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Atmospheric
Chemistry
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Discussions

Interactive comment on "Influence of semi-volatile species on particle hygroscopic growth" *by* P. Villani et al.

Anonymous Referee #2

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Villani and coauthors report on VH-TDMA results (Volatility-Hygroscopicity Tandem Differential Mobility Analysis) results from 4 sites in Europe. The experimental technique measures the hygroscopic growth factor for particles in the atmosphere with and without pretreatment in a heater, running at 70 to 110 degrees centigrade and a residence time of 1 second. The sites are a mountaintop site with free troposphere exposure (PD), a coast site (Mace Head, MH), a small town (Clermont-Ferrand, CF), and a city (Leipzig, LZ).

The authors do not present any time series results, but rather focus on the average properties of 100 nm particles at each location. At all sites, particles in a non-hygroscopic mode are identified, and at all sites a moderately hygroscopic mode is seen. The non-hygroscopic mode does not appear during all periods at PD and MH.

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When the non-hygroscopic mode is not present at these sites (presumably anthropogenic organics), a highly hygroscopic mode appears, with GF $>$ 1.6 at 90% RH.

Except for one instance, preheating enhances the hygroscopicity of non-hygroscopic particles, for example from a growth factor of 1.08 to 1.12 at CF. Preheating can either enhance or depress hygroscopicity of the intermediate hygroscopicity particles, although the changes are smaller than the margins of error of the technique shown in table 2. The ratio of hygroscopic growth factors is probably more accurate than the absolute value of the individual numerator and denominator (the authors allude to this on page 2031). Highly hygroscopic particles have their hygroscopicity suppressed by preheating.

The paper also includes a modeling exercise where binary mixtures of sulfuric acid and a nonhygroscopic inert material are simulated at different mass fractions. The mass fractions are selected to mimic the possible changes in particle composition in their preheating system. The conclusion of the modeling exercise is that 5% changes in particle diameter can (under their assumptions) only lead to 2% changes in the hygroscopic growth factor. Therefore, they conclude that, 'the change in Hgf cannot theoretically exceed 2% when a particle is not allowed to lose more than 5% of its original diameter' (page 2036). Since the average experimental values are often in excess of 2% (and sometimes go to 10%) and the short term enhancement/suppression can go to 20%, the authors claim that gentle volatilization has a 'drastic' effect on hygroscopicity.

The paper should be accepted with major revisions. This reviewer has no problems with the experimental data itself. It seems of high quality and is reported with error estimates that seem reasonable.

Concerns: —- ONE ——— The paper has a bias toward self-citations, and is missing some important V-TDMA and VH-TDMA works.

The following papers come to mind:

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Brooks, DeMott, Kreidenweis. Water uptake by particles containing humic materials Atmos. Environ 38 (2004) 1859-1868.

Fletcher et al. Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign. Environmental Chemistry (2007).

Huffman, J. A. et al. Development and Characterization of a Fast-Stepping/Scanning Thermodenuder for Chemically Resolved...; Aerosol Science and Technology (2008).

An, WJ et al. Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol. J. Aerosol Sci (2007).

Brooks et al. have experimental growth factors for mixtures of ammonium sulfate and fulvic acid, which would be useful to check the model results from this work. (which has growth factors for sulfuric acid and fulvic acid).

Huffman et al., through coupling of an aerosol mass spec to a V-TDMA system show what temperatures various compounds come off at. The Huffman work is relevant to the hypothesis regarding nitrate on page 2035.

Fletcher have similar results that can be compared to the European stations.

An et al. show an effect of heater residence time.

—- TWO ——— Line 10, page 2029 says that the paper will not investigate the temporal behavior of the parameters studied (only their averages). This is understandable, but there are problems with this. First, there is significant variability in particle sources and composition on a diurnal basis at several of the sites, and it is a shame not to look at it. Second, the reader is referred to Sellegri 2008 for more details on the temporal behavior during the campaigns, but the abstract of that paper refers to the PD mountaintop site only. Third, the paper refers to the short term and temporal behavior many times. For example, on 2029 line 25 (MH has different day and night properties). Page 2034 line 24 - discusses that average behavior is not really the whole story, there are patterns in the data (for the effect of the preheater) on timescales of hours, and the peak behavior is perhaps notable. Page 2035 (again on 2037) discusses the results as evidence of transient processes in aerosol growth and aging. Page 2036, mentions the peak enhancement and suppression values from the time series. It seems that the actual time series are informing the conclusions and the hypotheses for future work. I do not see why they should not be included in the paper, even though this would be a major revision. I would rather read about the temporal and average behavior in one paper, rather than having these split between two. If the temporal behavior is not included (for example, in tabular form, or through time series plots, or as an appendix) then the multiple sections where the higher time resolved results (see above) are mentioned or used to inform a conclusion must be revised.

