

**Hygroscopic
properties of Asian
aerosols**

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Hygroscopic growth of sub-micrometer and one-micrometer aerosol particles measured during ACE-Asia

A. Massling¹, S. Leinert², A. Wiedensohler¹, and D. Covert³

¹Leibniz-Institute for Tropospheric Research, Permoserstr. 15, 04318 Leipzig, Germany

²Environmental Protection Agency, Richview, Clonskeagh Road, Dublin 14, Ireland

³Department of Atmospheric Sciences, University of Washington, Box 354235, Seattle, WA 98195-4235, USA

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Correspondence to: A. Massling (massling@tropos.de)

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Abstract

Hygroscopic properties of aerosol particles in the sub-micrometer and one-micrometer size range were measured during the ACE-Asia study (Aerosol Characterization Experiment-Asia) in spring 2001. The measurements took place off the coasts of Japan, Korea, and China. All instruments contributing to this study were deployed in a container on the forward deck of the NOAA Research Vessel Ronald H. Brown.

Air masses with primarily marine influence and air masses from the Asian continent affected by both anthropogenic sources and by the transport of desert dust aerosol were encountered during the cruise.

Two different systems were used to determine hygroscopic growth of the ambient marine boundary layer aerosol at 90% relative humidity (RH). An H-TDMA-system (Hygroscopicity-Tandem Differential Mobility Analyzer) (Massling et al., 2003) and a newly developed H-DMA-APS-system (Hygroscopicity-Differential Mobility Analyzer-Aerodynamic Particle Sizer) (Leinert and Wiedensohler, 2006¹) were applied to analyze sub-micrometer and one-micrometer aerosol particles, respectively.

Results showed very different hygroscopic behavior in the sub-micrometer size range compared to the one-micrometer size range. In general, for all continentally influenced air masses, the one-micrometer particle population was characterized by two different particle fractions – a nearly hydrophobic fraction with growth factors around 1.0 representative of dust particles and a sea salt fraction with hygroscopic growth factors around 2.0. The number fraction of dust particles was generally about 60% independent of long-range air mass origin.

For sub-micrometer particles, a dominant, more hygroscopic particle fraction with growth factors between 1.5 and 1.9 (depending on dry particle size) indicating ammonium sulfate as major component was always found. In marine air masses and for larger sizes within the sub-micrometer range ($D_p=250$ and 350 nm), a sea salt fraction

¹Leinert, S. and Wiedensohler, A.: Hygroscopicity of aerosol particles around one micrometer – a new measurement technique, J. Aero. Sci., in review, 2006.

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with growth factors between 2.0 and 2.1 was also observed. For all other air masses, the more hygroscopic particle fraction in the sub-micrometer size range was mostly accompanied by a less hygroscopic particle fraction with growth factors between 1.20 and 1.55 depending on both the continental sources and the dry particle size. Number fractions of this particle group varied between 4 and 39% depending on dry particle size and air mass type. Nearly hydrophobic particles indicating dust particles in the sub-micrometer size regime were only found for particles with $D_p=250$ and 350 nm during a time period when the aerosol was significantly influenced by transport from Asian desert regions.

1 Introduction

Aerosol particles play an important role in the atmosphere, because they influence the radiative budget of the earth directly by scattering and absorbing the incoming sunlight and indirectly by serving as cloud condensation nuclei for the formation of fog and cloud droplets (Twomey, 1977). One of the important chemical aerosol properties that controls the magnitude of this effect is their hygroscopicity. Depending on the chemical composition, aerosol particles can take up large amounts of water compared to their dry state as relative humidity increases to 100% and thus radically increase their size and change their optical properties (Ogren and Charlson, 1992).

The hygroscopic behavior of aerosol particles also influences cloud formation processes and the resulting droplet size distribution and thus the cloud albedo. A change in the cloud albedo due to large-scale anthropogenic activities in Asia may significantly affect the regional climate.

Realistic hygroscopic growth data are needed to simulate microphysical aerosol properties such as number-size distributions and scattering and absorption coefficients at ambient conditions in meso-scale and global radiation transfer models.

In Asia and especially in China, high number and mass concentrations of aerosol particles together with water uptake at high RHs lead to reduced visibilities. Several

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studies in the past have shown, that a decrease of visibility is correlated with an increase of aerosol number concentration or aerosol mass (Noll et al., 1968; Charlson, 1969). One of the original reasons to study hygroscopic properties of aerosol particles was the dependence of visibility on the relative humidity (Kasten, 1968). It has been shown that the visibility continuously decreases with increasing relative humidity (Tsay et al., 1991; Horvath, 1995).

In addition to effects of aerosol particles on global climate and visibility, particles have been implicated as being detrimental to human health (Peters et al., 1997a, b; Cooney, 1998; Pope and Dockery, 1999). Investigations have shown that the hygroscopic properties of aerosol particles play an important role in this context (Ferron et al., 1998).

Hygroscopic properties of aerosol particles were investigated in marine environments in several field studies in the last ten years (e.g., Berg et al., 1998; Swietlicki et al., 2000; Massling et al., 2003). However, there have been no intensive investigations on this issue characterizing marine air masses which were affected by Asian dust regions and mega-cities in Japan, Korea, or China. In general, the knowledge of emissions in the Eastern Asian regions is limited. In Southeastern Asia, in countries like Indonesia the industrialization is rapidly increasing and their contribution to environmental pollution is not well known.

In this investigation, the common Hygroscopicity-Tandem Differential Mobility Analyzer-technique (H-TDMA) was used to measure hygroscopic characteristics in the sub-micrometer size range. Particles with initial dry sizes of $D_p=50$ nm (hereafter called Aitken mode particles) and $D_p=150, 250, \text{ and } 350$ nm (hereafter called accumulation mode particles) were investigated.

The H-TDMA-technique is usually instrumentally limited to particles less than 400 nm in dry diameter. In addition, the new Hygroscopicity-Differential Mobility Analyzer-Aerodynamic Particle Sizer-technique (H-DMA-APS) was employed to measure hygroscopic properties of $1 \mu\text{m}$ particles (hereafter called coarse mode particles).

