A. Laaksonen (Referee)

In this manuscript, the authors apply two techniques in order to obtain information about the volatility of newly formed atmospheric particles. They perform extensive aerosol dynamics modeling in order to mimic observed particle growth, and perform a number of sensitivity tests in order to find out how different values of effective saturation vapour density and other particle properties affect the growth. They also model particle evaporation in volatility TDMA to obtain constraints for the effective volatilities based on VTDMA measurements. I think that this is a well written (although there seem to be some typos and missing words) and valuable manuscript that fits the scope of ACP very well. However, I have some concerns that the authors should address before I can recommend publication.

I am very surprised, especially given the author list of the ms, that Kulmala et al. (Tellus 50B, 449,1998) has not been referenced. It should be referred to, and in fact it should be extensively discussed in the final paper. Kulmala et al performed very similar aerosol dynamics modeling as has been done here, albeit using a simpler model (three monodisperse modes instead of a spectrum of size classes). However, the simplicity of the model should not prevent the results they obtained to be in the same ballpark as the present results. But the fact is that the upper limit of effective saturation vapour density reported by Kulmala et al. (10ˆ5 molecules per cc) is almost two and half orders of magnitude lower than what is given in the present work. It appears to me that one reason for the discrepancy is that Kulmala et al. paid more attention to the growth rate of the nucleation mode in the beginning of the growth, while in the present work the main criterion appears to be the final size of the particles. Note that the final size depends on the integral of the condensable vapor production, and the same integral can be achieved with very different concentration profiles as a function of time - e.g. a flat and a strongly peaked profile can yield the same integral. However, the growth rate of the particles depends on the concentration of the vapour, and in these two cases the growth would appear quite different.

The lack of mention of Kulmala et al. (1998) was certainly on oversight. It is a very related paper and is now discussed and compared against in the text (shown later).

There are several other differences between Kulmala et al. (1998) study and the current study that are likely more important than the difference between the modal and bin structures. (1) In Kulmala et al. (1998) only one species (along with water) is allowed to condense in each simulation; however, in the present study, each simulation includes sulfuric acid condensation (constrained by CIMS or AMS) and condensation of at least one organic species (condensation rate constrained by AMS measurements). Even though sulfuric acid condensation was less than organic condensation during each of the chosen days, it will contribute to growth of the smallest particles. (2) The lower size cutoff for our model is 3 nm because the derived J3 values from measurements were used as a model input. The lower cutoff in Kulmala et al. (1998) was 2 nm. This would account for some difference in the predicted low-limit volatilities (a factor of 2-3). We have now addressed the 3 nm lower cutoff in our results. (3) The mass of total condensible material in the present study was constrained by dM/dt measured by the AMS and sulfuric acid vapor concentrations measured by the CIMS, whereas the amount of condensible material was a free parameter in Kulmala et al. (1998). With all else constant, these two approaches should converge to the same solution; however, I believe the risk of incorrect growth profiles (as mentioned in the reviewer comment) is reduced in the current analysis. (4) Finally, Kulmala et al. (1998) did not test the range of assumptions that would affect aerosol activity.

Towards the end of the introduction, we introduce the Kulmala et al., (1998) paper: “This paper is a continuation of our work in Riipinen et al. (2011) and builds off of earlier work of Kulmala et al. (1998). In Riipinen et al. (2011) we did not attempt to quantify the volatility (saturation vapor concentrations) or other properties of the condensing SOA beyond determining that half or more needed to condense based on surface area. Kulmala et al. (1998) used an aerosol dynamics model to determine a lower bound for the volatility for a single condensing species on nucleating particles;

