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Atmospheric
Chemistry
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Discussions

Interactive comment on “Hygroscopicity of the submicrometer aerosol at the high-alpine site Jungfraujoch, 3580 m a.s.l., Switzerland” *by* S. Sjogren et al.

S. Sjogren et al.

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Anonymous Referee #3

2.1 Page 13704, line 14: The assertion concerning the sampling efficiency of the inlet, an important parameter in the study (whether acknowledged as such or not), is not well supported. The given citation does not supply any data or detail concerning the estimated passing efficiency, which is in any case poorly characterized (e.g., what is the 50% cut point, what is the kurtosis of the presumably sigmoid efficiency curve, etc.). Mind you, there is noting intrinsically improbable about the somewhat vague, given efficiency for a stationary inlet but I have seen plenty of such inlets with 50% cut points well below 40 microns for wind speeds of 20 m/s. The authors must simply

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provide better support here.

Answer: The inlet has been designed to sample droplets $<$40 um at windspeeds up to 20 m/s. At higher windspeeds we cannot, with the design calculations used, ensure the sampling efficiency, as for example turbulence at the inlet has not been taken into account at such wind speeds. However, the percentage of time during which wind speeds above 20 m/s was encountered at the site over the last 9 years was low: 2.6%. In addition to the mechanical specifications of the inlet, it is also important to ensure that the heating does not disturb the particle distributions: Henning et al. (2002) showed by differentiating size distributions measured downstream of the inlets (total - interstitial) and comparison to cloud microphysical measurements (FSSP) that the total inlet has a very high sampling efficiency for cloud droplets. In our case we studied interstitial particles during 3 campaigns of 4 reported, so the PM1 and PM2.5 heads are of importance, and only during the fourth campaign 2005 the total (dried) particles were studied. This was in order to increase the particle counts during cloudy conditions, and as preliminary results have shown a negligible difference in hygroscopicity measured between interstitial and total aerosol, we assume that the aerosol properties with the total inlet are not that different from the preceding years. Moreover, if there would be a larger cutoff at lower windspeeds, then the campaign 2005 would only more approach the preceding campaigns, sampling interstitial aerosol. The functioning of the two inlets is now better described and it is more clearly detailed what type of inlet was used when.

2.2 Page 13706, lines 2-4: I find it at least mildly surprising that the hygroscopicity is insensitive to the BC concentration to within a factor of two (essentially the impact of varying the specific absorption by about a factor of two) and to the size distribution of that BC. After all, one can easily envision situations where there would be sensitivity (e.g., BC dominating the mass in a particular size range). The text suggests that authors have done sensitivity studies on this issue. They should report the results explicitly to support this claim.

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Answer: Certainly there can be cases where the BC concentration is large enough to influence the GF. In this case of atmospheric background aerosol though, the BC concentration varies between 0 to $<10\%$ mass. If we compare two model runs, one with BC up to 10% and one without, they give 1.289 and 1.310, respectively, difference 0.021, which is well within our stated uncertainty. This was during the first 12 hours of 28.02.2005, one of the occasions with most BC encountered during the campaigns. GF measured was at that occasion 1.325. Thus, with the assumption that BC distributes in the 100 nm range as it distributes in the whole PM1 range, the sensitivity to BC concentration up to 10%mass is delta GF$<$0.03 at the GF 1.3 level. This can be expected, as the ZSR model takes the GF of the pure component, which is 1.0 for BC, cubed, multiplied with the concentration of the pure component, $<10\%$. This sensitivity to BC will be added in the paper.

2.3 Page 13706, line 13: This is a minor organizational comment. One would normally expect temperature gradients in a TDMA system and such gradients in principle would produce errors in RH measurements. Hence, the assumption made here seems questionable. On the other hand, the authors DO provide good support for the assertion a bit further on (page 13707, lines 13-23). I would suggest a bit of a rewrite to more nearly juxtapose the assertion and its defense. Perhaps the insertion of a "see below for justification" would suffice.