The hygroscopic properties of Aitken mode, accumulation mode, and coarse mode

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particles are compared and discussed. This dataset gives a new overview about hygroscopic characteristics of sub-micrometer and one-micrometer aerosol particles having their origin in a region which has not intensively investigated up to now and which develops as a main emitter of anthropogenic aerosol in the world.

2 Experimental

An H-TDMA-system (Hygroscopicity-Tandem Differential Mobility Analyzer) and an H-DMA-APS-system (Hygroscopicity-Differential Mobility Analyzer-Aerodynamic Particle Sizer) were operated on board the US NOAA Research Vessel Ronald H. Brown to measure the hygroscopic growth of sub-micrometer and one-micrometer aerosol particles. During the experiment, air masses containing aerosols from different geographical origins were advected across the ship's cruise track and thus different aerosol types were investigated. The Hygroscopicity-Tandem Differential Mobility Analyzer (H-TDMA) was used to measure the hygroscopic characteristics in the sub-micrometer size range for particles with initial dry sizes of $D_p=50$, 150, 250, and 35 nm in dry diameter at 90% RH.

The Hygroscopicity-Differential Mobility Analyzer-Aerodynamic Particle Sizer (H-DMA-APS) measured the hygroscopic growth of aerosol particles at 1 μm in dry diameter.

The combination of both systems yielded growth factors determined at 90% RH and information about the mixing state of aerosol particles between 50 nm and 1 μm in dry size.

2.1 Location and air masses

The cruise of the Ronald H. Brown started in 14 March, in Pearl Harbor, Hawaii, and finished in 20 April, in the harbor of Yokosuka, Japan. During this time period, the ship crossed the western part of the Northern Pacific and then sailed within the coastal

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waters of Japan, Korea, and China.

The study region is illustrated in Fig. 1. The cruise was divided into seven consecutive time periods representing air masses with different aerosol sources and types (Bates et al., 2004). The geographical origin of the different aerosol sources and air mass types, that will be discussed in this work encountered during the cruise, is summarized in Table 1. Five of the seven time periods were selected for analysis of hygroscopic properties. At the beginning of the cruise, marine air masses having no land contact for six days were measured over a period of eleven days. The following time periods were characterized by air mass types, which were continentally influenced according to the back-trajectory analysis. These air masses were imprinted in terms of their aerosol chemistry by passing Japan and Korea, or China and crossing megacities in these countries or by entraining dust material over different Asian dust regions and volcano pollution. A more detailed characterization of the observed air masses is discussed in Bates et al. (2004).

2.2 Instrumentation

Both systems, the H-TDMA-system and the H-DMA-APS-system employed during the ACE-Asia field study will be explained in detail in the following chapter.

2.2.1 H-TDMA-system

The H-TDMA-system (Hygroscopicity-Tandem Differential Mobility Analyzer) consists of two Differential Mobility Analyzers (DMA) in series and an aerosol humidifier in between (Liu et al., 1978). Figure 2a shows a schematic drawing of the H-TDMA-system. In principle, the H-TDMA can be described by the following three parts:

Before entering the first DMA, the aerosol is conducted through a nafion dryer. Here, the RH of the aerosol is decreased to a value $<25\%$. Then, the aerosol flow is passed through a bipolar charger. Inside the first DMA, the aerosol is instantly dried by the sheath air to a $RH < 5\%$. The nearly monodisperse aerosol flow containing particles of

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the selected diameter leaving the DMA is then divided into two equal fractions. One part is conducted to the first CPC measuring the particle number concentration at the selected particle size (I).

The second part of the flow is directed to the aerosol humidifier. Here, it is humidified to a RH>85% to guarantee, that all particles have exceeded the deliquescence point independent of their chemical composition. The particles then are conducted to the inlet of the second DMA. The sheath air of the second DMA is brought to a final RH of 90% in a separate, second humidifier (II).

Inside the second DMA, the monodisperse aerosol is then exposed to the RH of the sheath air. The equilibrium RH in the second DMA is then close to 90%, because the volume flow of the sheath air is ten times greater than the monodisperse aerosol flow. The particles take up water depending on their hygroscopicity or chemical composition. The equilibrium size distribution of the humidified aerosol particles is finally measured by the second DMA and a second CPC acting as a mobility size spectrometer (III).

Because the particle number size distribution measured by a DMA is not the true number size distribution, but is a convolution of the mobility size distribution with the DMA transfer function and Boltzman-Fuchs charge distribution, a data inversion algorithm was applied to the data presented in this work. This inversion algorithm was developed by Voutilainen et al. (2000).

The result of an H-TDMA-scan is a hygroscopic growth distribution. According to their hygroscopicity, the particles within a selected diameter interval are classified into groups showing different hygroscopic behavior. These groups appear at different growth factors in the hygroscopic growth distributions depending on their chemical composition. Thus, the results also provide quantitative values of the aerosol's internal, external mixing state in terms of hygroscopicity.

During ACE-Asia, hygroscopic growth distributions were measured for particles with initial dry sizes of $D_p=50, 150, 250, \text{ and } 350 \text{ nm}$ at 90% RH. Hygroscopic growth distributions defined by the same parameters ($D_p, \text{ RH}$) were averaged over the time periods given in Table 1 above. Log-normal distributions were fitted to the data to describe the

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different hygroscopic groups.

The derived parameters by use of the H-TDMA technique are the hygroscopic growth factors gf_i of mode i defined by the ratio of the wet to the dry particle diameter (Eq. 1)

$$gf_i = \frac{Dp_{i,wet}}{Dp_{dry}}, \quad (1)$$

5 and the number fractions nf_i defined by the ratio of the number concentration of particles in each hygroscopicity group N_i and the sum of all observed particles (Eq. 2)

$$nf_i = \frac{N_i}{\sum_{i=1}^n N_i}. \quad (2)$$

The uncertainty of the measurements mainly depends on the uncertainty in RH within the system and possible size shifts of the two DMAs. In this study, size shifts of the specific DMAs used were calibrated before the experiment and all data presented here were corrected for those shifts. The system's uncertainty in RH was determined by atomizing sodium chloride particles at regular intervals during the campaign, and comparing their hygroscopic growth with theory. The calibration revealed, that the system RH was stable within $\pm 3\%$ RH. For the data analysis in this work, only spectra taken with an accuracy of $\pm 2\%$ in RH were used. The relative uncertainty in hygroscopic growth for a hygroscopic sodium chloride particle taken at 90% $\pm 2\%$ RH is about $\pm 6\%$. Because most particle fractions of the presented data were less hygroscopic than pure sodium chloride particles, the relative uncertainty of the results is less than 6%.

