**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

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

P. Villani et al.

The work of the reviewers on this paper was particularly well done and their comments exhaustive. We are very grateful for this and tried to follow most of their suggestions. We hope that the quality of the paper is significantly enhanced.

Reviewer #1

1. The text in the manuscript is often unclear about Kohler theory. In particular the introduction is confusing, mixing hygroscopicity, solubility, kinetic, and size effects. I recommend clarifying this section, also accounting for some literature that so far has not been included.

This is true, we clarified the introduction

(a) The closure study by Snider and Brenguier (2000) relied both on sizes and assumed

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chemical composition to predict CCN concentrations and this is as much a test of Kohler theory than challenging the accurate sizing of optical particle counters as well as number and supersaturation calibration of CCN instruments. We do not wish to detail the inaccuracies of the closure study from Snider and Brenguier here. Consequently, we decided not to cite their work following your suggestion.

(b) The study of Svenningsson et al. is not invalidating Kohler theory (pg. 2023, ln16); it merely demonstrates that the ZSR assumption may lead to some errors in predicted growth factors. However, as shown in Petters and Kreidenweis (2007) it is difficult to resolve this non-ideal mixing of compounds when propagating measurement errors into the prediction. Yes, we agree with you; we modified our text accordingly and clarified the confusion made between Kohler theory and ZSR rule.

(c) I am not aware of measurements that have demonstrated that organic compounds are more hygroscopic than inorganic compounds, as is insinuated on pg. 2023, ln 21. This is not what we meant, and we agree that the sentence was confusing. We modified the text accordingly.

(d) Hygroscopic growth and solubility are generally not related, contrary to the statement on pg. 2024, ln 3. True, particles must be sufficiently soluble to express their hygroscopicity and insoluble particles do not grow. However, insoluble compounds such as $CaSO_4$ have similar hygroscopicity than sulfuric acid, while infinitely soluble compounds, such as humic acid have low hygroscopicities. For detailed discussion on (sufficient) solubility and hygroscopicity see (Kelly et al., 2007; Laaksonen et al., 1998; Petters and Kreidenweis, 2008; Raymond and Pandis, 2003; Shulman et al., 1996) You are right and again, our sentence was misleading: we did not mean that the solubility determines hygroscopcity, but that water uptake measurements have been used in the literature to infer the aerosol soluble fraction in various environments. This is now better explained in the text earlier in the introduction.

(e) The fact that organic compounds may delay the growth rate is important (see also

Sjogren et al., 2007). However, it should be made clear that this study cannot address the role of this effect. Further, it is troubling if growth delays are asserted because this means that equilibrium concepts, such as Kohler theory, are not applicable to the data at all. I believe, however, that the situation is not so dire since all of the observations of organic aerosol hygroscopicity have similar growth times built in. This needs to be discussed in more detail in the manuscript. Our study can indeed not address the question of growth rates. However, changes in growth rates due to the volatilization of some trace species can affect our HGF measurement if the residence time in the humidified section of our VHTDMA is not sufficient. This question is now discussed in more details in the manuscript, in the discussion section

(f) It is stated that "synthetic particles" do not properly simulate the chemical complexity of organic aerosols (pg. 2024). Later it is said that thermodynamic data of organic compounds (ambient and synthetic) is largely lacking. I disagree. A lot of research has been done on organic compounds since the study of Saxena and Hildeman appeared first in 1996. Water uptake/activity data of pure and internally mixed dicarboxilic acids (Prenni et al., 2003; Prenni et al., 2001), saccharides (Chan et al., 2008; Rosenoern et al., 2005), humic and fulvic acids/HULIS, high molecular weight organics (Brooks et al., 2004; Dinar et al., 2007; Dinar et al., 2006; Gysel et al., 2004; Petters et al., 2006a; Wex et al., 2007; Ziese et al., 2008), polyols (Ekström et al., 2009; Marcolli and Peter, 2005), secondary organic aerosols generated from various precursors (Baltensperger et al., 2005; Meyer et al., 2009; Prenni et al., 2007; Varutbangkul et al., 2006), soot and primary organic aerosol (Dusek et al., 2006; Petters et al., 2006b; Weingartner et al., 1997) phenols and sparingly soluble/insoluble organics (Huff Hartz et al., 2006; Raymond and Pandis, 2002, 2003) and the ambient organic aerosol fraction (Shantz et al., 2008; Wang et al., 2008) are now available. Combined these measurements give an overview of organic aerosol hygroscopicity covering the range for organic aerosol kappa = 0 to _ 0.2 (with exception of oxalic acid which is more hygroscopic), characterizing their hygroscopic properties in the subsaturated range. I believe that it important to draw on this work in both the introduction and the analysis that follows in the

manuscript. We followed these suggestions and included most of the references in the manuscript, both in the introduction and further in the paper. We are gratefull for providing us with this nice overview.

