the model we use a salt mixture with $(NH_4)_2SO_4$ and NH_4NO_3 in equal amounts, based on measurements of the major ions in bulk aerosol samples from the field campaign (Hallberg et al., 1992). The calculations then use the Kelvin effect and corrected Raoults law to express the equilibrium relative partial pressure for water vapour in an aerosol with mixed droplets (Fitzgerald, 1975):

$$p/p_0 = \exp(4\sigma M_W/(\rho_W RTd)) \times \left(1 + \frac{i\varepsilon\rho_d M_W d_d^3}{M_S(\rho'[d^3 - d_d^3(1-\varepsilon)] - \varepsilon\rho_d d_d^3)}\right)^{-1}, \quad (1)$$

where

T = absolute temperature
R = gas constant
d_d = dry diameter
i = number of ions/molecule
ρ' = density of the salt solution
M_S = molecule weight of the salt
σ = surface tension
d = droplet diameter
ε = soluble fraction
ρ_d = dry particle density
ρ_W = water density
M_W = molecule weight of water.

The choice of salt mixture affects the calculations in three ways: (1) The calculated soluble fraction is affected. (2) The calculated super saturation is also affected. (3) The calculated activated fraction as a function of dry particle size (Fig. 5) is not sensitive to changes in the composition of the salt mixture as long as the salt mixture is the same in both hygroscopic modes. If this assumption is wrong, the predicted activation efficiency is also somewhat affected. The results are affected by the number of ions per volume in the assumed salt.

To be able to calculate the fraction of particles in a given size range that are activated to become fog droplets, we must know the maximum supersaturation to which the aerosol has been exposed. This information is not available, because it is not possible to measure. It is only known to be low, i.e., probably $<0.1\%$. Using the model described above and extrapolating the soluble fractions calculated above to larger particle diameters, the supersaturation needed for a particle to activate can be calculated, if the dry particle diameter is

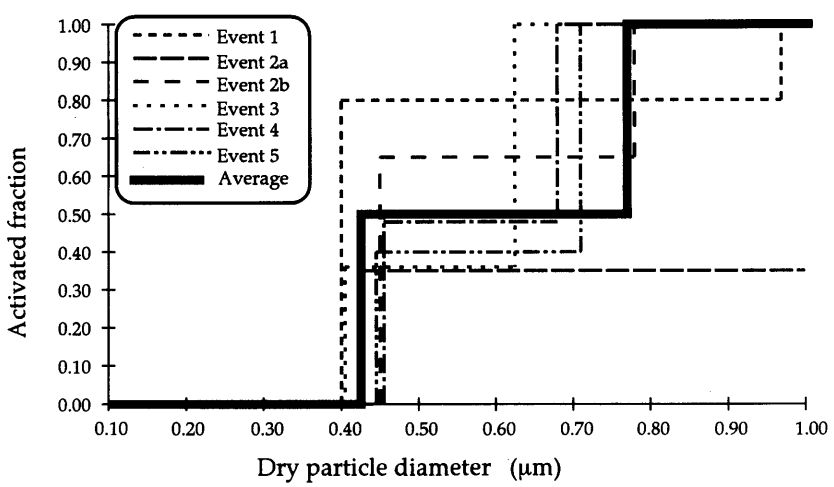

Fig. 5. Activated fraction of particles as a function of dry particle diameter, predicted from measured growth factors for the two hygroscopic modes, using the model described in Subsection 3.2.

known. The mean minimum dry diameter of activated particles in the investigated fogs was found by Noone et al. (1992) to be about 0.425 μm. Using this diameter for the more-hygroscopic particles, i.e., with growth factor of 1.44 and a soluble fraction of 43%, the supersaturation was calculated to be 0.03%. Using this supersaturation, we can calculate the minimum diameter for the less-hygroscopic particles that can activate. With a growth factor of 1.1 and a soluble fraction of 7%, we found this minimum activation diameter to be 0.775 μm.

