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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Thermal stability analysis of particles incorporated in cirrus crystals and of non-activated particles in between the cirrus crystals: Comparing clean and polluted air masses" *by* M. Seifert et al.

M. Seifert et al.

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6. mixing of particles

Reviewer: "Pg 3671 lines 5-9 Your arguments here do not take into account a significant fraction of your involatile material being internally mixed with sulfate/water solution drops. If, the particles are well aged this might be expected to be the case. These particles may well be homogeneously nucleated, you evaporate the volatile material but count the particle as it leaves an, albeit small, involatile core."

Reply: The reviewer is correct and we also mention this in the text (p. 3671 l. 29 - p. 3672 l. 2). It may appear as if making a lot a fuss about non-volatile particles if the

nucleating mechanism is homogenous (for small inclusions) is irrelevant, but is we wish to understand the relation between aerosols and cirrus and dare making some statements of what will happen in a future atmosphere this information is not so insignificant. If and at what mixture will a non-volatile core work as an IN. How will changes in aerosol particles and precursor gases influence the aging and transformation of aerosols in a future atmosphere?

Action: To make the limitations of the thermal denuder systems more clear we will add the following sentence to the text (p. 3672 l. 2):

"Recall that if the particles are composed of volatile material with a small non-volatile core, then the volatility system will detect them as non-volatile particles."

7. Discussion of the volatility technique

Reviewer: " Pg 3672 lines 5-10 The description of the effect of the volatility technique appears here, surely this should come much earlier. You also need to make the comment that as you donŠt measure the size you donŠt know the relative amounts of volatile and involatile material in the particles. If there some involatile material remains it is counted just the same if it were a 200 nm solution droplet with a 20 nm involatile core as if it is a 200 nm involatile particle."

Reply: OK

Action: The section addressing the limitations of the volatility technique (P. 3672 line 2-13) is moved to instrumentation section (paragraph 2.1.2):

8. Number of sea salt particles

Reviewer:"Pg 3673 line 4-5 I agree with referee 1. I donŠt think there are sufficient numbers of sea salt particles at these sizes to account for the very high numbers you observe. "

Reply: Reviewer 1 states in his/her referee:"According to various references from IN-

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DOEX and ACE there may exist 10 sea salt particles per cc less than 100 nm diameter in the marine boundary layer."

We are not aware of the publications from the INDOEX and ACE experiment that state what the reviewer says: ŞAccording to various references from INDOEX and ACE there may exist 10 sea salt particles per cc less than 100 nm diameter in the marine boundary layerŤ. However, we know of studies that do indicate large numbers of small sea salt particles. In remote marine air Murphy et al. (1998)* showed that although the sea salt mass fraction of the aerosol was larger at larger sizes, about half the mass near 100 nm was sea salt. These field measurements are in agreement with laboratory simulations by Mårtensson et al. (2003) as well as modeling results by Gong et al. (1997). Since sea salt is produced at the ocean surface by the bursting of air bubbles from entrainment of air induced by wind stress. The number and mass concentration of seal salt aerosol are strongly dependent on wind speed. The mean wind speed in the midlatitudes during fall is clearly different from the mean wind speeds observed during the ACE and INDOEX experiments

9. Conclusions

Reviewer: "Pg 3673 Your conclusions need to be amended given the above comments and certainly caveated with points raised about the technique not being sensitive to particles which are volatile but have small involatile cores. Your parting comments are very valuable, a tandem DMA would help greatly to understand the measurements you have made."

Reply: We have tried to make these points more clear.

Action: P. 3674 line 10-14 now reads:

"The simple thermal denuder system used in this study is limited by only treating integral number densities. It was not possible to identify the effect of aerosol mixing on cirrus formation, since we can not distinguish between particles which were volatile

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but have small non-volatile cores and entirely non-volatile particles. Hence the above presented conclusions must be tempered with the caveat that the thermal composition of residual and interstitial particles was not measured size dependent. A system that would provide size resolved information would really help in understanding the link between aerosols and cirrus formation. A volatility tandem DMA technique would not only provide size resolved information, but would also give a direct measurement of the internal and external mixture of the aerosol. ”

Minor comments:

1. References

Reviewer:“Pg 3663 line 5 the instruments have already been described elsewhere. Where? Give references”

Reply: Since all the instruments are described in the paper we remove the sentence “The instruments have already been described, however a short description is provided below.” in line 5/6 on page 3663.

2. Calculating the enrichment factor

Reviewer:“Pg 3663 line 15-19 You need to state and reference the method you used for calculating the enrichment factor and correcting it.”

Reply: OK

Action: P. 3663 line 15-16 now reads:

ťťThe design of the CVI probe causes an enrichment of the crystal number density in the sample air compared to ambient conditions (Ogren et al., 1985; Noone et al., 1988).”

References:

Noone, K.J., Ogren, J.A., Heintzenberg, J., Charlson, R.J., and Covert, D.S.: Design

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and Calibration of a Counterflow Virtual Impactor For Sampling of Atmospheric Fog and Cloud Droplets, Aerosol Sci. Technol., 8, 235-244, 1988.

Ogren, J.A., Heintzenberg, J., and Charlson, R.J.: In-situ sampling of clouds with a droplet to aerosol converter, Geophys. Res. Lett., 12, 121-203, 1985.

