Atmos. Chem. Phys. Discuss., 6, S7291–S7299, 2007
www.atmos-chem-phys-discuss.net/6/S7291/2007/

Atmospheric
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Discussions

Interactive comment on “Closure between measured and modelled particle hygroscopic growth during TORCH2 implies ammonium nitrate artefact in the HTDMA measurements” *by* M. Gysel et al.

M. Gysel et al.

Received and published: 17 March 2007

General reply:
First of all we want to thank the referees for their detailed reviews, which certainly will improve the quality of this manuscript.

Apparently we have put too much emphasis on the nitrate artefact in the manuscript title leading to thoughts that the paper might possibly be published as a technical note. However, we are convinced that the manuscript is still worth more than just a technical note, as the nitrate artefact is just one outcome of this study. Other major results are:

- High resolution in time and size for both hygroscopic growth factors and chemical composition is crucial for a valid hygroscopicity closure, whenever particle properties vary with time.
- The ZSR approach – one possible simplification in the modelling approach to allow for high time and size resolution – is a valid tool to predict growth factors of aged ambient pollution particles based on their chemical composition when there is a mixture of inorganic and organic material.
- The organic compounds in aged ambient particles have a growth factor in the order of 1.20 at 90% RH.
- Quantification of relative contributions of inorganic versus organic compounds to overall water uptake shows that the inorganic salts clearly dominate in the observed aged air masses.

These outcomes are already pointed out in the manuscript. In the revised manuscript the nitrate discrepancy will be discussed first and a shorter discussion of the other, discounted possibilities will follow. More emphasis will be put in discussing the other outcomes of this study

We acknowledge the common judgment of the referees that the manuscript is rather long. Figures 2 (back trajectories)and 7 (fraction of non-hygroscopic particles and HOA markers) will be removed and the text will be worked over in order to further shorten it.

After realising that most likely a nitrate artefact occurred in the HTDMA measurements, our first thought was to run laboratory experiments to prove and quantify the effects of this artefact. Qualitatively the magnitude of the artefact is reasonable based on our general lab experiences with pure NH_4NO_3 and e.g. the literature on TDMA measurements of NH_4NO_3 cited in this paper. However, when it comes down to an exact quantification, the issue becomes somewhat complicated. The

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evaporation rate of NH_4NO_3 depends on temperature, RH, and also on the gas phase concentrations of ammonia and nitric acid. Dealing with these three dependencies might still be feasible. However, the major influence on evaporation rates probably comes from the actual composition of the particles. This is nicely shown in the abstract amended by referee #2, where the evaporation rate for mixed NH_4NO_3 / $(NH_4)_2SO_4$ particles was found to be distinctly different from pure NH_4NO_3 particles. We do not see that it is possible to find adequate surrogate particles and an appropriate experimental set-up such that the corresponding result can be compared to our field data quantitatively. This is the reason for not adding specific laboratory experiments. The problem is certainly worth a set of laboratory experiments but that should be the topic of a comprehensive separate study.

The referees asked whether the mass fraction of ammonium nitrate might have been overestimated due to different collection efficiencies of different compounds. The Q-AMS's signal intensity depends on the collection efficiency, the fraction of a species successfully vaporized on the heater, and the ionization efficiency (standard 70eV electron impact ionization is applied). Collection efficiencies less than unity in the AMS are thought to be a result of particle bounce on the heater, and so affect all species in the bouncing particle equally (Matthew et al., submitted to Anal. Chem., 2007). Particles containing substantial amounts of NH_4NO_3 have higher collection efficiency than e.g. solid sulphate particles. Mass fractions of different species obtained by the AMS can potentially be biased towards NH_4NO_3, but only if the NH_4NO_3 is externally mixed. If the discrepancy between HTDMA and AMS/ZSR prediction would have been caused only by higher collection efficiency of externally mixed ammonium nitrate particles, then the growth distributions were to have a signal at GF$\sim$1.8, which is clearly not the case (see dC/dGF in Figure 3). The collection efficiency can vary with time due to variations in composition. This does not affect ZSR-prediction made with high time resolution, because only mass fractions are required as input data, which are independent of the collection efficiency for internally mixed particles. In the case of a clear breadth of the growth factor distributions, which has not been observed for the nitrate containing particles, the nitrate mass fractions could become somewhat biased because those particles with high nitrate/low sulphate mass fraction could have a higher collection efficiency than the low nitrate/high sulphate particles.