2.2.2 H-DMA-APS-system

20 The Hygroscopicity-Differential Mobility Analyzer-Aerodynamic Particle Sizer (H-DMA-APS) is a new system for measurements of hygroscopic properties of aerosol particles around $1\mu\text{m}$ in dry diameter. The system is based on the comparison of diameters

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measured for particles in dry and humidified state by two Aerodynamic Particle Sizers (APS). A schematic of the system is shown in Fig. 2b.

First, particles of a given Stokes equivalent diameter interval are selected by means of a High Aerosol Flow-Differential Mobility Analyzer (HAF-DMA) at a dry state (I). The aerosol flow from the DMA is then split in two fractions. One half of the aerosol flow is directed to the first APS, which characterizes the aerodynamic equivalent diameter of the selected aerosol particles in their dry state at low RH (II).

The second half of the aerosol flow is humidified to a defined, higher *RH* and conditioned to a defined final RH (III).

The second APS measures the final size distribution of the selected aerosol at higher RH (IV). The sheath air of this APS is also humidified to the same RH as the conditioned aerosol flow. Humidification and conditioning are accomplished by use of nafion humidity exchangers. At the intermediate state, the particles can be humidified to about 90% RH or dried to about 10% RH before being conditioned to a selected relative humidity. This procedure allows measurement of hygroscopic growth on both branches of a possible hysteresis curve.

The main differences with regard to the H-TDMA-technique that allow measurement of hygroscopic growth information of particles around $1\ \mu\text{m}$ in dry diameter, are:

1. use of a custom built DMA for the selection of $1\ \mu\text{m}$ particles with an aerosol flow rate of 2 lpm, and a ratio of the aerosol to sheath air flow rate of 1:10,
2. use of two APS as detectors instead of a second DMA and CPC,
3. measurement of the dry and hydrated aerodynamic size distribution after the DMA.

The comparison of the particle diameters measured in dry and hydrated states with the two APS units yields the aerodynamic growth factor gf_{aero} .

During ACE-Asia, particles with an initial dry size of $Dp=1\ \mu\text{m}$ were selected in the DMA, and subsequently sized at 30% and at 90% RH using the second APS unit.

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The measurement RH was changed periodically, with individual measurements at a specific RH lasting for 15 min. The first APS unit, measuring the size distribution of the particles selected by the HAF-DMA in their dry state, showed sizing problems during this campaign. Therefore, in this study, the first APS was used for comparison only.

- 5 The growth factor was calculated by using the measurements from the second APS unit alone, by comparing the aerodynamic particle size measured at 90% RH to the one measured at 30% RH using the following Eq. (3):

$$gf_{\text{aero},i} = \frac{Dp_{\text{aero},i,\text{wet}}}{Dp_{\text{aero},\text{dry}}} \quad (3)$$

10 Because the particle concentrations in the coarse particle mode were very low, humidified size distributions for the same parameters (Dp , RH) were averaged for the time periods to yield one average distribution for the dry state and one for humidified state for each air mass type. The particles in the humidified size distribution appeared in groups according to their differing hygroscopic properties. The averaged size distributions were fitted with log-normal functions to determine the aerodynamic growth factors of different hygroscopic growth groups and their corresponding number fractions via Eq. (2).

15 The uncertainty in the RH measurement is given as $\pm 1\%$ RH in the range up to 90% RH, and $\pm 2\%$ for 90% and above from the manufacturer. The RH control feedback maintained the relative humidity, as measured with the RH sensor, to within $\pm 0.2\%$ RH of the set point relative humidity. In this study, as for the H-TDMA system the relative uncertainty for the aerodynamic growth factor was estimated to be smaller than 6% considering the hygroscopic growth of a pure sodium chloride particle measured at 90% $\pm 2\%$ RH.

20 For comparison with H-TDMA measurements, the aerodynamic growth factor was converted to a growth factor based on the Stokes diameter using Eq. (4):

$$gf_{\text{Stokes}} = gf_{\text{aero}} \times \text{sqrt} \left(\frac{\rho_{\text{dry}}}{\rho_{\text{wet}}} \right) \quad (4)$$

Here, the wet density ρ_{wet} is a function of the growth factor gf_{Stokes} . Therefore, this equation has to be solved iteratively. For this purpose, the dry density ρ_{dry} of dry particle needs to be known. The bulk density ρ was determined by Quinn et al. (2004) by gravimetric and chemical analysis for the defined time periods and the selected size range. Because of uncertainties calculations of the Stokes equivalent growth factor for nearly hydrophobic particles were sometimes less than 1.0. Calculated Stokes equivalent growth factors undershooting this value were set 1.

3 Results and discussion

In the following chapter, hygroscopic growth distributions, derived growth factors of particles of different hygroscopic behavior, and their corresponding number fractions will be presented and discussed as a function of dry particle size and air mass type. A range of hygroscopic behavior was observed for the particles encountered depending on their size and also within a size class depending on chemistry and external mixing. Particles exhibiting only small growth factors around 1.1 are called “nearly hydrophobic”. Particle groups with growth factors much smaller than ammonium sulfate (around 1.2 to 1.5) are classified as “less hygroscopic”. Particles with growth factors close to that of ammonium sulfate (around 1.6 to 1.8) are called “more hygroscopic”. A fourth group of particles showing growth factors around 2.0 are categorized as sea salt particles or particles composed of sulfuric acid depending on air mass type.