3. Interpolation between the CPCs with 5 nm and 14 nm to 10 nm

Reviewer: "Pg 3664 line 14: The interpolation between the CPCs with 5 nm and 14 nm to 10 nm only works if there is no recent new particle formation or pollution in the sampled region. If the dN is small relative to N then the correction may be valid but not if dN/N is larger than say 10-20% How large was this difference? "

Reply: We do not agree with the reviewer. The ratio dN/N is no measure for the validity of the preformed approximation. Whether this approximation affects the outcome of the volatility analysis depends very much on how much the result of our approximation deviates from deriving N10 based on the actual interstitial size distribution. We may try to estimate this deviation by using DMA and PCASP size distribution data from the INCA campaigns (Seifert et al. 2003). The combined data from DMA, PCASP as well as N14 and N5 yields a composite aerosol size distribution between 0.005 and about 1 μm which is fitted by lognormal distributions. The mode for particle diameters smaller than 25 nm is constrained by the shape of the distribution in the Aitken mode, and the difference between N14 and the DMA integral as well as the difference between N5 and N14.

For an assumed relative difference between the two counter of 50% N*10 derived based on a lognormal size distribution and N10 approximated from N5 and N14 differ less than 10%. In more than 80% of the time the relative difference between these two counter (N5-N14)/N5 *100 was less than 50%. Most of these cases occurred in polluted air determined from CO. We therefore believe that using a proxy for N10 did not influence our analysis in any substantial amount.

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References: Seifert, M., Ström, J., Krejci, R., Minikin, A., Petzold, A., Gayet, J.-F., Schumann, U., and Ovarlez, J.: In situ observations of aerosol particles remaining from evaporated cirrus crystals: Comparing clean and polluted air masses, Atmos. Chem. Phys., 3, 1-13, 2003.

4. Counting efficiencies of the CPC

Reviewer: " Pg 3664 were the counting efficiencies of the CPCs (say at 30 nm) the same for all the counters? An offline DMPS test would be sufficient here."

Reply: Post campaign laboratory calibration showed that the TSI 3010 and the two modified TSI 3760 had the same 50% efficiency cut-offs, but the slope of the efficiency curve was flatter for the two modified counters. At larger particle sizes (D > 20 nm) the counting efficiency curves were essentially the same for all counters.

5. Trends in the color plots

Reviewer: "Pg 3667 lines 9-11. I donŠt agree with the statement that for volatile particles the gradient from warm to cold colors occurs with increasing Ncvi and also slightly with RHi. Rather there is a band of warm colors with an increased fraction of the involatile particles occurring closest to the regions of cloud formation and evaporation (are these the first to nucleate, largest and therefore last to evaporate?) and also occurring at the maximum ice number concentration. Is this not surprising? I donŠt believe you have discussed this adequately."

Reply: We do not agree with the reviewer comment that there is no gradient from warm to cold colors with increasing Ncvi and also slightly with RHi for the volatile residual fraction plotted in Figure 1 left column. Furthermore the reviewer is incorrect when stating that the increased fraction of the involatile particles occurring closest to the regions of cloud formation and evaporation.

We believe that the reviewer is misinterpreting Figure 1. To make the concept of Ncvi, RHi diagram more clear we added a new paragraph to the draft (paragraph 3.1 in the

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revised version of the paper)

6. expression " ambient air"

Reviewer: "Pg 3669 line 13 in the ambient air should read in the out of cloud total aerosol population."

Reply: OK

Action: Pg 3669 line 12-15 reads now:

"In the cold cases the non-volatile fraction in residual particles is about 15 (NH) and 30 (SH) percent units higher than in the out of cloud total aerosol population."

7. selecting data 95-105%

Reviewer: "Pg 3669 lines 20-23 A discussion of the meaning of the figures 1 and 2 (see above) should be sufficient to rule out any formation/growth and evaporation of the crystals in the region 95-105% you are selecting. "

Reply: OK. This point should be clear after adding section 3.1 in the revised version of the manuscript.

8. Differences between NH and SH aerosol

Reviewer: " Pg 3672 line 17 not necessarily more aged but greater heterogeneity of sources. What evidence do you have for the increased age of SH aerosol? It needs to be presented in the paper, as far as I know this is not common knowledge."

Reply: Recently, Williams et al. (2002) studied aerosol variability as function of particle size for data collected over the Northern Indian Ocean. It was found that for particles believed to be of terrestrial or oceanic origin, the variability correlated with the average number density. What regards particles that are thought to be formed and grow in the atmosphere through coagulation and condensation an anticorrelation was observed, the minimum in variability coinciding with the maximum in the number concentration.

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Nevertheless, since we did not perform a variablitiy analysis of the INCA data the statement Şa more aged aerosol in the SHŤ (p. 3672 line 17) will be removed.

Action: Page 3672 line 13-21 reads now:

“But why is the non-volatile fraction so pronounced in the SH cold case? Recently, Minikin et al. (2003) has shown for the INCA data that the aerosol number density in the NH is more variable and typically a factor of 2Ű3 higher than in the SH. According to Williams et al. (2002) who examined aerosol variability as function of particle size, variability can be related to the origin of particles. The authors found that for particles believed to be of terrestrial or oceanic origin, the variability correlated with the average number concentration. For particles that are thought to be formed and grow in the atmosphere through coagulation and condensation anticorrelation was observed, the minimum in variability coinciding with the maximum in the number concentration. Hence one might speculate that in the SH the aerosol properties are more characterized by long-range transport compared to the NH where sources at the surface may play a larger role. ”

References:

Williams, J., de Reus, M., Krejci, R., Fischer, H., and Ström, J.: Application of the variability-size relationship to atmospheric aerosol studies: estimating aerosol lifetimes and ages, Atmos. Chem. Phys., 2, 133Ű145, 2002

Typographical errors

Reviewer: “Pg 3663 line 13 should read: downstream of the inlet”

Reply: OK

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3659, 2003.