General comments of referee #1:
1) The AMS measures NH_4, NO_3, SO_4 amongst other compounds. In case of an acidic aerosol, the measured ammonium is smaller than the number of number of moles of ammonium, m_{NH_4,neutr}, that would be required to fully neutralize a given number of moles of sulphate and nitrate ions (m_{NH_4,neutr}=2*m_{SO_4}+m_{NO_3}). Doing these calculations for this data set shows that the aerosol was always fully neutralized when a substantial nitrate mass fraction was observed, whereas clearly acidic aerosol was only found in nitrate free cases. This means that virtually all measured SO_4 is attributed to $(NH_4)_2SO_4$ in the model calculations, whenever NO_3 is present, the latter being attributed to NH_4NO_3. This means that altering the SO_4 attribution in the model calculations would further increase the predicted growth factors and thus the difference between growth factor prediction and measurement would become even larger in the presence of NH_4NO_3.

2) See above in general reply regarding lab experiments quantifying possible ammonium nitrate artefacts.

Specific comments and technical corrections of referee #1:
The specific comments and technical corrections will be taken into account

General comments of referee #2:
1) See above in general reply regarding length of the paper. Figure 3 does indeed contain lots of information. We take into consideration reducing the number of dry sizes shown, even though it is an important to see that the growth characteristics

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change with only small differences in dry size. The mean growth factor asked for by the referee is already shown in Figure 3. The standard deviation is not a helpful quantity in case of multimodal growth distributions. Growth distributions with clearly separated modes have been found in this study (see Figure 3). Therefore we prefer showing the growth distributions dC/dGF along with the mean growth factor and the fraction of particles with GF>1.15.

2) See above in general reply regarding lab experiments quantifying possible ammonium nitrate artefacts.

Specific comments of referee #2:
p. 12505) Revision of references in the introduction will be done.

p. 12506) The results by Carrico et al. (2005) indicate a growth factor of ∼1.16 (1.11) for the organic material present in the 100 (200nm) particles at **80% RH**, which translates roughly into 1.22–1.30 **at 90%** (see p. 12528). This can be called “contribution to hygroscopic growth” to my understanding. Further references supporting this statement are already given in the last paragraph of the discussion section. The two studies mentioned by the referee measured the optical growth factor f(RH). They indicate only a small contribution of the organic compounds to f(85-90% RH). However, the error bars in both RH and f(RH) are relatively large and translation of such optical measurements on polydisperse size distributions into monodisperse diameter growth factors is not straight forward. Therefore these studies are not in contradiction with a small contribution of organic compounds to hygroscopic growth factors.

p. 12510) The closure could be done at the RH of measurement for every point. However, we clearly prefer reporting HTDMA data corrected to a constant RH, in order to remove systematic offsets and variations in growth distributions induced by RH variations during measurements. Only in this way growth factors become directly comparable to growth factors of other studies reporting data at 90% RH.

p. 12512) Correct treatment of equation 2 regarding water activity and relative humidity is not simple (it requires an iterative solution) and its usage is usually not detailed in publications. Here we make a simplification which has to be justified. Equation 3 is not a repetition from literature to my knowledge. Therefore we will keep this discussion, but we will try to clarify the text and equation 4 will be removed.

p. 12513) See above in general reply regarding mixing state and collection efficiency. A major outcome of this study is that high resolution in both time and size of chemical characterisation is crucial for a valid hygroscopicity closure, unless the variability of particle properties over the averaging interval is small. Sufficient time an size resolution for a variability as found in the TORCH2 experiment is very hard to achieve with conventional methods, which themselves are not always artefact free regarding organics and ammonium nitrate.

