Atmos. Chem. Phys. Discuss., 9, S965–S976, 2009
www.atmos-chem-phys-discuss.net/9/S965/2009/

Atmospheric
Chemistry
and Physics
Discussions

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

M. Petters (Referee)

petters@atmos.colostate.edu

Received and published: 21 March 2009

The authors present observations of hygroscopic growth factors and volatility growth factors for ambient aerosol at four different field sites in Europe. The data are grouped into different growth classes and are stratified by air mass origin. Data analysis focuses on relating volatility and hygroscopicity through a modeling exercise considering mixtures of sulfuric and fulvic acid in various mass fractions. Based on the model results the authors conclude that the observed changes in growth factor are in part due to changes in the vapor pressure lowering ability of the remaining mixture (Raoult effect). Changes in surface tension and kinetic limitations to hygroscopic growth are invoked because the Raoult effect could not fully account for the observed changes in growth factor due to volatilization.

This is a timely paper and the data are highly relevant to the readers of Atmospheric Chemistry and Physics. Unfortunately, the conclusion reached in the manuscript are not fully supported by the analysis. Numerous conceptual, typographical, and grammatical mistakes make it unnecessarily difficult to fully appreciate the quality of the experimental work. I recommend the manuscript for publication after the authors address the following concerns.

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.
    (a) The closure study by Snider and Brenguier (2000) relied both on sizes and assumed 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.
    (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.
    (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.
    (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 CaSO4 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)

(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.

(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 $\sim$ 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.

   (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).

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?

   (b) What does that mean then that HGF decreased by a certain fraction after volatilization?

   (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.

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

$gf^3 - 1 = \kappa\frac{a_w}{1-a_w}$.

where gf is the growth factor, κ is the hygroscopicity parameter, and a_w 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 $dln(gf)/dln(\kappa)$ is

$\frac{dln(gf)}{dln(\kappa)} = 1/3\frac{a_w\kappa}{1-aw-\kappa aw}$

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 $\sim$ 90% and hence aw $\sim$ 0.9. In this case:

$$\frac{dln(gf)}{dln(\kappa)} = \frac{3\kappa}{1+9\kappa}$$

Taking Puy de Dome, period 1, and assuming a_w = 0.9 I calculate κ = 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 κ (or Raoult term) for Class 3 but only a 0.6% change in κ 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 κ_1 and a non volatile component having κ_2, the volume fraction of the non volatile component ϵ. (1-ϵ is then the volume fraction of the volatile component). This results in

$$\kappa_{overall} = \epsilon\kappa_1 + (1-\epsilon)\kappa_2$$

This expression assumes ZSR mixing and zero volume change due to mixing. The relative sensitivity is

$$\frac{dln(\kappa)}{dln(\epsilon)} = \frac{(\kappa_1-\kappa_2)\epsilon}{\kappa_{overall}}.$$

For simplicity we may assume that κ_2 = 0, in that case the sensitivity is

$$\frac{dln(\kappa)}{dln(\epsilon)} = \epsilon$$

This equation implies that a 10% change in kappa is equivalent to a 5% change in ϵ if the volume fraction of the non volatile compound is 0.5. For different choices of

κ_2 the system is less sensitive. How does this sensitivity compare to the volatility growth factor?

$$\epsilon_{new} = D^3_{nonvolatile}/D^3_{90}$$

$$\epsilon_{old} = D^3_{nonvolatile}/D^3$$

$$\epsilon_{new}/\epsilon_{old} = Vhgf^3$$

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.

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).

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.

Pg. 2032, 18: Fulvic acid is hygroscopic and has kappa ~ 0.05 (Petters and Kreidenweis 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

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

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).

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%. 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?

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).

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

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).

References

W.J. An, R.K. Pathak, B.H. Lee and S.N. Pandis, Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol, J Aerosol Sci 38(2007), pp. 305-314.

A. Asa-Awuku, G.J. Engelhart, B.H. Lee, S.N. Pandis and A. Nenes, Relating CCN activity, volatility, and droplet growth kinetics of 946;-caryophyllene secondary organic aerosol, Atmos Chem Phys 9(2009), pp. 795-812.

U. Baltensperger et al., Secondary organic aerosols from anthropogenic and biogenic precursors, Faraday Discuss 130(2005), pp. 265-278.

S.D. Brooks, P.J. DeMott and S.M. Kreidenweis, Water uptake by particles containing humic materials and mixtures of humic materials with ammonium sulfate, Atmospheric Environment 38(2004), pp. 1859-1868.

C.M. Carrico et al., Aerosol hygroscopicity and cloud droplet activation of extracts of filters from biomass burning experiments, J Geophys Res 113(2008), p. 08206.

M.N. Chan, S.M. Kreidenweis and C.K. Chan, Measurements of the Hygroscopic and Deliquescence Properties of Organic Compounds of Different Solubilities in Water and Their Relationship with Cloud Condensation Nuclei Activities, Environ Sci Technol 42(2008), pp. 3602-3608.

E. Dinar et al., Hygroscopic growth of atmospheric and model humic-like substances, Journal of Geophysical Research-Atmospheres 112(2007), p. D05211.

E. Dinar et al., Cloud Condensation Nuclei properties of model and atmospheric HULIS, Atmospheric Chemistry and Physics 6(2006), pp. 2465-2481.

J. Duplissy et al., Cloud forming potential of secondary organic aerosol under near atmospheric conditions, Geophys Res Lett 35(2008), p. L03818.

U. Dusek, G.P. Reischl and R. Hitzenberger, CCN activation of pure and coated carbon black particles, Environ Sci Technol 40(2006), pp. 1223-1230.