Answer: We tried to keep the technical comments of the HTDMA setup to a minimum in the paper and referred to the references. The point mentioned above is rectified by indicating to the technical description with a "see below", as the reviewer proposes. We agree that there are certainly gradients in the system. However we meant to a smaller amount than what has a large influence on the RH measurement. We have specified our expected quality now as being : "The accuracy of the RH measurement at higher RH is for example 85+/-1.1%, assuming no temperature gradients in the DMA2. Our temperature gradients were $<$0.1K, when the DMAs were inserted in water baths (see below).". This is shown in Weingartner et al. (2002), and also T. Hennig et al.

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(2005) have shown similar results (although the gradient is differing depending on water circulation flowrates and insulation properties of each individual instrument, ofcourse).

2.4 Page 13708, lines 3-13: The inversion technique used here is not really clearly delineated. The reference to a manuscript in preparation is, of course, not adequate and, recognizing this, the authors have tried to characterize their procedure by comparison with Cubison et al (2005). However, the characterization is a bit obscure. They say that the inversion has "similarities" to Cubison et al. This is not very enlightening since it does not preclude quite substantial differences between the two approaches. The only difference apparently given is the non-linearity of the inversion function. Is this all that differs? If not, what else is different? The authors need to clearly show exactly how the procedure they employ here differs from the only actual literature reference they supply.

Answer: This is an important point, and we hope that we with the proposed text below are more specific with how the inversion functions and how it is related to the one of Cubison et al. and Stolzenburg & McMurry. We hope the reference to the manuscript in preparation (Gysel et al.) will obtain a correct reference status when the future proofs are ready for this article. New text: "Atmospheric particles of a defined dry size typically exhibit a range of growth factors or even clearly separated growth modes, because of external mixing or variable relative fractions of different compounds in individual particles (hereinafter referred to as quasi-internally mixed). Growth factor probability density functions (GF-PDF) c(GF)=dC/dGF are retrieved from each measurement, and normalised such that C=[integral]c(GF)dGF=1. The inversion method applied to the raw data (Gysel et al., in prep.) has been tested and applied to ambient HTDMA data previously (Gysel et al., in press). This method uses a full TDMA transfer forward model in combination with a X2 minimisation algorithm to retrieve the GF-PDF c(GF). This is basically the same approach as the "TDMAfit" algorithm by Stolzenburg and McMurry (1988) with the difference that the GF-PDF is assumed to be a piecewise linear function, similar to the inversion algorithm described by Cubison et al. (2005),

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instead of a superposition of multiple Gaussians. A bin resolution of delta GF=0.15 was chosen for the inversion because of counting statistics as well as being small enough to separate the mode of the inorganics from that of the organics in a potentially externally mixed aerosol. The AMS provides chemical composition data for the bulk submicron aerosol in the air sample, whereas no information on the mixing state of the aerosol is obtained. GF-PDFs obtained with the HTDMA provide some information on the mixing state. The ensemble mean growth factor GF* is defined as the 3rd-moment mean growth factor (i.e. weighted by the volume) of c(GF):

GF*=([integral]GFˆ3 c(GF)dGF)ˆ0.3333 (1)

GF* represents the growth factor that would be observed if the absorbed water were equally distributed among all particles in a sample. Thus GF* is the quantity to be compared with growth factor predictions based on composition data obtained by the AMS (see below). Thus even if the measured GF is broad or even clearly bimodal GF* would represent the hygroscopicity as predicted from the AMS data as long as the AMS can measure all the relevant chemical components in both modes. This is not the case if some of the material sampled is composed of a refractory component such as dust or sea salt, that cannot be observed by the AMS. The standard deviation sigma of the inverted GF-PDF c(GF) is used as a measure for the spread of growth factors. With a resolution of delta GF=0.15 as chosen here for the HTDMA data inversion, any sigma$<$0.10 means that the aerosol is either quasi-internally mixed with limited growth spread (no distinct growth modes) or even perfectly internally mixed. The sigma obtained with pure ammonium sulfate at 85% RH is $<$0.05, however, such small sigma can only be detected when the counting statistics allow for data inversion with higher resolution. Any sigma $>$ 0.15 shows that the aerosol is externally mixed or quasi-internally mixed with substantial spread of growth factors."