p. 12515) See general reply above regarding the mixing state. With “not completely mixed” I tried to say that individual particles may contain the same compounds but in different ratios. Is there at all clear definition whether “internally mixed” means just presence of all compounds in all particles or more strictly equal fractions of every compound in every particle? We will clarify this by using “quasi-internally mixed” for the former and “internally mixed” for the latter interpretation.
We will keep Figure 5 containing the hydration-dehydration curves, because there is not too much ambient HTDMA measurements available in the literature regarding suppression of efflorescence-deliquescence hysteresis along with measurements of chemical composition.

p. 12517) See above in general reply regarding mixing state and collection efficiency. As ammonium nitrate is most likely internally mixed with the other aerosol compounds, it does have the same collection efficiency (Matthew et al., submitted to Anal. Chem., 2007). If ammonium nitrate would be externally mixed, then the growth distributions were to have a signal at GF$\sim$1.8, which is clearly not the case (see dC/dGF in Figure 3).

p. 12518) Figure 2 will be removed in order to shorten the manuscript. Back trajectories were not shown to validate the measurements – such good closure achieved at all sizes and times when no nitrate was present can hardly be expected to be caused by measurement errors – but rather to explain why the particles did have the composition and physical properties as found.

p. 12521) The standard errors will be included.

p. 12523) The effect of setting the organic growth factor to 1.0 is illustrated in Figure 8, where the reader gets a chance to make his personal judgment. The effect on the regression statistics will be added in the form of numbers to the text.

p. 12524) We thank the referee for pointing out our error in labelling the right hand side panels in Figure 9. It should read: "AMS/ZSR: ignore nitrate, HTDMA: hygroscopic particles only." It can be seen that nitrate is ignored in the calculations for the scatter plots on the right hand side and centre panels, since predicted growth factors are equal for equal dry size. Therefore our statement that closure is only achieved by ignoring nitrate also when just considering the more hygroscopic particles was correct. This can also be seen from Figure 10.

p. 12525 and 12526: We will adapt the formulations.

The technical corrections will be considered in the revised manuscript.

General comments of referee #3:

1) Rearranging the evaporation artefact hypothesis will be taken into consideration. See general reply above regarding extra lab experiments. NH_4NO_3 is indeed the calibration substance for the AMS and evaporation artefacts between DMA and AMS could also occur. Therefore the connecting tube between DMA outlet and AMS inlet was kept very short, such that no significant size reduction occurred as could be seen from the independent sizing by the AMS.

2) 20-25 °C in the measurement container accommodating all instrumentation would have been desirable. The container was equipped with air conditioning, but the difference to outdoor temperature remained considerable due to the excess heat of all instruments and the sun radiation absorbed by the container. In the case of low outdoor temperatures the measurements are often done at considerably higher temperature since the instrumentation is rarely kept at temperatures below 20°C.

3) See general reply above regarding length and form of manuscript.

4) The deviations between HTDMA measurement and AMS/ZSR predictions in cases of acidic aerosols are likely to be due to reduced measurement statistics under these conditions as the number concentrations are very low. The deviations are not systematic and not as pronounced as when nitrate is present.

The aerosol was fully neutralised by ammonium when substantial amounts of nitrate were present (see reply to first general comment of referee #1 above) and therefore the presence of ammonium nitrate is plausible. Figure 6 sometimes suggests incomplete neutralisation by ammonium when small amounts of nitrate are present, which is probably caused by averaging over finite size and time intervals. Speculations about other forms of nitrate are discussed and dismissed on p.12523 in the manuscript.

Specific comments of referee #3:

p. 12508) The description of the HTDMA is just 7 lines long, part of which is relevant instrument specific information such as the residence time. We will try to shorten a bit further.

p. 12510) NR-PM1 is already defined at page 12506. A comprehensive discussion of what compounds not being detected is given on page 12520 along with potential consequences for the closure.

p. 12522) The most likely cause of evaporation artefacts is listed last because it was the last one we thought of. We will rearrange the list.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 12503, 2006.

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