—- THREE — At first, it was unclear what the modeling section's purpose was. Although the reference is given, the model calculation is not developed enough (some equations and preliminary calculations/parameters) are needed so that someone else could repeat the calculation. Third, it would seem easy to add the relevant model equations. The model employed is very simplistic, and only when I realized the point was to give an upper bound estimate on enhancement or suppression, then it made sense to me. This purpose should be made clear at the beginning of the modeling section. The difference in the Kelvin effect between 100 and 93 nm is not significant enough to matter and does not need further discussion. Along similar lines, is really the Raoult effect that is called into question here (e.g. page 2036)? The authors should define the Raoult effect mathematically and discuss it in more detail. I think the basic issue is just the loss of nonhygroscopic organics leading to enhancement of hygroscopicity (in some cases) and the loss of hygroscopic salts in other cases (particularly ammonium nitrate) in other cases leading to suppression.

— FOURTH — At times in the modeling section, a 5% diameter change is referred to, and at other times, a 7% diameter change. This should be standardized to one value.

— FIVE — It does not seem fair to compare a fixed 5% (or possibly 7%) diameter change in the model, with diameter changes in the model that may be different during

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peak times. For example, when the large enhancement and suppression effects were seen (fig 1), what were the diameter changes due to volatilization during those periods? Correlation between enhancement/suppression and diameter loss would significantly strengthen the main result of the paper; that the gentle volatilization has important effects on physical properties.

— SIX — It seems problematic to use sulfuric acid as a species in the RH-TDMA model, since sulfuric acid has been shown to resist dehydration and crystallization at low RH. (e.g. Seinfeld and Pandis, and Tang JGR 101(D14) 19245 (1996). When the growth ratio is figured for the sulfuric acid mixture, is it assumed to have water or be water free at RH of 10%?

— SEVEN — Why is the 60/40 mixture selected as the starting point for the model? By using other starting mixtures, one can tune the suppression and enhancement effects.

— EIGHT — Using the simple additive model for organics and inorganics used in Brooks et al. (2004), my calculations show that a 7% diameter decrease (by evaporation of a non-volatile organic) can give a 4% increase in hygroscopicity at 90% RH, and that this works for inorganic fractions of ammonium sulfate or sulfuric acid. (The mass fractions start at 60/40, similar to the current work). This calls into question the statements that a 5% diameter change is never consistent with more than a 2% enhancement or suppression. Furthermore, by tuning the starting composition, one can match the initial GF and the change in GF for the average behavior for the intermediate hygroscopicity mode. However, I do show that the enhancement in hygroscopicity for the non-hygroscopic particles is much harder to explain. Loss of appreciable amounts of nonhygroscopic organics are necessary (13-14% diameter change) would be needed to get a 10% enhancement in hygroscopicity. The Brooks et al. model does not account for any interactions in solution between dissolved salts and the organics. There are several models (not cited in the work) more recent than Saxena and HIldemann that can take into account salt-organic interactions.

— NINE — Is there any lab data to support a 90% RH growth factor of 1.71 for a 40/60 fulvic acid-sulfuric acid mixture? Using the simple additive model of Brooks et al., I calculate a growth factor of 1.49-1.61 for this system (depending on whether crystallization is assumed). The authors should explain this discrepancy, even if it is just a feature of the thermodynamic model used in this work.

— TEN — Considering the combined questions around the model (mainly concerns 5-8), and the issue of temporal variability (concern 2), I think that the statements on the drastic and/or difficult-to-explain effects of semivolatile evaporation are not supported in the manuscript.

Technical corrections: on page 2035, a citation is needed for the nitrate volatilization. on pages 2023 and 2024 the phrase 'a certain number' is overused on page 2026, should it be T-naught $>$ T-amb at line 4 (the text has T $>$ Tamb) page 2028 line 14 should be parish not perish

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 2021, 2009.