In Figs. 3a, b, hygroscopic growth factors and their number fractions for a clean, marine air mass (period 1) for particles with initial dry sizes of 50, 150, 250, and 350 nm are presented. Calculated boundary layer back-trajectories showed that the observed air mass had no land contact during the five previous days (Bates et al., 2004). For all particles in the sub-micrometer size range, a more hygroscopic particle group was found. Within our experimental uncertainties, growth factors corresponded to those of pure ammonium sulfate. The factors for specific diameters were 1.58 (50 nm), 1.82 (150 nm), 1.83 (250 nm), and 1.86 (350 nm) which correspond well to the results of

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Swietlicki et al. (2000) for clean marine aerosol in air masses over the Eastern North Atlantic where hygroscopic growth factors of 1.64 (50 nm), 1.77 (150 nm), and 1.80 (250 nm) were observed during the Second Aerosol Characterization Experiment. Particles with initial dry diameters of 250 and 350 nm divided into a more hygroscopic particle group and a sea salt particle group that showed growth factors higher than 2.0. The number fraction of the sea salt particles was less than 35% indicating, that most particles in this size range can be assigned as ammonium sulfate. For 1 μm particles, no data were available for the marine case.

Measurements for the air mass type which was strongly influenced by Korea and Japan (period 2) are presented in Figs. 4a, b. During this time period, the ship was located southeast of the Japanese island of Honshu. The back trajectory analysis for this air mass showed that the observed air masses passed first over Korea and then Japan before reaching the location of the ship. The figure shows growth factors and number fractions for particles with initial dry sizes of 50, 150, 250, 350 nm, and 1 μm . In general, a more hygroscopic particle group was observed for all sizes of measured sub-micrometer particles with growth factors similar to those measured during the clean marine period. However, for particles of 150, 250, and 350 nm, a less hygroscopic particle group was also apparent. For this group, growth factors were in the range between 1.4 and 1.5 and their number fractions varied between 15 and 30% depending on the initial dry particle size. The latter group is assumed to consist of combustion-related particles with sources over Korea and Japan. Their slightly hygroscopic behavior can be attributed to modifications by condensation from the gas phase or liquid phase processes during transport. These particles might be a mixture of elemental carbon and organic material coated by soluble substances.

For 1 μm particles, a nearly hydrophobic particle group occurred that can be attributed to dust particles from continental sources, which are known to be mainly hydrophobic. The number fraction of these particles was found to be approximately 64%. The remaining fraction of the second particle group showed a calculated Stokes diameter growth factor of 1.97. Based on this high value of hygroscopic growth, these

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particles are strongly suspected to be largely composed of sea salt material.

In Figs. 5a, b, hygroscopic growth factors and their number fractions are presented for an air mass, which was highly influenced by emission sources in Japan (Table 1: period 3). In general, hygroscopic behavior similar to that of the continentally air mass influenced by Korea and Japan (period 2) was found. In addition to the occurrence of a more hygroscopic particle group, a less hygroscopic particle group with growth factors smaller than those of ammonium sulfate appeared for all sub-micrometer sizes. Here it is noticeable, that growth factors of this particle group with values of 1.2 to 1.3 were slightly smaller than those of the corresponding group of the air mass influenced by Korea and Japan. This finding can be explained by different aging times and residence times of both air mass types over the continent. Based on air mass back trajectory analysis, the processing time for the air mass encountered during period 2 (Polluted Korea/Japan) was longer with 24 to 48 h than for air mass during period 3 with 6 to 12 h (Polluted Japan) after continental influence resulting in a slightly more hygroscopic particle group during period 2.

Also, for the $1\ \mu\text{m}$ particles two distinct groups of particles, one corresponding to sea salt aerosol and one nearly hydrophobic corresponding to dust aerosol was found.

In Figs. 6a, b, growth factors and number fractions are illustrated for the air mass having crossed the Miyakejima volcano and Japan (period 4). The situation looks very similar to the marine case. For sub-micrometer aerosols, a more hygroscopic particle group was found for all dry sizes. Growth factors were in the range between 1.59 and 1.73. Based on these values it can be assumed, that these particles were mainly composed of ammonium sulfate. Additionally, these particles are characterized by the appearance of a second particle group with growth factors slightly larger than the first one (1.77 to 1.96). Volcanoes are a significant emission source for SO_2 , which typically is oxidized in the atmosphere to sulfuric acid. High concentrations of sulfuric acid intensify the formation of particles composed of sulfate and also enable the mass transfer of sulfate on existing particles. These processes lead to a hygroscopic particle population mainly composed of sulfate and are a simple explanation for the appearance of

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this hygroscopic particle group. However, the existence of sea salt can not be excluded within these considerations, because the hygroscopic growth of sea salt and sulfuric acid particles is nearly the same.

The hygroscopic growth distribution of $1\ \mu\text{m}$ particles shows a split into two groups of different hygroscopic behavior. Again, a nearly hydrophobic group of aerosol particles is observed with a number fraction of 66%. The second group of more hygroscopic particles shows a calculated growth factor (Stokes diameter) of 1.75, which indicates ammonium sulfate as main compound. Also, the large fraction of sulfate can be explained by volcano emissions in this size range.

In Fig. 7a, examples of averaged hygroscopic growth distributions measured at 90% RH for sub-micrometer particles are presented for the air masses, which was again continentally influenced, period 5. When the ship was sampling in the Korean Strait, the air mass back trajectory analysis showed the air coming from Northern China and Mongolian dust regions before they passed over Shanghai to reach the ship location. The distributions split into different groups of hygroscopic behavior. Nearly hydrophobic particles here strongly linked to dust only occurred for larger sizes ($D_p=250$ and $350\ \text{nm}$). In comparison, the hygroscopic growth distribution of $1\ \mu\text{m}$ particles is presented for this air mass taken at dry conditions ($<5\% \text{RH}$), at $30\% \text{RH}$, and at $90\% \text{RH}$. The distribution taken at dry conditions only shows one major group of particles at about 1.2 to $1.3\ \mu\text{m}$ in aerodynamic diameter. A second mode at greater diameters can be assigned to doubly-charged particles leaving the DMA. The distribution taken at $30\% \text{RH}$ shows a small growth shift towards larger sizes. Data taken at $90\% \text{RH}$ show a split into two groups with different hygroscopic growth. One group shows no growth in comparison to 30% and the other one shows a significant growth towards larger diameters. The latter group can be assigned to sea salt particles, which are known to be very hygroscopic. The first group can be attributed to dust particles, which are known to be hydrophobic. This number fraction of the latter particles is greatly increased compared to those found in the sub-micrometer size range because dust particles have their maximum of emission at diameters $D_p \geq 1\ \mu\text{m}$.