The similarity in the calculated growth of the two types of droplets discussed above as a function of the relative humidity, i.e., the Köhler curves, is illustrated in Fig. 6. From Fig. 6 we can also see that these particles activated at a droplet size of about 5 μm. Particles with less soluble material were not activated and were smaller than 5 μm at this supersaturation, and those with more soluble material were activated and larger, if they had had enough time to grow. This means that the upper particle size cut-off of 5 μm of the interstitial inlet was a good choice.

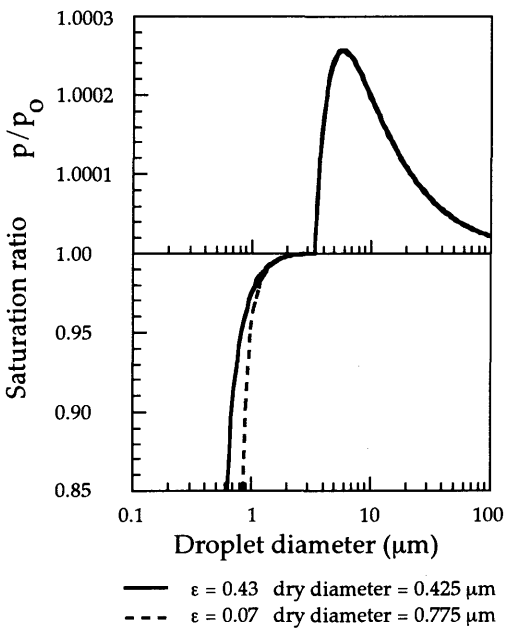

Fig. 6. The equilibrium saturation ratio of water vapour, as a function of the particle size. Calculations made with eq. (1). The soluble fraction assumed to be 50% $(NH_4)_2SO_4$ and 50% NH_4NO_3. Soluble fractions (ε) of 0.43 and 0.07 correspond to growth factors 1.44 and 1.1 respectively at 85% RH. The two curves overlap at saturation ratios over 1.

The fractionation between the two different hygroscopic modes is then, together with the above calculated data, used to predict how large a fraction of the total number of particles at a certain dry particle size, will activate to fog droplets (Fig. 5).

The calculations were repeated for the separate events. The minimum diameter of the activated particles, used to calculate the supersaturation needed to activate the more-hygroscopic particles, was the estimated mean minimum dry diameter of the activated particles (see Noone et al., Fig. 4, 1992). The particle diameters were 0.40 μm for fog events 1 and 3, and 0.45 μm for fog events 2, 4 and 5. The resulting supersaturation varies in the range 0.018 to 0.03%. The calculated supersaturations give the minimum activation particle diameter, ranging from 0.62 to 8 μm, for the less-hygroscopic particles in each event.

The calculated activated fraction as a function of particle diameter for the mean and for the separate events is illustrated in Fig. 5 and shows good agreement with simultaneous measurements of the droplet residual fraction performed by Noone et al. (1992) as presented in their Fig. 4, which is analogous to our Fig. 5.

4. Discussion

The general picture of atmospheric aerosols shows two modes of particles with different growth factors, which is in agreement with similar earlier measurements from such different areas as Los Angeles, the Grand Canyon, Hamburg and the Arctic (McMurry and Liu, 1978; McMurry et al., 1989; Covert et al., 1991). However, Sekigawa (1983) reports measurements from Japan, where no particles with a low growth factor were found. This can be in agreement with measurements by Covert et al. (1991) from Ny Ålesund, Svalbard, where a small fraction of less-hygroscopic particles appeared only when the air mass trajectory indicated recent transport of air from northern Europe.

The existence of 2 separate modes of particles

with different hygroscopic properties is difficult to explain. The known physical and chemical processes, e.g., nucleation, condensation, coagulation and heterogeneous reactions, in the atmosphere tend to force the development of the atmospheric aerosol into a more internal mixture, i.e., different particles have a similar chemical composition and thus hygroscopic behaviour. Specific source processes can produce particles with specific hygroscopic properties, e.g., combustion of fossil fuels gives considerable amounts of soot and organic components that are hydrophobic as found by McMurry and Liu (1978). Other processes, resulting in formation of different inorganic salt, e.g., nitrates and sulphates, give hygroscopic particles. So one reason for the observed two modes in the hygroscopic growth spectra can be mixing between particles from different sources or source processes. But it is still not evident why only 2 modes occur and several modes do not, or why a continuum is not found.

