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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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General comment: It was encouraging to read the positive statements the reviewers made on the results in our paper. We thank the referees for their help which certainly will improve the quality of the article. Below we describe how we will accommodate the referees comments in the revised version.

Anonymous Referee #1

Point 1: First, please be more specific with the term "aerosol loading" on page 13703 (line 16), since this may mean different thing depending on the research topic (PM mass concentration, AOD, aerosol extinction, total particle number concentration etc.).

Answer: We have now done so. In the description of the Jungfraujoch site we wanted to introduce its seasonality, and for this paper the accumulation mode mass concentration and composition (basically organics and inorganics fractions in mass, for instance) are of importance. Both of these, but also AOD and number concentration do vary from winter to summer. This is now clarified in the paper: "The aerosol at the JFJ shows an annual cycle with highest mass concentrations in August to July and minimum concentrations in January to February, furthermore the organics fraction increases during summer season (e.g. Cozic et al., 2007c; Nyeki et al., 1998; Weingartner et al., 1999). These are the major factors influencing the hygroscopic properties studied in this article."

Point 2: Second, please define AS (apparently ammonium sulfate) on page 13707.

Answer: Is defined in Introduction, line 8, p 13702.

Point 3: Third, the discussion on the concept "GF" on page 13708 may not be clear for most of the readers. The authors might consider opening it a little bit more.

Answer: We will in the revised version further a) explain how we interpret an externally or quasi-internally mixed distribution, as opposed to a mono-modal distribution, as well as b) connect this paragraph to lines 1-5 of p 13707, where GF is introduced and defined in Eq. 1. c) A suitable reference for how modes appear as internally or externally mixed can be found in e.g. Buzorius et al., 2002, which is added for further information in our article. Also reviewer #3 required more clarity on the description of the inversion algorithm (second half of p 13708). That part of the text is extended and can be found under reviewer #3 (point 2.4), below.

Point 4: Fourth, the assumed growth factor of 1.2 for organic compounds at RH=85% seems rather high (page 13714) compared with the values observed in most laboratory experiments conducted for organic particles. This should be mentioned in the paper and a potential explanation for this difference would be useful. Answer: We acknowledge that the ensemble GF of the organics should be related to findings of other

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laboratory and field experiments (see also reviewer #2, point 4), which will be done in the revised manuscript. An ensemble GF for the organics of 1.2 at aw=0.85 (1.181 at RH=85% for D=100 nm) is indeed at the upper end of the range reported in laboratory experiments for SOA (e.g. Varutbangkul et al., 2006) or humic-like substances (HULIS) extracted from ambient samples (e.g. Gysel et al., 2004). However, Duplissy et al. (in press) have shown that the GF of SOA measured in smogchamber experiments can be substantially higher when using atmospherically relevant precursor concentrations. Furthermore the SOA GF increases continuously with ongoing photochemical reaction and can reach ˜1.2 at RH=85% for a-pinene SOA after 11 hours of illumination. Ensemble GFs reported for the organic fraction in previous field studies looking at SOA dominated or aged are masses are slightly smaller (Aklilu et al., 2006; Gysel et al., in press) or comparable (Carrico et al., 2005) to the findings in this study. The air masses at the JFJ are representative of a highly aged aerosol and therefore a relatively high ensemble organic GF is not surprising.

Point 5: Finally, on page 13716 (lines 15-17) it is stated that "The hygroscopicity for summer indicates a similar chemical composition for different sizes, while during winter the hygroscopicity increases with size". On the other hand, on page 13713 (lines 18-20) it is stated that "It is hypothesized that smaller particles contain a larger fraction of organic compounds from secondary organic aerosol (SOA) formation". Taken together, these two statements would indicate little SOA formation during summer and effective SOA formation during winter, which does not sound quite correct. Could there be other reasons for the observed size dependence of the growth factors beside SOA formation? For example, what could be the role of aging and associated sulfate formation by cloud processing in larger particles?