S. Ekström, B. Noziere and H.C. Hansson, The Cloud Condensation Nuclei (CCN) properties of 2-methyltetrols and C3-C6 polyols from osmolality and surface tension measurements, Atmos Chem Phys 9(2009), pp. 973-980.

C.A. Fletcher, G.R. Johnson, Z.D. Ristovski and M. Harvey, Hygroscopic and volatile properties of marine aerosol observed at Cape Grim during the P2P campaign, Environ Chem 4(2007), pp. 1628211;171

M. Gysel et al., Hygroscopic properties of water-soluble matter and humic-like organics in atmospheric fine aerosol, Atmospheric Chemistry and Physics 4(2004), pp. 35-50.

K.E.H. Huff Hartz et al., Cloud condensation nuclei activation of limited solubility organic aerosol, Atmospheric Environment 40(2006), pp. 605-617.

J.T. Kelly, C.C. Chuang and A.S. Wexler, Influence of dust composition on cloud droplet formation, Atmospheric Environment 41(2007), pp. 2904-2916.

A. Laaksonen, P. Korhonen, M. Kulmala and R.J. Charlson, Modification of the Köhler equation to include soluble trace gases and slightly soluble substances, Journal of the Atmospheric Sciences 55(1998), pp. 853-862.

C. Marcolli and T. Peter, Water activity in polyol/water systems: new UNIFAC parameterization, Atmos Chem Phys 5(2005), pp. 1545-1555.

N.K. Meyer et al., Analysis of the hygroscopic and volatile properties of ammonium sulphate seeded and unseeded SOA particles, Atmos Chem Phys 9(2009), pp. 721-731.

M.D. Petters and S.M. Kreidenweis, A single parameter representation of hygroscopicity growth and cloud condensation nucleus activity, Atmos Chem Phys 7(2007), pp. 1961-1971.

M.D. Petters and S.M. Kreidenweis, A single parameter representation of hygroscopic growth and cloud condensation nucleus activity 8211; Part 2: Including solubility, Atmos Chem Phys 8(2008), pp. 6273-6279.

M.D. Petters et al., Cloud droplet activation of polymerized organic aerosol, Tellus Series B-Chemical and Physical Meteorology 58(2006a), pp. 196-205.

M.D. Petters et al., Chemical aging and the hydrophobic-to-hydrophilic conversion of carbonaceous aerosol, Geophys Res Lett 33(2006b), p. L24806.

A.J. Prenni, P.J. DeMott and S.M. Kreidenweis, Water uptake of internally mixed particles containing ammonium sulfate and dicarboxylic acids, Atmospheric Environment 37(2003), pp. 4243-4251.

A.J. Prenni et al., The effects of low molecular weight dicarboxylic acids on cloud formation, Journal of Physical Chemistry A 105(2001), pp. 11240-11248.

A.J. Prenni et al., Cloud drop activation of secondary organic aerosol, J Geophys Res 112(2007), p. D10223.

T.M. Raymond and S.N. Pandis, Cloud activation of single-component organic aerosol particles, J Geophys Res 107(2002), p. 4787.

T.M. Raymond and S.N. Pandis, Formation of cloud droplets by multicomponent organic particles, Journal of Geophysical Research-Atmospheres 108(2003), p. 4469.

J. Rissler et al., Size distribution and hygroscopic properties of aerosol particles from dry-season biomass burning in Amazonia, Atmos Chem Phys 6(2006), pp. 471-491.

T. Rosenoern, G. Kiss and M. Bilde, Cloud droplet activation of saccharides and levoglucosan particles, Atmos Environ 40(2005), pp. 1794-1802.

N.C. Shantz, W.R. Leaitch, L. Phinney, D. Toom-Sauntry and M. Mozurkewich, The effect of organic compounds on the growth rate of cloud droplets in marine and forest settings, Atmos Chem Phys 8(2008), pp. 58698211;5887.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

M.L. Shulman, M.C. Jacobson, R.J. Carlson, R.E. Synovec and T.E. Young, Dissolution behavior and surface tension effects of organic compounds in nucleating cloud droplets, Geophysical Research Letters 23(1996), pp. 277-280.

S. Sjogren et al., Hygroscopic growth and water uptake kinetics of two-phase aerosol particles consisting of ammonium sulfate, adipic and humic acid mixtures, J Aerosol Sci 38(2007), pp. 157-171.

V. Varutbangkul et al., Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds, Atmos Chem Phys 6(2006), pp. 2367-2388.

A. Vestin, J. Rissler, E. Swietlicki, G.P. Frank and M.O. Andreae, Cloud-nucleating properties of the Amazonian biomass burning aerosol: Cloud condensation nuclei measurements and modeling, Journal of Geophysical Research-Atmospheres 112(2007), p. D14201.

J. Wang, Y.N. Lee, P.H. Daum, J. Jayne and M.L. Alexander, Effects of aerosol organics on cloud condensation nucleus (CCN) concentration and first indirect aerosol effect, Atmos Chem Phys 8(2008), pp. 6325-6339.

E. Weingartner, H. Burtscher and U. Baltensperger, Hygroscopic properties of carbon and diesel soot particles, Atmospheric Environment 31(1997), pp. 2311-2327.

H. Wex et al., Hygroscopic growth and measured and modeled critical supersaturations of an atmospheric HULIS sample, Geophys Res Lett 34(2007), p. L02818.

M. Ziese et al., Hygroscopic growth and activation of HULIS particles: experimental data and a new iterative parameterization scheme for complex aerosol particles, Atmos Chem Phys 8(2008), pp. 1855-1866.

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

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper