**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Particle hygroscopicity during atmospheric new particle formation events: implications for the chemical species contributing to particle growth" *by* Z. Wu et al.

Anonymous Referee #1

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Wu et al. performed measurements of aerosol particle size distributions, hygroscopicity and chemical composition at a mid-level mountain range in Germany, as part of a larger HCCT-2010 campaign. They use the data to interpret two very different new particle formation (NPF) events. The measurements and data seem of good quality, but both the methods and interpretation of the results leave much to be desired. While the subject of the study would fit the scope of the journal very well, I have several major comments that should be addressed before publication in ACP can be considered.

General comments:

Many of the methods used in this study are over-simplified, which by itself would not

be a problem if the interpretation of the results would be made accordingly. However, the authors seem to take the results almost at face value, discuss each individually, and do not try to combine all the results into any kind of larger picture which would increase our understanding of NPF. The conclusions in practice state that two different NPF events were observed, with the condensing vapors changing over time in both, and that some methods indicate strong H2SO4 involvement, while some indicate the opposite. This is not enough to warrant publication in ACP, and the analysis should be expanded and improved.

The authors measured growth rates during two NPF events. Then the composition of 10-50 nm particles is estimated using three different methods: 1) Calculating the contribution to growth from H2SO4 and coagulation. 2) Measuring the changes in hygroscopicity of 25-45 nm particles. 3) Measuring the changes in PM1 composition. During neither event do these methods agree. During the first event (Oct 12), method 1) suggests marginal contribution from sulfate, while 2) and 3) suggest a more pronounced contribution. On Oct 14, 1) shows that sulfate could explain the entire growth (though there was in fact none), while 2) shows that organics might be more important, and 3) is undecided. The authors add some speculation after each method, but there is practically no discussion on the discrepancies between the methods. Possible errors rising from the methods, calculations or interpretation need to be addressed for the reader to know if indeed any of the methods are actually reliable/applicable for getting information on the composition of 10-50 nm particles.

As a clear example of the lack of error analysis in the paper, at the end of section "2.5. Estimation of H2SO4 concentration", the authors claim that due to the high radiation during the events, the "proxy is accurate". Later the growth rate by H2SO4 during Oct 12 is reported to be 0.28 nm/h without any uncertainties discussed. Mikkonen et al (2011) gave an overall "relative error" of about 40% for the proxy, and also concluded that the proxy was worst at predicting H2SO4 concentrations at another mid-level mountain site in Germany. Based on Fig. 7 in that paper, one could conclude

that the error in the proxy might be up to a factor of 5 at times.

The homogeneity of the surroundings is a strongly underlying assumption throughout the paper, and this should be discussed in more detail, starting from a more detailed site description. To me, a mode of 25 nm particles appearing, remaining without growing for 4 hours and then disappearing, suggests inhomogeneous surroundings causing particle formation and growth. And if this is indeed the case, the NPF event on Oct 12 may also be influenced, and the observed GR may be an over- or underprediction of the real particle GR. Here the authors should make more use of the actual aim of the campaign, and do Lagrangian studies. The three stations are relatively close, but as the average wind speeds were around or below 1 m/s during both events, differences should be visible between the size distributions. This would give an independent GR measurement which should add valuable information to the interpretation. Additionally, I am extremely confused about Fig. S1. I am aware that the color scale is different, as well as the y-axis scale for some reason, as compared to Fig. 1, but should not the top two plots in Fig. 1 be the same as in Fig. S1? The modal diameter during Oct 12 seems to be clearly larger in Fig. 1 than in Fig. S1. Also, the top and bottom right plots in Fig. S1 are identical!

Another opportunity to make better use of the acquired data is to go further in calculating the "soluble fraction". The use of a "soluble fraction" is questionable, but it should be pointed out in the text that the main benefit of that term is that it is independent of particle size and the RH at which the GF was measured. The authors could try to relate the GF of the organics in the AMS to the measured GF based on O:C ratios (according to e.g. Massoli et al., 2010, Geophys Res Lett, Relationship between aerosol oxidation level and hygroscopic properties of laboratory generated secondary organic aerosol (SOA) particles).