Answer: Indeed a sharp observation and an intriguing question. The first sentence (p. 13716) describes how an increased inorganics content increases GF (or, less possible to that large degree, how GForganics would have to increase) in winter, and also how this, presumably, inorganics content increases with size (as k-value increases with size,

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fig 3, panel a). During summer the organics content is larger and thus the GF remain lower and fairly similar for all sizes. This will be written more clearly as indicated above. We agree that the second sentence mentioned ("small particles, SOA", p. 13713) is not optimally written (e.g. "larger fraction" meant "increased fraction"). Moreover, the context of that section is still concerning the winter FT period, but actually our focus has now in this sentence shifted to summer campaigns. We propose to delete that sentence, especially as that topic is also again discussed on lines 7-11 on p. 13714, where it fits better with the context. In general we assume a model of the aerosol would include a fix part of black carbon with a relatively fix part of condensed OC and an inorganics fraction increasing with size. Added to that would be, when temperature, pre-cursors and sunlight allow, a proportional increase of SOA with these parameters.

Anonymous Referee #2

Point 1: One of the important findings that was highlighted in the conclusion is the choice of the two primary components for ZSR in the proton-ammonium-bisulfate-sulfate system. Kim et al. (1989) arrived at the same conclusion when they compared the ZSR predictions with the SCAPE predictions and EDB measurements.

Answer: That paper is now included as a reference, as indeed it is highlighting and treating that topic. Also reviewer #3 (point 2.7) required some more details here. The original manuscript was not quite clear regarding two different aspects: Firstly, the ZSR mixing rule is an approximation and it requires an ion pairing scheme, if different ions are possible. The differences between the ZSR approximation and full thermodynamic models can be kept small with an appropriate ion pairing scheme. The equations of the ion pairing scheme used in this study are provided in the study by Gysel et al., in press. Secondly, the GF of mixed particles is most sensitive to variations in the inorganic composition (e.g. (NH4)2SO4 versus NH4HSO4 or (NH4)2SO4 versus NH4NO3. Therefore a detailed speciation of the inorganic fraction is important to improve GF predictions of ambient particles. The points are clarified in the revised manuscript.

Point 2: What is the relationship between GF* and a volume or mass averaged growth factor? That would help readers relate the analyses of hygroscopic growth and chemical composition measurements.

Answer: See answer below (reviewer #3, point 2.4).

Point 3: The statistical analysis involves the use of a delta GF of 0.15 as a criterion for differentiating external and internal mixtures after hygroscopic growth. This is reasonable because the GF of the inorganics is sufficiently different from that chosen for the SOA. It may be a point that is worth highlighting.

Answer: Indeed we are thankful for a further argument in supporting our choice of size of GF bins. This has been added in the following sentence(s): Page 13708, line 12: "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."

Point 4: In the paper, the choice of GF=1.2 for organics is based on GF measured for SOA. Without a further elaboration on the chemical compositions and trajectory analysis to reveal the sources and reactions involved of the organics found in the campaign, the choice of GF=1.2 is not as justified as it should be. However, the choice of another GF value would probably not make a difference in the results presented because the overwhelming dominance of the inorganics in GF.

Answer: We have indeed used reported measured GF values of SOA as a guideline for the choice of GF organics, but furthermore chosen the GF organics that gives a best fit of the modeled GF values to the measured values. The choice of GF organics influences the results of the model (if GF at aw=0.85 is varied from 1.2 to 1.15, the slope of predicted versus measured GF is reduced from 0.99 (current choice) to ˜0.93). The influence is somewhat larger during summer, as the organics content then is higher. This text has been added to the paper. See also reviewer #1 (point 4) above for further clarifications on the GF of the organics.

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Point 5: From Figure 3, there appears bimodal distributions of GF near the period of 13.3.00 to 15.3.00 too. Answer: We agree. We cannot confirm any SDE there, however the angstrom exponent of the single scattering albedo, varies from 0.08 to -0.20 during that time period, but fluctuating hourly, making it difficult to determine the 3h air type. With the current instrument sensitivity (requiring 3 h averages) and method of evaluation we cannot with certainty label that air parcel as a well-defined SDE.

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