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In Figs. 8a, b, growth factors and their number fractions are illustrated for the air mass discussed above. Here, the sub-micrometer aerosol always showed a dominant, more hygroscopic particle group with growth factors between 1.62 and 1.75. For 50 nm particles, this was the only observed group. Accumulation mode particles ($D_p=150$, 250, and 350 nm) were subdivided into a less hygroscopic particle group with growth factors slightly smaller than those of ammonium sulfate as was the case for other continentally air masses discussed before. The observed hygroscopic growth factors for these particles varied between 1.37 and 1.55 with number fractions between 30 and 40% and the particles can be assigned to anthropogenic aerosols, which were modified by condensation from the gas phase or liquid phase processes. Additionally, a small (less than 10%) number fraction of nearly hydrophobic particles occurred for the 250 and 350 nm particles. This group corresponds to the presence of dust particles that were mixed into the air mass when it passed over the Asian dust source regions. Dust particles are not expected to extend to the Aitken mode size range.

With regard to the $1\ \mu\text{m}$ particles, a sea salt group with a corresponding growth factor of 1.98 (Stokes diameter) and a number fraction of 36% was also observed. Nevertheless, a nearly hydrophobic particle group also occurred at this particle size.

4 Summary and conclusions

During ACE-Asia, an H-TDMA-system and an H-DMA-APS-system to measure hygroscopic properties of particles in the sub-micrometer and one-micrometer size ranges were deployed on the US Research Vessel Ronald H. Brown. The ship started its cruise from Hawaii (USA) to Japan and included legs to the Sea of Japan. During the route, seven distinct air mass types of different origin were observed, five of which were used in our analysis. At the beginning of the cruise, air masses of marine origin having no land contact for five days were encountered over a period of eleven days. This period was followed by air mass types with continental influence from Korea and Japan and air masses, which had crossed Asian desert dust regions in Northern China

and/or Mongolia.

In general, different hygroscopic behavior of atmospheric particles was observed for dry sizes ($D_p=50, 150, 250, 350$ nm, and $1 \mu\text{m}$) within one air mass type as well as between different air mass types. This result was obtained for measurements done at 90% RH. This set of results implies, that particles of different dry size had varying chemical composition with a high degree of external mixing within a given air mass type.

For all air mass types, a dominant, more hygroscopic particle fraction indicative of ammonium sulfate particles was found for sub-micrometer particles and a fraction indicative of sea salt particles was found for one-micrometer particles. Sea salt particles in the sub-micrometer size range were only identified for $D_p=250$ and 350 nm during the clean marine period.

Less hygroscopic sub-micrometer particles only occurred for those cases when air masses with continental influence were observed. They are assumed to have their origin in relatively recently emitted aerosol which was modified during transport from its source to the ship by condensation from the gas phase or liquid phase reactions or by cloud processing resulting in particles showing less growth than expected discussed above for pure ammonium sulfate particles. This hygroscopic growth group was not observed for $1 \mu\text{m}$ particles at all. For sub-micrometer aerosol, number fractions of the less hygroscopic group varied between 10 and 50% depending on dry particle size.

Additionally, sub-micrometer particles that had a nearly hydrophobic behavior, can likely be assigned to freshly emitted soot particles or dust particles and were only found during one time period when air masses were influenced by Shanghai anthropogenic sources and Asian desert dust regions for larger particle sizes $D_p=250$ and 350 nm. These particles can be assigned to dust particles that are known to be non-hygroscopic and that also were found in the one-micrometer size regime. But, $1 \mu\text{m}$ dust particles were observed in all of the continentally influenced air masses, some of which did not show a clear trajectory over the major Asian dust source regions. These observations imply that dust particles seem to be a major constituent of coarse mode particles in

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this region independent of the air mass imprint. Number fractions of this particle group were about 60% for 1 μm particles and all observed air mass types.

Acknowledgements. We are grateful for the support and cooperation of the NOAA PMEL group, who gave us the opportunity to participate in this field study. We also thank the participants of the cruise from the University of Washington and PMEL for the excellent and effective teamwork and brilliant scientific guidance during the cruise.

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Table 1. List of time periods with different air mass origin during ACE-Asia.

Time period	DOY	Air mass type
1	75–84	Marine
2	91–94	Polluted Korea/Japan
3	96.4–99.2	Polluted Japan
4	99.3–100.5	Volcano + Polluted
5	103.4–104.5	Dust + Shanghai

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Appendix A

The Appendix includes all values of growth factors and number fractions of different dry sizes and air mass types as individual values. The growth factors one through four are assigned to nearly hydrophobic, less hygroscopic, more hygroscopic, and sea salt particle groups.

Table A1. Growth factors and corresponding number fractions for particles of different size measured at 90% RH (marine air mass, period 1).

<i>D_p</i> [nm]	<i>gf_1</i>	<i>gf_2</i>	<i>gf_3</i>	<i>gf_4</i>	<i>nf_1</i>	<i>nf_2</i>	<i>nf_3</i>	<i>nf_4</i>
50	–	–	1.58	–	–	–	1	–
150	–	–	1.82	–	–	–	1	–
250	–	–	1.83	2.03	–	–	0.67	0.33
350	–	–	1.86	2.11	–	–	0.76	0.24

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Table A2. Growth factors and corresponding number fractions for particles of different size measured at 90% RH (pollution from Korea/Japan, period 2).

<i>D_p</i> [nm]	<i>gf</i> _1	<i>gf</i> _2	<i>gf</i> _3	<i>gf</i> _4	<i>nf</i> _1	<i>nf</i> _2	<i>nf</i> _3	<i>nf</i> _4
50	–	1.42	1.61	–	–	0.29	0.71	–
150	–	1.46	1.72	–	–	0.13	0.87	–
250	–	1.47	1.71	–	–	0.17	0.83	–
350	–	–	1.64	–	–	–	1	–

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Table A3. Growth factors and corresponding number fractions for particles of different size measured at 90% RH (pollution from Japan, period 3).