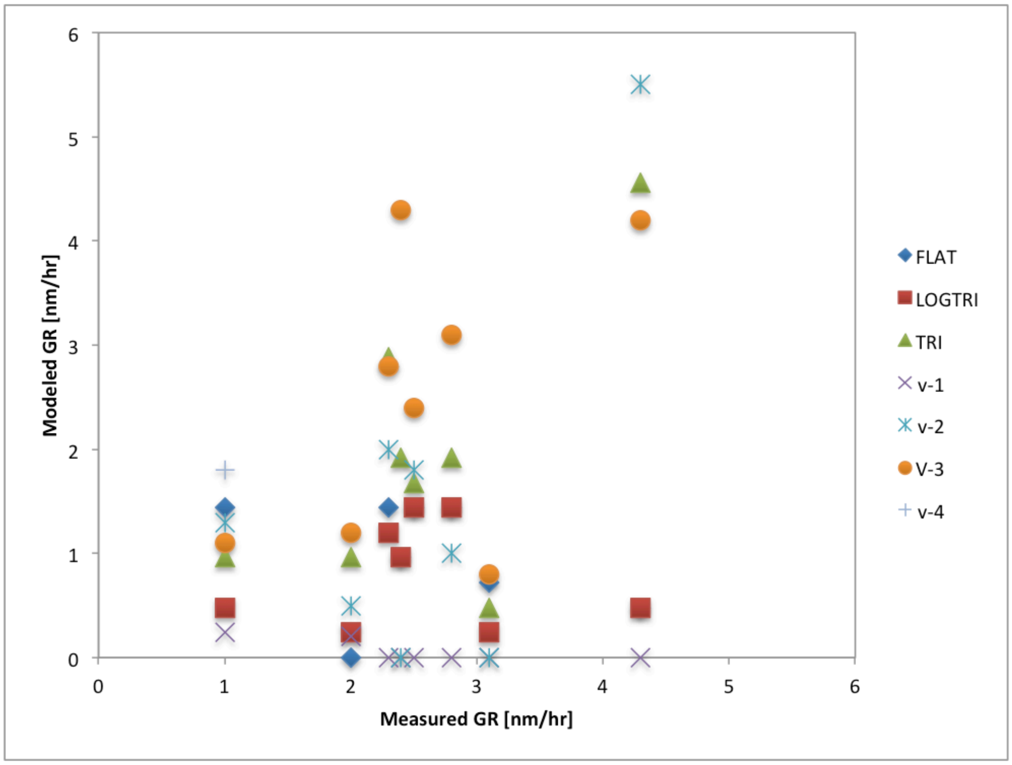
however, because measurements of time-resolved sulfuric acid and organic aerosol mass were not standard practice at the time of the study, the results were limited."

At the end of Section 3.1.1 we add: "These upper-bound volatilities are about 30-300 times more volatile than the results presented by a related study, Kulmala et al. (1998), using a similar technique. Some possible reasons for the differences are: 1) In Kulmala et al. (1998) only one species (along with water) is allowed to condense in each simulation; however, in the present study, each simulation include sulfuric acid condensation and at least one organic species, (2) Kulmala et al. (1998) had a lower diameter cutoff of 2 nm, while the current study has a lower diameter cutoff of 3 nm, and (3) Kulmala et al. (1998) did not nest the range of assumptions that would affect aerosols activity. Also, our results indicate the maximum volatility of the condensing molecules could in theory have to be able to condense on the nucleation mode. It is well possible that the actual compounds are even less volatile than the conservative estimates we are giving."

Finally, in the conclusions, we add: "From both methods we found that the average saturation concentrations (C^*) of organics in the aerosols likely needs to be around 10^{-3}-10^{-2} μg m^{-3} or less to facilitate growth of freshly nucleated particles starting at 3 nm. If organics are condensing onto particles smaller than 3 nm, as shown to be likely by Riipinen et al. (2011), these saturation vapor concentrations would necessarily be even lower as suggested by Kulmala et al., (1998)."