2.5 Page 13708, lines 17-26: I found the discussion of the "ensemble mean growth factor" a bit confusing. This apparently refers to the mass mean GF, important since the AMS was used in scanning mode. The authors then state that this corresponds to the GF if water were "equally distributed among all particles." This will be true only if the particles are both of the same composition and size. Of course, this is all one can really get from a bulk measurement. On the other hand, it is not the same as the average of the hygroscopicities (and mass hydration) of individual particles of differing composition and size. I THINK that the authors are trying to say this but I am not sure. The discussion needs to be clarified.

Answer: This has been clarified (see text at point 2.4 above), and the reviewer has described correctly what we tried to express. It is important to state that the chemical composition data refers bulk aerosol composition, not distinguishing any potential external mixtures.

2.6 Page 13710 - 13711, section 2.6 (ZSR relationship): A major assumption is implicit in the adoption of the ZSR mixing rule, namely the independence of organic and inorganic effects on water activity. The authors do state this (essentially) but do not discuss it at all adequately, in my view. First, of course, such independence is not generally correct, even as an approximation, it is simply difficult to deal with the alternative. Perhaps the best attempt at incorporating organic-inorganic ion interactions into a prognostic model was the modified UNIFAC model of Ming and Russell (JGR, 106, 28259-28274,2001). This effort suggests that substantial errors may be incurred using an approximation such as ZSR, perhaps 30% or so. Similarly, even studies that do indicate that the ZSR relationship can be useful, suggest errors on the order of 20% or so due to organic-inorganic interactions (cf. Cruz and Pandis, Environ. Sci. Technol., 34, 4313-4319, 2000). Furthermore, it is not simply the presence of organics that can invalidate the mixing rule. Aklilu et al (Atmos. Environ., 40, 2650-2661, 2006) have found that high nitrate levels will also render the ZSR mixing rule suspect. Of course, there is relatively little nitrate in the aerosol presented here (at least ostensibly), but there is certainly plenty of organic matter, typically at or in excess of a 50% mass fraction according to Figure 4. As noted by the authors, the ZSR mixing rule is relatively insensitive to this large organic fraction due to the cubic weighting of the GFs - and the assumed relatively low hygroscopicity of the organic fraction. However, this is not true of less approximate methods and the high organic mass fraction dictates that this issue be explored. I am not unalterably opposed to the use of the ZSR rule but its use needs to be justified here.

Answer: We agree that the ZSR model is a simplification, and do not intend to display that it in any way describes solute-solute interactions, which indeed it does not. It is also true that solute-solute interactions in specific inorganic/organic mixtures can have a substantial effect on the water uptake in terms of mass. These differences are much smaller in terms of diameter growth factors. The ZSR mixing rule has been shown to predict GFs of inorganic mixtures of atmospheric importance within +/-3% (Topping et al., 2005b). Inorganic/organic interactions may have somewhat larger effects, however, it may be better to ignore them fully if the specific system is not characterized than to use a different mixtures as a proxy because the sign of the interactions my be different (Choi and Chan, 2002; Topping et al., 2005a). The chemical information required for UNIFAC predictions is not available in this study. Therefore the ensemble organic GF has been optimized towards minimal differences between measurement and model prediction. This value gives an indication of the organic contribution to the hygroscopic growth, which includes the potential effect of organic/inorganic interactions. A discussion of the fitted organic GF in context to previous studies has been added (see reply above). The diameter growth factor of mixtures is always much more sensitive to the contributions of the most hygroscopic compounds. This is not a specific feature of the ZSR mixing rule. In this study we have used the ZSR rule along with a constant ensemble GF for the organic fraction in order to investigate, whether hygroscopic growth factors of an aged atmospheric aerosol can be predicted with a simplified, computationally efficient approach.

2.7 Page 13712, lines 1-11: I am not sure I follow the argument here concerning the partitioning of NH3 in solution. Thermodynamic equilibrium for the nitrate-sulfate-ammonia-water system has been studied for some time (cf. Seinfeld and Pandis, Atmospheric Chemistry and Physics, 2nd ed, Wiley InterScience,1998). The relative concentrations of the various aqueous ionic species will be determined by the absolute masses in the system (i.e., masses per unit volume of sampled air) together with the RH and temperature. Presumably, the authors have this information and there should therefore be no ambiguity in the speciation. Are there substantial organic acids present to complicate matters? Is there some question as to the validity of the nitrate measurements? Again, it has been known for sometime that one can evaporate nitrate particles in DMAs - and thus presumably in HTDMAs (cf., Khlystov et al, J. Aerosol Sci., 28, S1, s59-s60, 1997). If there is an issue here, it must be discussed. The Gysel et al citation simply, in so far as I can tell, reiterates the statement already in the text that the given choice of partitioning yields the best closure. I do not find this very satisfying. Why not do the detailed thermodynamic calculation and put the issue to rest?