<i>D_p</i> [nm]	<i>gf</i> _1	<i>gf</i> _2	<i>gf</i> _3	<i>gf</i> _4	<i>nf</i> _1	<i>nf</i> _2	<i>nf</i> _3	<i>nf</i> _4
50	–	1.20	1.52	–	–	0.04	0.96	–
150	–	1.29	1.61	–	–	0.13	0.87	–
250	–	1.26	1.65	–	–	0.17	0.83	–
350	–	1.28	1.71	–	–	0.19	0.81	–

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Table A4. Growth factors and corresponding number fractions for particles of different size measured at 90% RH (volcano imprinting, period 4).

<i>D_p</i> [nm]	<i>gf</i> ₁	<i>gf</i> ₂	<i>gf</i> ₃	<i>gf</i> ₄	<i>nf</i> ₁	<i>nf</i> ₂	<i>nf</i> ₃	<i>nf</i> ₄
50	–	–	1.59	1.77	–	–	0.55	0.45
150	–	–	1.59	1.83	–	–	0.25	0.75
250	–	–	1.62	1.88	–	–	0.23	0.77
350	–	–	1.73	1.96	–	–	0.45	0.55

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Table A5. Growth factors and corresponding number fractions for particles of different size measured at 90% RH (pollution from Shanghai and dust, period 5).

<i>D_p</i> [nm]	<i>gf_1</i>	<i>gf_2</i>	<i>gf_3</i>	<i>gf_4</i>	<i>nf_1</i>	<i>nf_2</i>	<i>nf_3</i>	<i>nf_4</i>
50	–	–	1.62	–	–	–	1	–
150	–	1.55	1.73	–	–	0.29	0.71	–
250	1.12	1.49	1.75	–	0.06	0.38	0.56	–
350	1.10	1.37	1.75	–	0.10	0.39	0.51	–

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Table A6. Growth factors, corresponding number fractions, and densities for particles of different air mass origin measured at 90% RH.

Air mass	ρ	$gf_{\text{aero}-1}$	nf_{-1}	$gf_{\text{Stokes}-1}$	$gf_{\text{aero}-3}$	nf_{-3}	$gf_{\text{Stokes}-3}$	$gf_{\text{aero}-4}$	nf_{-4}	$gf_{\text{Stokes}-4}$
Polluted Korea/Japan (2)	1.63	1.00	0.58	(1.00)	–	–	–	1.61	0.42	1.98
Polluted Japan (3)	1.91	0.95	0.64	(1.00)	–	–	–	1.51	0.36	1.97
Volcano + Polluted (4)	1.72	0.87	0.66	(1.00)	1.42	0.34	1.75	–	–	–
Dust + Shanghai (5)	2.36	0.92	0.64	(1.00)	–	–	–	1.40	0.36	1.98

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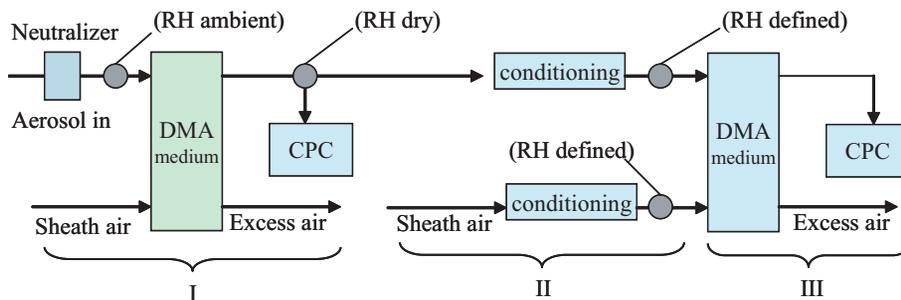


Fig. 2a. Schematic drawing of the H-TDMA-system.

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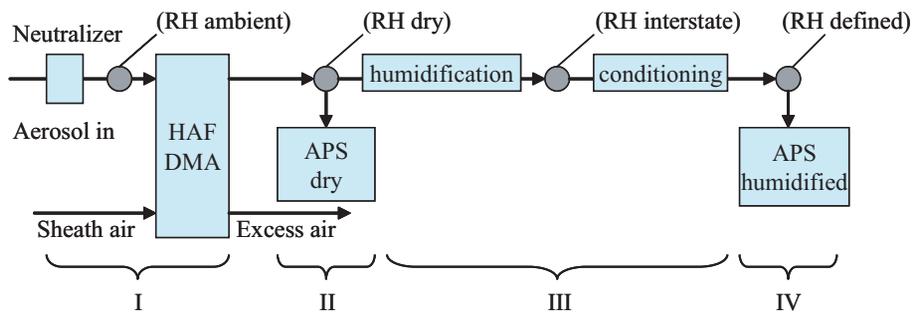


Fig. 2b. Schematic drawing of the H-DMA-APS-system.

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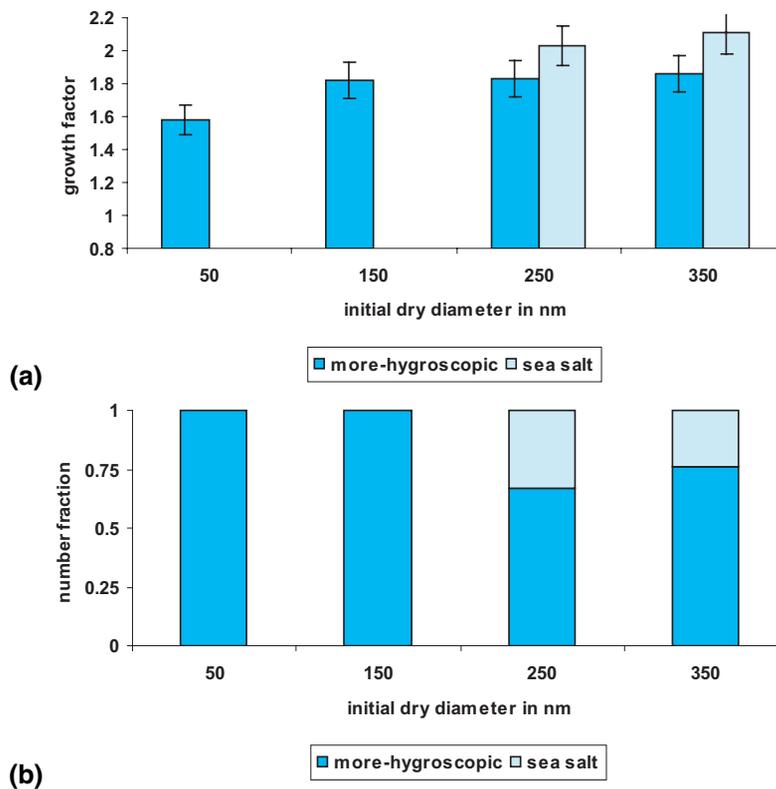