Specifically, in such a case that the effective saturation vapour density is relatively high, the Kelvin effect may prevent the growth altogether unless the concentration of the condensable vapor peaks at a high value, which on the other hand can easily lead to an "overshoot" in the growth rate as the particle size increases to around 3 nm and the Kelvin effect is already smaller than at 1.5 nm. The limit given by Kulmala et al. is based on that: When the saturation vapor density was set to 10^7 (i.e. still 3 times lower than the highest number given in the present ms), the peak vapor concentration needed to initiate growth was so high that the nucleation mode "shot straight up" once the growth began. Thus, I think that in this ms, the authors should also compare the modeled growth rate (and specifically, the growth rate during the first 1-2 hours) to the measured, and based on the comparisons, re-asses the upper limit of their stated saturation vapour density.

We have performed a growth rate comparison and found the results to be similar to our analysis in the paper ($C^*=10^{-3}$ is about the cutoff). See the figure below:



As discussed above, the total condensible material as a function of time is constrained in the model by AMS and CIMS measurements, thus the risk of incorrect growth profiles is somewhat reduced. We feel that the differences between model results are due to the other model differences described above, most likely the 3 nm starting size of the current model and the presence of condensing sulfuric acid.

Additionally, because we constrain the amount of condensible material based on dM/dt measurements by the AMS, the risk of "overshoot" growth because of gas-phase concentrations that are far too high is greatly reduced.

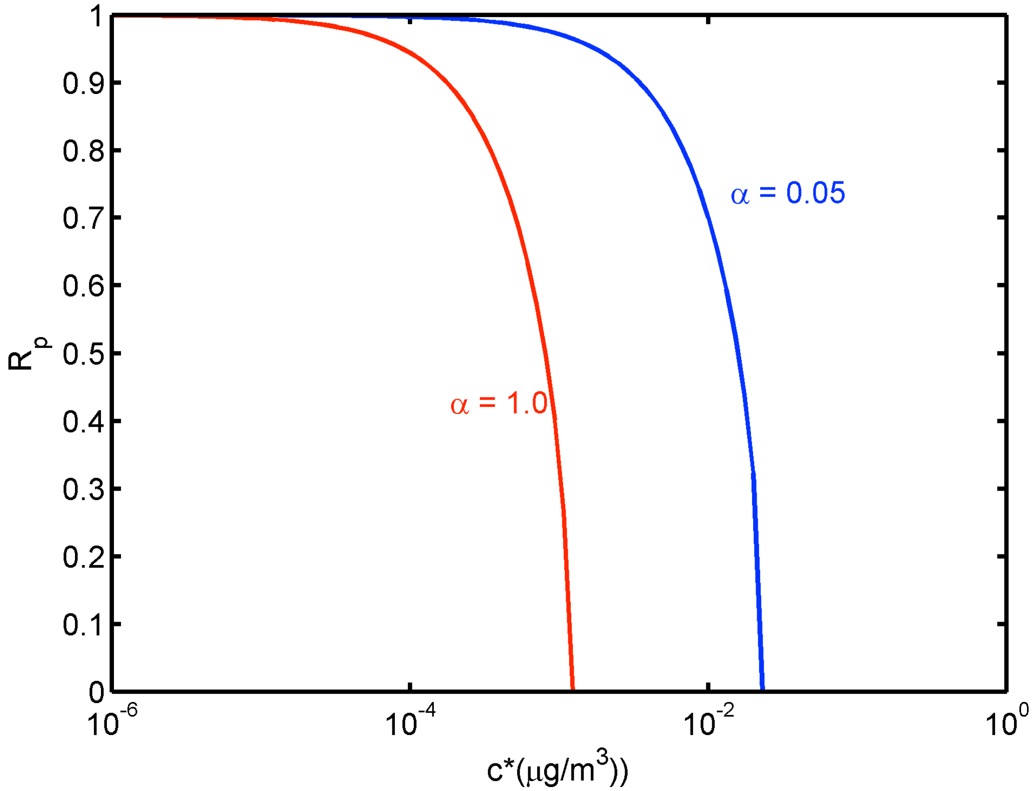
Regarding the Kelvin effect, I see no basis for the simulations in which the surface tension has been set to zero (the authors themselves note that "The surface tension of the aerosols cannot be 0"). They should be removed, or at least it should be made sure that they do not affect the assessment of the upper limit of the effective saturation vapour density. If the simulations are retained, it should at least be explained why they are useful.