(g) There is no discussion on previous VTDMA work (e.g., Fletcher et al., 2007). A paragraph summarizing previous similar observations would be helpful. Especially the relationship between volatility and hygroscopicity has also been discussed by (Asa-Awuku et al., 2009). It should strongly be noted that VTDMA do not necessarily measure equilibrium states and residence time plays an important role in interpreting volatility data (An et al., 2007). We now acknowledge the work of Fletcher et al. 2007, as well as previous work on volatility studies. The relationship between volatility and hygroscocpicity is also mentioned, although our goal here is to investigate the role of ageing on the hygroscocpic properties of aerosols, and not document the relationship between volatility and hygrosoccicity.

2. I am not sure on how to interpret the disappearance of number fractions. It is troubling that Class III aerosol are destroyed and Class II aerosol is generated. Since there is only one VHGF mode this implies that volatility is distributed homogeneously for the 100 nm particles. The differential change in HGF (some grow a lot less than their original class, some a little less and remain in the same class) suggests otherwise. (a) How can these two points be reconciled? (1) Volatility is not as discriminating as hygroscopicity regarding the chemical composition of an aerosol particle: it happens frequently that an external mixing of particles observed from hygroscopicity measurements have the same volatility. It is hence possible that two aerosol populations have the same volatility but not the same hygroscocpicity. Moreover, at 100$°$C, two different volatility properties are hardly discriminated in the V mode (we tried to keep the fraction of volatilized mass low). (2) One moderately hygroscopic particles mode can also be composed of two sub-populations of aerosols found as an external mixture, but having similar hygroscopicities (inorganic/organic mixtures with different ratios and hygroscopic properties). One of these two sub-populations can be significantly modi-

fied by the condensation of a compound which will modify its surface/kinetic properties. This is now better explained in the text.

(b) What does that mean then that HGF decreased by a certain fraction after volatilization? The Class III aerosols are not necessarily homogeneous. In the Case of Mace Head, they can be a combination of NH4SO4+organics or NaCl+organics with proportions that give similar HGF (not distinguishable within the VHTDMA accuracy). Once volatilized, the different organics leave the "pure sea salt" on one hand (which end up in class III) and the Nh4SO4-like aerosols on the other hand. This hypothesis is now explained in the text.

(c) To me it seems that the classification into Class I-III is not necessarily helpful. Instead it would be better to plot a distribution of HGF change after volatilization and report the moments of this distribution. The data sets which are used in the present paper covers several field campaigns and it is more synthetic to use a table for presenting the hygroscopic changes due to volatilization. Figures would give qualitative information and we wanted to be quantitative here. We however plot one example for the Mace Head data set though.

3. The modeling analysis relating HGF and VHGF is not very clear and the two model mixtures are not sufficient to draw the sweeping conclusion that the Raoult effect is insufficient to explain the change in HGF after volatilization. Assertions about surface tension and kinetic effects (pg. 2034) are not sufficiently supported by the data analysis. Further, using relative changes in growth factor are not very meaningful as I discuss later. I have outlined both my objections and how I would analyze the data below, making use of the single parameter hygroscopicity framework (Petters and Kreidenweis, 2007, 2008; Rissler et al., 2006; Vestin et al., 2007; Wex et al., 2007). I realize that this analysis does reflect in part my own biases on how I think about modeling hygroscopicity and other equivalent methods may be employed by the authors instead. Finally, given my previous comment the authors should consider if the question that I answer below based on the information of the manuscript is not ill-posed. If