Section 2.6: I had to look up Stoltzenburg et al (2005) to understand what calculations were actually made based on this section. As written now, the section is confusing, at least for readers who have not done these specific calculations themselves. Several

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equations are listed without a good explanation how one ties into the other, and the actual important steps are left unmentioned. The flow chart in Fig. A1 in Stoltzenburg et al (2005) is an extremely efficient way of showing what is actually done, and something similar would fit better into this paper than listing some equations that can be used to calculate different quantities. The authors should clarify this section, either by rephrasing the text and perhaps adding a flow chart, or as I would recommend, remove at least equations 5, 7 and 8, and just shortly explain the important steps and refer the interested readers to Stoltzenburg et al (2005). Lacking major points that definitely should be explicitly mentioned are that modes were fit to the SMPS data, and that the GR from H2SO4 is calculated based on the H2SO4 proxy. Finally, I do not understand the end of the section, where intramodal coagulation "can contribute to sulfate fraction". Intramodal coagulation should not change any fractions inside the mode.

The grammatical errors were too numerous to list in the technical corrections, and the language needs to be improved before publication in ACP is possible.

Specific comments:

Page 11416, line 5: HCCT should be written out or just not mentioned in the abstract.

11417, 6-17: In a list of instruments capable of measuring ultrafine particles, the NAMS should also be mentioned. See e.g. Zordan, C. A.; Wang, S.; Johnston, M. V. Time-resolved chemical composition of individual nanoparticles in urban air. Environ. Sci. Technol. 2008, 42 (17), 6631−6636.

11418, 22-24: Why do the authors talk about upwind and downwind sites? Does this not imply a constant wind direction? Now Goldlauter is named an upwind site, but at least in Fig. 2a, it should be downwind of the other sites.

11419, 10: What is an "automatic" silica gel dryer?

11419, 17-18: If you are going to talk about DMA1 and DMA2, they need to be mentioned earlier. Overall a 2-3 sentence explanation of the working principle of an HTDMA

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would be useful.

11420, 2: Draxler

11420, 18 & 22: First the authors state that SOA is typically hydrophobic, and then that SOA typically has a growth factor > 1. The intent with the soluble fraction needs to be clarified, together with an improved discussion on the organic growth contribution.

11424, 6-7: Are the authors implying that the end of the event and increase in wind speed are related? If so, please state how. Otherwise rephrase.

11424, 26-28: on Oct 14?

11425, 8: decreasing

11425, 15-16: If the mode was internally mixed, why does the GF at 30 nm differ so much from the rest?

11425, 25: I recommend that you do not speculate on which species took part in the actual nucleation based on the soluble fraction of 25 nm particles. What does the Zhang 2004b citation refer to in this sentence?

11426, 1-4: Certainly all these reaction would decrease the GF of H2SO4, but they would probably increase the GF contribution of any reacted organics. Are the authors sure that these reactions would cause a net decrease in GF of a particle?

11426, 13: Why only use 12:00-17:00. Earlier it is stated that the event continues until 20:00. The period 17-20 may be more interesting as the calculated H2SO4 is much lower (zero at the end of the event).

11427, 13: The authors seem to state that the derivative of a constant "cannot be calculated". It can, and the answer is zero, as also the authors deduce from their data.

11428, 17: I would not talk about "addition" when the rise in acidity is accompanied by a dramatic drop in concentration of all AMS species. Generally, the absolute concen-

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trations should also be taken into account in the interpretation of the data.

Fig. 2: Although it can be figured out, the position of the station should be clearly marked in the figure. Also, there is no need to show all of Europe in these maps. The different trajectories could be made out much better if the maps were zoomed in to e.g. 0-25 long, 50-60 lat.

Fig. 5 caption: The "ion molar ratio" should be explained here.

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