We include this simulation for the purpose of isolating the effect of surface tension the effect of differences in activity, volatility and accommodation coefficient. We have made this point clearer in the paper: "We test values of, 0, 0.025 and 0.05 N m^{-1}. While the surface tension cannot be 0 N m^{-1}, we include this case for the purpose of isolating the surface tension effect from other effects."

It already was not being counted when determining the possible volatilities, "The surface tension of the aerosols cannot be 0. It is likely that mixtures of aerosol organics have surface tensions in the range of 0.02-0.05 N m^{-1} (Alvarez et al., 1997, Egemen et al., 2000), and when mixed with water the surface tension of the particles can approach 0.07 N m^{-1}. For some solid phases, the surface tensions may even be higher. Our analysis showed that when surface tension is 0.025-0.05 N m^{-1}, the cases with low-volatility ($C^* \leq 10^{-3}$ µg m^{-3}) condensing SOA agree best with the observations. There are still many input cases where $C^* = 10^{-2}$ µg m^{-3} or the mixtures of volatilities also gave good agreement, so these cannot be ruled out."

In my opinion, the authors downplay the importance of the results obtained from the TDMA results. It is true that the size change can take place because of other reasons than evaporation - for example, ammonium sulfate will decompose at 280 centigrades, but such an effect will only cause an overestimation of the saturation vapour pressure. Pyrolysis is somewhat more complicated as it leaves a non-volatile char residue. A sensitivity calculation could be done: pyrolysis should not take place below 200 centigrades, and if the particle undergoes pyrolysis, it should be stable until its temperature reaches at least 200 centigrades. Thus, a high estimate of the vapour pressure could be reached by assuming that a complete evaporation takes place at 200 degrees.

We appreciate this comment as we also think that the VDMPS data gives more insight that is typically given credit of, and we think it is a useful way to indirectly proble the composition and properties of the smallest particles. Following the suggestion of Prof. Laaksonen, we also ran the VDMPS analysis assuming that the TD temperature was 200 centigrade. We found that if it is assumed that the aerosol would evaporate at 200 centigrade (in other words used 200 centigrade as the TD temperature) the upper limit of the volatility of the material shifts with roughly an order of magnitude upwards (towards higher maximum volatilities) as compared with the results presented in Fig. 8, i.e. around 10^{-3} to 10^{-2} $\mu g/m^3$ depending on the assumptions about the mass accommodation coefficient and surface tension. We have somewhat softened the discussion of the uncertainties related to the pyrolysis to the revised version of the manuscript.



Rn vs C* for 200 Celsius. This should be compared to Figure 8 in the manuscript. The predicted volatilities are about 1 order of magnitude higher than 280 Celsius.

Note also that Raatikainen et al. (ACP 10, 2063-2077, 2010) found that measured volatilities of Hyytiälä aerosols can be correlated rather well with AMS organic and inorganic groups, which suggests that pyrolysis might only play a small role if any.

We have added the reference to the paper by Raatikainen et al. (2010) to the revised MS. “However, we feel that the results from the VDMPS strongly support the nucleation-mode growth calculations above – particularly as in their parallel analysis of the VDMPS data and AMS data from Hyytiälä, Raatikainen et al. (2010) saw no significant indications of pyrolysis.

Regarding the aerosol-phase chemistry calculations, I wonder what would the reaction rate coefficients need to be for the reactions to proceed rapidly enough to be able to drive particle growth? See Vesterinen et al. (Atmos. Environ. 41, 1768, 2007) for some discussion on these matters.

This is a very important question. As a rule of thumb, the time scale of evaporation should be much longer than the time scale of the reaction. The time scale of evaporation can be estimated based on the saturation concentrations. If the parent molecules follow equilibrium partitioning, the residence time of the parent molecule in the aerosol will depend on the volatility of the parent molecule and the corrected surface area of the particle. Because the volatilities of the parent molecules could span orders of magnitude, the necessary reaction rate coefficients would similarly span orders of magnitude. This is something that needs to be addressed in future work.