We have found a mean growth factor of 1.10 for the less-hygroscopic particles, indicating that they had some (ca. 7%) soluble material. Zhang and McMurry (1991) report a growth factor of 1.15 for the less-hygroscopic particles. Covert et al. (1991) report for Hamburg a growth factor of 1.06, and 1.10 for influxes of European long-range transported air to the Arctic site Ny Ålesund at Svalbard. In the earlier TDMA measurements the growth factor is just reported as low. The difference between a particle composed of only insoluble material and a particle with a few percent soluble material might not seem to be so important, but it is! It is the small soluble part that controls the uptake of water and determines the particle size at relative humidities close to 100% and, therefore, the potential for the particles to activate. The minimum dry diameter of a particle with no soluble material, that will activate at 0.03% supersaturation, is over 5 μm, while with 7% soluble material it is 0.73 μm.

The growth factor for the more-hygroscopic particles is an average of 1.44 in this study. This is in agreement with most earlier measurements. In Los Angeles McMurry and Stolzenburg (1989) found a mean growth factor of 1.49 ± 0.08 for 0.4 μm particles, but a significantly lower value of 1.12 ± 0.05 for 0.05 μm particles. On the other hand, Covert et al. (1991) report from Hamburg a growth factor of 1.38 ± 0.08, detecting no size dependence. In Ny Ålesund, a mean growth factor of 1.5 for the Arctic spring aerosol was found. In the Grand Canyon, Zhang et al. (1991) found growth factors that increased with size from 1.36 ± 0.02 to 1.51 ± 0.02 and 1.44 ± 0.04 for 0.05, 0.3 and 0.4 μm particles respectively. All these values are too low to be explained only by a mixture of the major ions, e.g., NH_4, SO_4, NO_3, Na and Cl. In the case of Ny Ålesund, we can not exclude the possibility of a pure H_2SO_4 aerosol, but in the other sites an insoluble component in the more-hygroscopic particles must be considered. The results of McMurry and Liu (1978) contrast somewhat with the above. Close to the freeway they mostly found only nonhygroscopic particles. Occasionally a mode of particles that grew like H_2SO_4, i.e., a growth factor of 1.5 at 85% r.h., also occurred. In the Tennessee haze, 20 miles downwind of a steam plant, they found only particles growing like a mixture of H_2SO_4 and $(NH_4)_2SO_4$, i.e., 1.64 at 85% r.h. Sekigawa (1983) also found only one mode, but its soluble fraction varied in the range of 20%–100% and had a tendency to increase as particle diameter increased from 0.04 to 0.2 μm.

There is surprisingly good agreement between mean values from the different sites for both modes. The mean values of the growth factors for each mode do not vary more than $\pm 5\%$ for the Po Valley, Hamburg, Ny Ålesund and the Grand Canyon, while these sites vary quite significantly in natural source background and distance to anthropogenic sources and their influence. A prerequisite for both modes to occur seems to be an anthropogenic influence. The measurements concerning Tokyo and Los Angeles probably fit into the group as well. Unfortunately, appropriate information is lacking in the articles.

The particles in the more-hygroscopic mode can consist of three different types of particles: (1) pure mixtures of inorganic salts, (2) a mixture of salt together with minor compounds, e.g., surfactants, that strongly affect the hygroscopic growth, and (3) a mixture of salts together with major inactive and insoluble components. The previous discussion shows that particle type 1 is probably not so common, except at specific sources. The regularity in the growth factor spectra also makes particle type 2 not so probable. Thus, we come to the conclusion that particle type 3 is the most probable, even though a rather large variation is seen in

the relative amount of insoluble material. Bulk analyses of the major ions can probably provide a good model for the soluble part of these particles, as most of the soluble material is in the most hygroscopic particles, but the composition of the insoluble part is unknown.