not the following or similar analysis should be included in the manuscript. The observations presented in the manuscript are: A 3-11 nm reduction of a 100 nm particle leads to changes in relative change growth factor from -10% to +4%. To address whether this can be explained only by the Raoult effect, or surface tension and/or kinetic effects should be considered we can convert the growth factor data into hygroscopicity space using gf3 − 1 = _ aw 1−aw where gf is the growth factor, _ is the hygroscopicity parameter, and aw is the water activity (calculated from removing the Kelvin effect from the grown droplet as shown in PK07). Here kappa denotes the Raoult driving force that is expressed in the form of the growth factor. The relative sensitivity dln(gf)/dln(_) is dln(gf) dln(_) = 1/3 aw_ 1−aw−_aw If the relative sensitivity dlnX/dlnY evaluates to a number (e.g. 1/2), then a 10% change in X, corresponds to 5% increase in Y. Here it can be seen that the relative sensitivity of the growth factor depends on the absolute value of kappa, or the growth factor itself. The measurements were taken at RH _ 90% and hence aw_ 0.9. In this case: dln(gf) dln(_) = 3_1+9_ Taking Puy de Dome, period 1, and assuming aw = 0.9 I calculate _ = 0.569, 0.175, 0.025 for Class III, II, and I, respectively. Correspondingly, the relative sensitivities are 0.28, 0.20, and 0.06. This implies that a 10% change in growth factor corresponds to a 2.8% in _ (or Raoult term) for Class 3 but only a 0.6% change in _ for Class I. This is why I consider the relative changes in growth factor plotted in Figure 2 and presented in the manuscript misleading. Showing them in kappa space (or equivalent) is more meaningful from a physical perspective. The second question is whether the underlying changes in kappa values are consistent with changes in particle diameter. The modeling presented in the manuscript is a first step. However, I believe the problem can be solved more generally. For a mixed particle the overall hygroscopicity of the particle can be written as the volume weighted hygroscopicity of its individual components. For the following discussion we may consider to conceptually split the particle into a volatile component having _1 and a non volatile component having _2, the volume fraction of the non volatile component _. (1-_ is then the volume fraction of the volatile component). This results in _overall = __1 + (1 − _)_2 This ex-

pression assumes ZSR mixing and zero volume change due to mixing. The relative sensitivity is dln(_) dln(_) = (_1−_2)_ _overall For simplicity we may assume that _2 = 0, in that case the sensitivity is dln(_) dln(_) = _ This equation implies that a 10% change in kappa is equivalent to a 5% change in _ if the volume fraction of the non volatile compound is 0.5. For different choices of_2 the system is less sensitive. How does this sensitivity compare to the volatility growth factor? _new = D3 nonvolatile/D3 90 _old = D3 nonvolatile/D3 _new/_old = V hgf3 This implies that Vhgf = 0.96 (upper bound in Table 2) corresponds to a 12% change in non volatile component volume fraction. A 10% change in growth factor corresponds at maximum to 2.8% change in kappa. At epsilon = 0.5 this corresponds to a necessary 1.4% change in epsilon to explain the growth factor change by the Raoult effect. This compares to a 12% change that can be sustained by even a modest volatility growth factor. Based on this, the volatility growth factors can fully explain the change in hygroscopicity. Reference to surface tension or kinetic effects is not required, although it can of course not be excluded based on this analysis alone. Your analysis is perfectly right; we agree that the HGF change when a fraction of the aerosol is volatilized can be explained by the raoult effect. This is now better explained in the text. However, the raoult effect can not explain the change of hygroscopicity class for a fraction or the totality of an aerosol class. We now provide an analysis similar to yours, and make clear that the raoult effect can explain most changes (on averages) expect the Mace Head and PDD cases. Figure 2 was consequently not necessary and do not appear anymore in the paper.

4. A similar analysis is necessary to show that the volatilization of nitrates can explain the decreased growth factors (Class III to Class II conversion). Done for both cases.

Other comments Pg. 2032, 15: The description of "fully hygroscopic" and "fully hydrophobic" does not make sense to me. To my mind the hygroscopicity is a property of a compound that ranges from non-hygroscopic (no growth factor), to varying degrees of hygroscopicity, which is expressed by the compounds growth factor. corrected

Pg. 2032, 18: Fulvic acid is hygroscopic and has kappa _ 0.05 (Petters and Krei-

denweis and references therein). Pg. 2033: I am skeptical about the chosen model compounds. Fulvic acid does not seem volatile to me; it also is not non-hygroscopic. Are the model results in agreement with data for this system? The choice of example models strikes me as somewhat arbitrary and not validated against data (see also comment of the other reviewer). This is correct. We now use model imaginary compounds with kappa of 0 for the hydrophobic fraction and 0.8 for the hygroscopic fraction.

Pg. 2034: "presence of HNO3 on the particle surface, even at low concentration, is likely to increase hygroscopic growth (Kulmala et al., 1998)". This can be assessed quantitatively. A fraction of XX% nitrate increases the hygroscopicity of a kappa = YY particle by ZZ %, corresponding to a change in growth factor by a AA%. The extreme values of kappa used for the hygroscopic and hydrophic fraction now stand for upper limits of the effects that could be due to the raoult term and no kinetic parameter.The effect is higher than what HNO3 could lead to if no kinetic or surface effect was taken into account.