Fig. 3. (a) Hygroscopic growth factors and (b) number fractions for particles with initial dry sizes $D_p=50, 150, 250,$ and 350 nm measured at 90% RH for a clean marine air mass during period 1.

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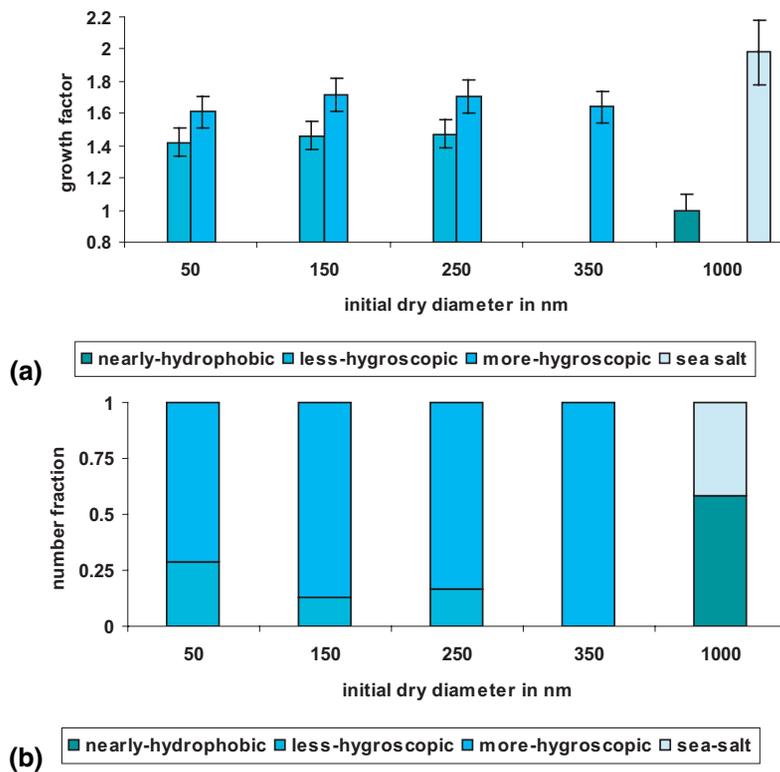


Fig. 4. (a) Hygroscopic growth factors and (b) number fractions for particles with initial dry sizes $D_p=50, 150, 250, 350$ nm and $1 \mu\text{m}$ measured at 90% RH for period 2 in an air mass with pollution sources from Korea/Japan .

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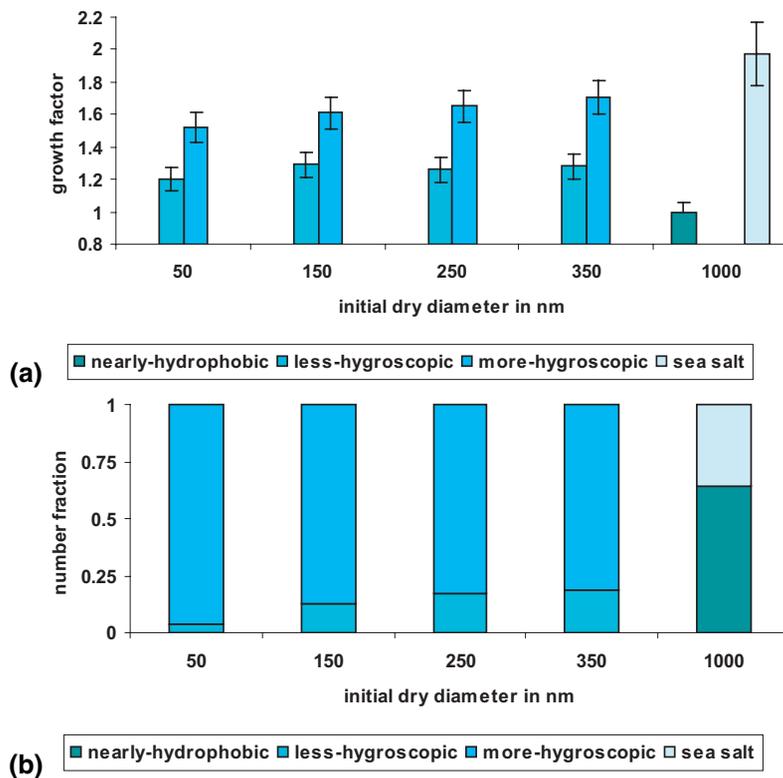


Fig. 5. (a) Hygroscopic growth factors and (b) number fractions for particles with initial dry sizes $D_p=50, 150, 250, 350$ nm and $1 \mu\text{m}$ measured at 90% RH for period 3 in an air mass with pollution sources from Japan.

