

## ***Interactive comment on “Hygroscopic growth of sub-micrometer and one-micrometer aerosol particles measured during ACE-Asia” by A. Massling et al.***

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General comments:

The paper by Massling *et al.* presents a study of particle hygroscopic growth factors observed during a ship cruise in the western part of the Northern Pacific and the coastal waters of Japan, Korea and China. The measurements include submicron and 1  $\mu\text{m}$ -particles using the H-TDMA and the recently developed H-DMA-APS techniques, respectively. This paper focusses on reporting the growth factors for different air masses which, by covering this wide size range, nicely illustrates how the

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particle composition and therefore the hygroscopic properties are often very different between the Aitken, accumulation and coarse mode particles. Observed properties are only linked to one single other study. I could imagine that there is potential to expand the discussion of the results a little in the context of previous studies.

Below I provide a number of specific comments particularly dealing with the fact the authors appear to draw conclusions on the particle's composition solely based on the observed growth factors. The corresponding statements need supporting information from chemical analysis or measurements of other physical properties, otherwise they remain speculative.

Specific comments:

Abstract, line 24, "with growth factors between 1.5 and 1.9 (...) indicating ammonium sulfate as major component ...": The theoretical growth factor at 90% RH of ammonium sulfate is 1.74 or less. Therefore growth factors of  $>1.74$  indicate that either the sulphate is not fully neutralised by ammonia or the presence of e.g. sodium chloride or sodium sulphate. Furthermore a growth factor of  $\sim 1.7$  is a necessary condition for ammonium sulphate being the major component, but it is not sufficient. A mixture of sodium chloride with organic compounds can also result in a growth factor of  $\sim 1.7$ . There one needs corroborating information to make such a statement possible.

Page 12271, line 23: The year of the cruise might be repeated here.

Page 12273, lines 2–3: "...to the first CPC measuring the particle number concentration at the selected particle size (l)." To my understanding this should rather be: "...to the first CPC measuring the number concentration of particles leaving the first DMA at the selected particle size (l)."

Page 12273, lines 7–8 and Fig. 2a: Why is the reference RH not measured in the excess air, which is the mixture of the sample and sheath flow? Furthermore, the laminator mesh in the DMA for the sheath air often causes a small overpressure at the sheath air inlet, where every 10 mbar overpressure cause a systematic offset of 1% of the actual RH. However, such potential biases are corrected for by calibrating the RH with the actual observed growth of NaCl.

Page 12273, lines 15–19: It might be worth adding two or three sentences explaining what the inversion algorithm does. For example the wording chosen here appears to imply that the inversion algorithm corrects for the issue with multiple charges. However, I can see no straight forward way to correct for the particles carrying multiple charges in an externally mixed aerosol. The only thing one can do, if parallel particle number size distributions are available, is to judge, whether a particular measured growth spectrum is mainly from particles carrying a single charges or whether the fraction of particles with multiple charges is too big for a valid measurement.

Page 12273, line 29: The question that always arises when multi-modal distributions are fitted is, how sensitive are the fit results to the initial guess and to the choice of fit function. Can the authors elaborate on this issue for the growth distribution observed in this study?

Page 12274, lines 2–3: It might be worth mentioning whether number mean diameters or volume mean diameters, which would be needed for a hygroscopicity closure study, are reported.

Page 12274, Eq. 2: Confusing indices. It should be:

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$$nf_i = \frac{N_i}{\sum_{k=1}^n N_k} \quad (1)$$

Page 12274, line 11: The RH measurement for DMA2 is calibrated by measurement of the growth factor of sodium chloride (what dry size?). The measured growth factor is translated into a RH using theoretical growth curves. While volume equivalent growth factors of sodium chloride are well known, there is the issue with the shape of the particles. Sodium chloride particles are understood to be cubic and therefore mobility growth factors measured by a H-TDMA must be corrected for shape effects. Was such a correction applied and were the size dependence of the dynamic shape factor as well as appropriate Cunningham slip corrections applied (see e.g. inset of Figure 1b in Biskos et al., 2006)? - I have to admit that I also didn't do it correctly in earlier work.

Page 12274, lines 14–15: Only measurements when the RH in DMA2 was within the band 88–92% were used for the further data analysis. Was the deviation from the nominal 90% RH random for all events, or was it sometimes systematically offset on the low or high side? In the latter case one could apply a correction to the measured growth factors in order to minimise systematic biases.