For the less-hygroscopic particles our knowledge is even more limited. The small soluble part of these particles is only a minor part of the bulk sample. We do not know if these particles contain any NH_4, SO_4, NO_3, Na or Cl. The soluble material might even be organic. The chemical composition of the insoluble part is unknown, but it probably contains substances like soot and organics. But soot can be only a minor fraction of the insoluble material because soot is just a few percent of the total mass (Hallberg et al., 1992).

We have used a model which assumes that the soluble material is 50% $(NH_4)_2 SO_4$ and 50% NH_4NO_3. With this model we predict the shape of the activated fraction as a function of particle diameter (Fig. 5). We use the minimum diameter for the activated more-hygroscopic particles to fix the particle diameter scale and estimate the maximum supersaturation. Our calculations are simplified by using only the measured mean values. When comparing with the measurements of the droplet residual fraction (number of residual droplets/total number of particles) as a function of particle diameter (Fig. 4, Noone et al., 1992), it must be remembered that we are comparing mean values of different time periods, even though they are related to the same fog periods. Still, the agreement is good. Clear deviations are found only in fog event 1 where the plateau between 0.5 and 0.7 μm is measured to be about 60% activated, while our prediction shows 80%. This difference can be explained by entrainment of aerosol from above the fog, since fog event 1 had its top only 8–10 m above ground, i.e., only 2–4 m above the interstitial inlet. In fog event 2, the aerosol changed significantly from the first day to the second, and thus, the predicted shape of the activated fraction curve is different for events 2a and 2b. The prediction for 2b is in good agreement with the measurements. 2a is in the beginning of fog event 2 while 2b is after 24 h of fog.

Another explanation of the plateau in the size dependence of the activated fraction is entrainment of aerosol that has been exposed to a lower maximum supersaturation. Sampling this mixture of aerosols with different history gives a curve with a shape similar to the curve obtained from the measurements (Noone et al., 1992). However, it is difficult to understand how the entrainment could be so similar for all the fog events studied.

Although other explanations for the observed scavenged fractions are possible, the good agreement between the model and the measurements is a strong indication that the hygroscopic properties of the individual particles are very important in estimating the scavenging efficiency. Thus, the particle size, the fraction of soluble material in the particle and the composition of this material seem to be the only clearly observable parameters that govern the particle's potential to form a fog droplet.

The existence of 2 hygroscopic modes implies that the activation efficiency, and thus the scavenging efficiency, is different for differential chemical compounds. Such differences in scavenging efficiency for sulphur and soot have been observed by Hallberg et al. (1992) during the field campaign. Considering the total particle size distribution (Noone et al., 1992) and assuming that both modes have the same particle size distribution, a rough calculation shows that about half the mass of the more-hygroscopic particles was activated, while less than 10% of the mass of the less-hygroscopic particles was.

5. Conclusions

The atmospheric aerosols before fog and in the interstitial air were found to consist of 2 modes of particles differentiated by their hygroscopic properties: at 85% r.h., the mode with less-hygroscopic particles has a growth factor of 1.10 and the more-hygroscopic mode has a growth factor of 1.44. In the Po Valley aerosol the modes contain about the same number of particles. Comparison with other studies gives support for the hypothesis that the occurrence of these two hygroscopic modes is a general behaviour of an atmospheric aerosol influenced by anthropogenic sources.

The chemical composition of the less-hygroscopic particles is unknown, but they probably contain substances like soot and organics. The chemical composition of the more-hygroscopic mode is better known. This mode

contains most of the soluble material, e.g., the major ions. However, it also contains hygroscopically inactive and insoluble material which may account for up to 50% of the volume. The composition of this insoluble fraction is not known, but it most likely consists of organic compounds.

With simple model calculations, assuming particles with an insoluble core covered with a salt solution of 50% NH_4NO_3 and 50% $(NH_4)_2SO_4$, it is found that the hygroscopic growth of the individual particles gives a good prediction of how the fraction of activated particles is related to dry particle size.

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