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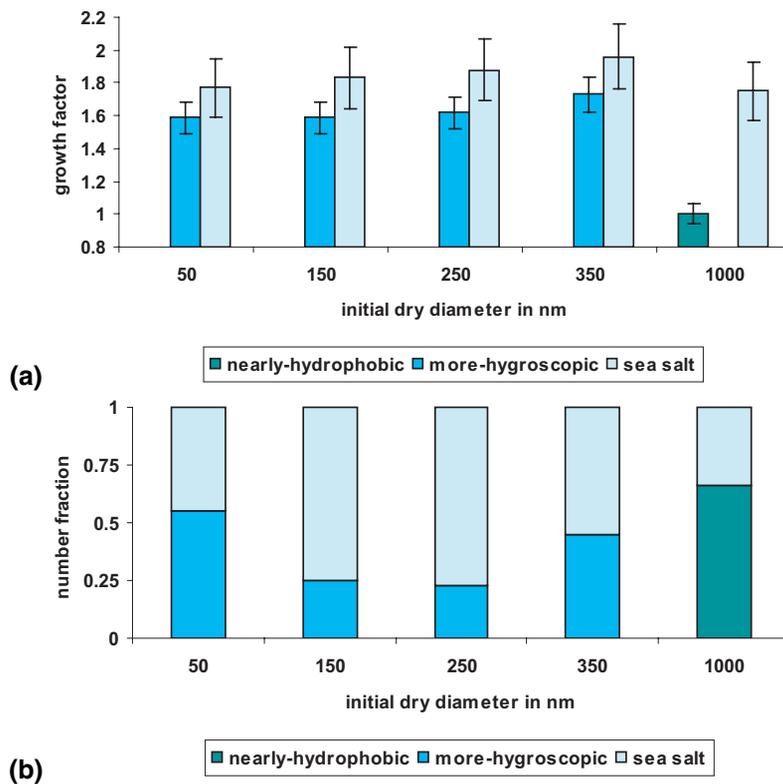


Fig. 6. (a) Hygroscopic growth factors and (b) number fractions for particles with initial dry sizes $D_p=50$, 50, 250, and 350 nm and $1\ \mu\text{m}$ measured at 90% RH for an air mass that advected across Miyakejima volcano and Japan to the ship during period 4.

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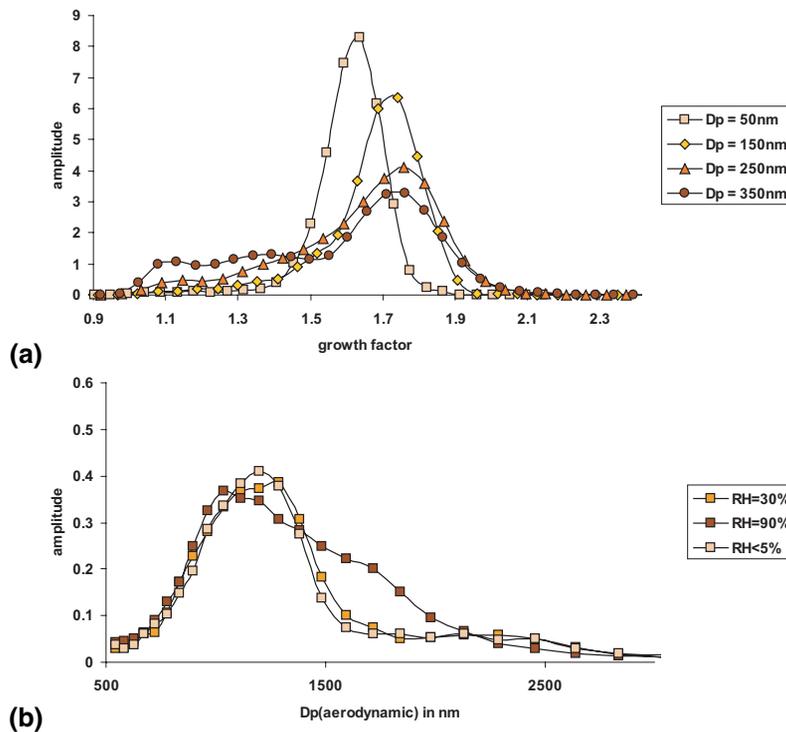


Fig. 7. Hygroscopic growth distributions for particles with an initial dry size of **(a)** $D_p=50, 150, 250, 350$ nm measured at 90% RH and **(b)** $D_p=1$ m measured at 90, 30, and <5% RH for an air mass influenced by sources from Asian dust regions and Shanghai during period 5.

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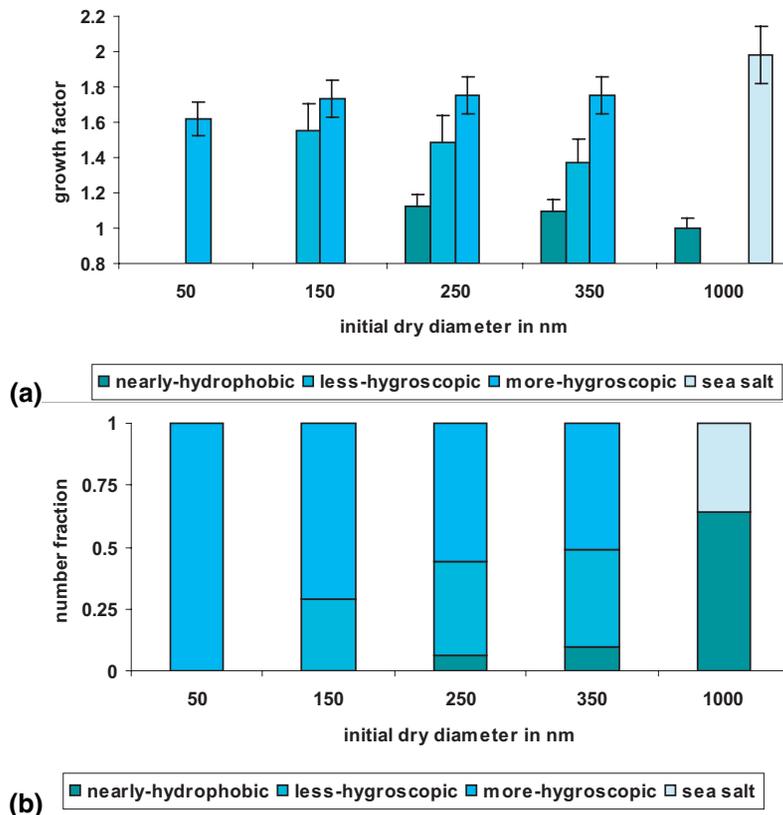


Fig. 8. (a) Hygroscopic growth factors and (b) number fractions for particles with initial dry sizes $D_p=50, 150, 250, 350$ nm and $1 \mu\text{m}$ measured at 90% RH for an air mass influenced by sources from Asian dust regions and Shanghai during period 5..

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