Page 12274, lines 17–18: The relative growth factor uncertainty associated with the RH uncertainty is:  $\Delta g_f = \Delta RH \frac{dg_f}{dRH} g_f^{-1}$ . Therefore the statement "...were less hygroscopic than pure sodium chloride particles, the relative uncertainty of the results is less than 6%" is not quite true. For example  $\text{NaNO}_3$  and  $\text{NH}_4\text{NO}_3$  are less hygroscopic than sodium chloride but the resulting relative growth factor uncertainty is 7.4 and 7.6% at 217 nm, respectively, for  $\Delta RH = 2\%$ . For other salts of atmospheric importance it is also  $>5.5\%$ .

Page 12276, line 4: "Therefore, in this study, the first APS was used for comparison only." - Comparison with what? The data from the first APS aren't mentioned

anywhere else.

Page 12776, Eq. 3: Is  $D_{p_{aero,dry}}$  variable in time because of density variations?

Page 12276, lines 13–16: Does the H-DMA-APS need some sort of data inversion similar to the HTDMA?

Page 12777, lines 6–7: Doesn't this introduce a systematic bias because only points of one side of the random scattering are corrected?

Page 12277, lines 25ff.: These growth factors are higher than those of pure ammonium sulphate though not significantly regarding the measurement uncertainty. However, in a clean marine case one can well imagine that the sulphate is not fully neutralised by ammonia, therefore resulting in larger growth factors.

Page 12278, lines 11–13: The transport time of the air masses from Korea past Japan to the ship's location might be mentioned already here.

Page 12278, lines 18–24: These statements sound like pure speculation, unless there is further corroborating knowledge on e.g. the chemical composition behind it. In principle a particle having a growth factor of 1.4-1.5 can be composed of a combination of any hygroscopic salt (sulphate salts, nitrate salts, sodium chloride, ...) with less or non-hygroscopic compounds (organics, elemental carbon, mineral dust). One can think of original particle sources other than combustion such as biomass burning, mineral dust or secondary organic aerosol nucleation.

Page 12279, lines 2–4: The transport time of the air masses from Japan to the ship's location might be mentioned already here.

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Page 12279, lines 10–11: Different ageing times is one possible explanation but there is an alternative explanation: The emission ratio of less and non-hygroscopic compounds to more hygroscopic compounds or their precursors contributing to the particulate matter might have been different between these two periods.

Page 12279, lines 21–23: Again, e.g. mixed NaCl/organic particles can also have growth factors of 1.59-1.73. This statement needs corroborating information, otherwise it is speculation.

Page 12279, line 23: Why not: "Additionally, this aerosol is characterized by ...".

Page 12279, lines 23–30: These particles could also be partially neutralised to ammonium bisulphate. Pure sulphuric acid may exhibit similar growth factors to ammonium sulphate in a HTDMA due to the residual water retained on the particles even at  $RH < 10\%$ , whereas ammonium bisulphate is expected to exhibit larger growth factors.

Page 12280, lines 4–9: Would you expect that the  $1\ \mu\text{m}$ -particles are neutralised by ammonia while the submicron particles are not? Or do the  $1\ \mu\text{m}$ -particles contain substantial amounts of less or non-hygroscopic material?

Page 12280, lines 27–29: What about the sea salt particles, where do they have their maximum in number? Isn't it also at large sizes?

Page 12281, lines 7–10: Again, I don't think that the growth factor alone is sufficient to conclude that the particles are of anthropogenic origin.

Page 12281, lines 10–14: Can soot particles be excluded?

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Personal interest: Sea salt particles or only sometimes seen in the large accumulation mode size range. Does the data set allow to say more about when they are observed and when not? Are there links to parameters such as wind speeds along the back trajectory?

Tables A1–A5: The mean growth factor of the whole growth distribution might also be added, possibly even weighted by number and volume if sufficient space is available.

Figures 3–6, 8: What are the error bars? The variability of the group's growth factors during a period or the accuracy of the reported values? If it is the variability, can it also be shown for the number fractions.

Figure 7 caption: It should be mentioned that these growth distributions, and therefore also the spread of growth factors, are the sum of whole sampling period.

Figure 7b: The Stokes diameter scale corresponding to the aerodynamic diameter scale might be added.

Technical corrections:

Page 12269, line 17: "...as relative humidity (*RH*) increases ...", in order to define "RH".

Page 12271, line 3: "... which has not *been* intensively investigated ..."

Page 12278, line 2: "... Eastern North Atlantic, where ..."

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Page 12278, line 7: "... can be assigned to ammonium sulfate ..."

Page 12280, line 18: "... , and at 90% RH (*Fig. 7b*)."

Page 12282, line 17: "... less growth than *expected* for pure ammonium sulfate ..."

## References

Biskos, G., Russell, L. M., Buseck, P. R., and Martin, S. T.: Nanosize effect on the hygroscopic growth factor of aerosol particles. *Geophys. Res. Lett.*, 33, L07801, doi:10.1029/2005GL025199, 2006.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 6, 12267, 2006.

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