It should be noted that nitric acid is water soluble and dissolution of the gas in the aqueous solution by Henry’s law partitioning, followed by dissociation, is also a mechanism that may need to be accounted for (Laaksonen et al., 1998). Could it be that the thermodenuder scrubs the gas phase nitrate, but this is not the case when measuring regular growth factors? We do not believe so. The dissolution of gas phase nitrate into hydrated aerosols in the second DMA can not occur during regular growth factor measurements, because the gas phase is not representative eof the ambient atmosphere but the one of the sheath air in the DMA. The fact that the aerosol flow is passing through a thermodenuder or not should not change the gaz phase composition of the sheath air in the second DMA.

Pg. 2037: "Because the link between hygroscopic growth and CCN activity is not linear, it is, however, difficult at this point to predict this effect on CCN activation from our measurements." I slightly disagree with that statement. If particle size and kappa are known it is trivial to calculate CCN activity. Although this estimate does fail for some

secondary organic aerosols and aerosol water extracts (Prenni et al., 2007; Ziese et al., 2008) it generally gives predictions within 30% (Carrico et al., 2008; Chan et al., 2008; Duplissy et al., 2008; Petters and Kreidenweis, 2007). Most of the literature cited is dealing with laboratory generated aerosols while we are dealing with atmospheric natural aerosols; Hence, we are not sure that, in our case, sub-saturation behaviour would be reliable for an extrapolation to sur-saturation conditions, especially when the sub-saturation behaviour is not quite understood. However, we agree with you that the sentence is not adequate and we not precise it following his advises.

The terms hydrophobic/hydrophilic; hygroscopic/nonhygroscopic, soluble/insoluble, should be defined and not used synonymously. Corrected

The meaning of Figure 1 is not clear to me. As shown by the equations above there is some relationship between VHGF and HGF, and such a space would make sense for the plotting (either individual data pairs or perhaps averages, although averages may obscure the physical interpretation). Superimposed could be predictions for certain model assumptions. Before submitting a revised manuscript the authors should carefully proofread the manuscript to eliminate spelling mistakes (for example Kohler, Köhler, Kolher, Prenny). Figure 1 is replaced by numbers in the text. Spelling mistakes corrected.

Reviewer #2

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: 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. We now refer to most references cited above. We did not use the work of Brooks et al. because we do not use fulvic acid anymore, and we refer to Huffman et al. 2009 instead of Huffman et al. 2007.

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. Even if the main goal of the paper is to show the effect of semivolatile compounds on the particle hygrosocpicity, we now show the temporal behaviour of the HGF over each site and briefly discuss them..

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. Yes this is an error, only Sellegri et al 2003, dealing with chemical analysis at pdd is referenced, while Sellegri et al. 2008, which deals with VHTDMA measurmetns at Mace Head has been omitted in the reference list; this is now corrected.

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.

We agree with the reviewer and added a section on the variability of the H to VH changes. We focused on the sub-data set for which we identified a clear change be-tween HGF and VHGF (Mace Head period 1). First we provide average HGF and VHGF distribution with standard dev for each of this period. Then, we study the scan-to-scan variability. The Delta GF (=VHGF-HGF) and delta nf (nf(VH)-nf(H)) are indeed very much more variable when observed scan by scan than when observed on an average. In order to illustrate this variability, we plotted (nf3-nf2) vs time.

The uncertainty due to the fitting procedure is of course stronger than when the analy-sis is performed on an average GF distribution, but we still can observe that the gain (or loss) of hygroscopicity is persistent only over three or four successive series of scans (about three hours), which points to transient phases of condensation of vapours during a few hours rather than stable chemical composition effects.

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 some-one 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 mod-

eling section. Yes it is now made clearer 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. Yes this is exactly what we meant by choosing sulphuric acid and fulvic acids as model salts. We now, as suggested by M. Petters use imaginary model compounds with extreme hygroscopic behaviours in order to evaluate if kinetic or surface effects are needed to explain our results.

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. done

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 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. Yes this is now addressed in details in the paper: the volatility growth factors are carefully studied at times when the volatilization has the highest impact (change of hygroscopicity classes). We did not find any correlation between the Vgf and the gain/loss of hygroscopicity. This implies that the gain/loss effects are not driven by the raoult effect due to a change of mass but rather by surface/kinetic parameters.

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%? Low RH effects are not taken into account in the model, simply the equilibrium at 90% RH is calculated

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. We now model the amount of aerosol mass which would need to be volatilized to explain the hygroscopicity change.

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. Again, we fully agree with both the reviewers. As mentioned earlier, the conclusions stating that HGF changes could not be explained by the raoult effect have been modified. We now discuss only the change in hygroscopicity class and corrected our calculations according to the suggestions.

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. We now include new calculations and temporal variability; the statement stands only for a fraction of the data set.

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 done

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