Answer: We will improve clarity and readability of that section. The paragraph about the ion-pairing in the ZSR prediction for the nitrate-sulfate-ammonia-water system has been clarified (see reply above to point 1 of referee #2). Ammonium nitrate evaporation artifacts in the HTDMA are a potential issue as shown by Gysel et al. (in press). However, the nitrate fractions at the JFJ are fairly low. Careful analysis of the closure results in this study did not show any indication of such an evaporation artifact. In this study the HTDMA was operated at lower temperature thus minimising possible evaporation artifacts.

2.8 Page 13714, lines 11-20: In the abstract to this study, the authors state that hygroscopic closure was done using the HTDMA and AMS data by means of the ZSR mixing rule and that, "in general, a good agreement between measured and modeled data was found." One would expect that this apparently major theme would be reflected in the content of the paper but this does not seem to be the case. Here, we finally return to this topic but in a very vague and indecisive manner. Firstly, the closure is not actually presented except in a form that is difficult to quantitatively assess (the time series of Figure 4). Indeed, no quantitative assessment is given, at least in so far as I can see. There is nothing at all wrong with showing the time series of Figure 4 (though the figure should really be a bit larger). However, in addition, standard regression plots of the observed vs predicted values of GF should be given, showing the regression line(s). The R2 value(s) for the regression(s) should also be given, together with the regression coefficients and their uncertainties. Furthermore, I would have expected to see some discussion of the chemical composition characteristic of both good and bad closure. There IS some discussion of poor closure on page 13715, vis a vis nitrate evaporation as examined by Gysel et al but it is, again, non quantitative. This should be rectified.

Answer: To increase the discussion of the influence of the chemical composition, which would be advantageous to the paper, one could list the possible errors in the closure, namely: bimodality, chemical composition, GF measurement, ZSR model etc. A sensitivity could then be done by varying these parameters within their variability, which would have to be limited with reasonable assumptions. This would give each parameter's contribution to errors. We propose to do that and present that in a table, together with the values from the comparison predicted/measured for the FT and PBL INF cases. That would be the slope of the regression line, and Pearsons R-value. Concerning the nitrate question: we found no correlation between error model/measurements to nitrate concentration for the closures.

2.9 Page 13714, lines 20-23: The authors state that the absence of the m/z=57 peak indicates that there is little unprocessed, primary organic material present and that the majority of the organics are oxidized. I think that these assumptions are not warranted. The 57 peak is certainly associated with a commonly occurring hydrocarbon fragment - essentially a CH3CH2CH2CH2 group - but there are plenty of other fragment of different m/z associated with HCs (e.g., 41, 43, 55, 69, 71, etc.). Similarly, I do not understand at all the reasoning that says that the absence of this peak implies that the bulk of the organic material present is oxidized. The references cited certainly do not claim this. It may well be true, of course, that the organic matter present IS mostly oxidized, but the presence or absence of the 57 peak does not in itself determine this. The authors need to supply more support for their assertion.

Answer: We agree with the reviewers comment. The focus of this discussion should really be on the mass spectral pattern as a whole rather than on one specific mass fragment. We have now addressed this comment in the revised manuscript and replaced the original sentence with the following discussion:

"The mass spectra obtained by the AMS at the Jungfraujoch are characterised by the absence of the hydrocarbon mass fragments pattern from the ion series CnH(2n+1)+ (i.e. m/z 43, 57, 71, 85), indicating that little unprocessed primary organic material is present (Alfarra et al., 2004; Zhang et al., 2005). On the other hand, the spectra are dominated by mass fragment 44 which arises from CO2+ as a result of the thermal decomposition of highly oxygenated organic compounds in the AMS. This mass spectral pattern is typical for processed and aged organic aerosol (Alfarra et al., 2004; Zhang et al., 2007."

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