What we assumed in the paper is instantaneous reactive uptake (rate coefficients of infinity). The results may change drastically once real composition-dependent rate coefficients are used. We now have the text, "The choices of cut-off diameter, instantaneous reaction and volatility are arbitrary but they illustrate the potential implications of particle-phase chemistry in the freshly nucleated particles. If finite reaction rate constants were used, the results of these tests could change. This additional detail is left to future work; however, the main conclusions regarding the necessary low volatilities of the reaction products would not change."

In the introduction, three (numbered) complications are mentioned. As shown by Virtanen et al. (Nature 2010), the growing particles are solid at least when they are larger than about 30-40 nm. I believe this may cause a severe complication to the growth calculations, as the mixture of different organics and sulfate may not be homogeneous throughout the particle, but the particle could have a layered structure. Furthermore, it may be the case that when the particles are in the few nm size range, they are still liquid, and a phase change takes place while they are growing. These possibilities should be mentioned.

Yes, this is a very good point. We have added this complicating factor: "Organic aerosols may form complex multi-phase mixtures. SOA is typically modelled as a pseudo-ideal single-phase liquid mixture, but recent results show this may not always be correct (Virtanen et al., 2010; Cappa and Wilson, 2011)."

In the second paragraph, the authors refer only to modeling papers when noting that new particle formation can produce CCN. Before the modeling papers, this was shown in a number of experimental papers (Lihavainen et al. JGR 108, 4782, 2003; Kerminen et al. GRL 32, L14803, doi:10.1029/2005GL023130; Laaksonen et al. GRL 32, L06812, doi:10.1029/2004GL022092).

The references are now included.

B. Bonn (Referee)

General comments:

The authors address the very important aspect of mass contribution by secondary organic compounds (SOCs) to new aerosol particles in their early stage. The study is well written (with some minor typos) and aims to investigate the volatility of organic compounds contributing to ultrafine particulate mass, which is one of the important unknowns besides their chemical identification. From numerous earlier studies it is well established that both, i.e. sulphuric acid and SOCs contribute significantly to the masses of freshly nucleated particles. However as sulphuric acid is only a single compound already causing a notable difficulty to measure the situation is much worse for organics. As the authors state correctly there are at least several 1000 different organics compounds of low or semi-volatility present, with most of them participating in the growth process but not being analysed just speculated. Thus, the present approach trying to lump the tremendous number of compounds to 8 ideal compounds of a specific volatility is necessary and reasonable. The applied kinetic approach is most welcome, since the former secondary organic aerosol (SOA) community use an equilibrium approach only, representing an approximation only and ignoring the size dependent change in physico-chemical properties. This includes chemical composition as well. However a basic equilibrium (non-kinetic) between gas- and aerosol- phase is certainly reached much more rapid for the tiniest particles than for larger or 'grown-up' ones. Nevertheless, the kinetic approach allows to calculate growth rates accurately and to investigate the effect of chemical reactions in the aerosol phase. Using a box model allows to investigate different impacts of various assumptions made. This is what the authors do and which provides them a good basis for their conclusions. One essential point of this study is the assumption of growth caused by condensation only, not by chemical reactions, which is a kinetic phenomenon too. The authors thus use measured nucleation events at two different boreal locations and a box model to figure out the essential volatility of organic compounds required to explain the early growth/activation. From this they conclude that the initial contributions by SOC are of extremely low volatility and thus so far unknown organic substances or cluster compounds are needed. Because of the achievements made and the carefull discussion this study merits publication in Atmos. Chem. Phys. after addressing some minor remarks given further below.

Comments:

One aspect to be discussed at least during this review process deals with the reactivity of small clusters and aerosol particles. We have published a modelling study investigating the reactive uptake of organic peroxy radicals (RO2) in a smog chamber study several years ago, indicating that those reactions can overcome the initial barrier for the oxidation products to condense caused by the Kelvin effect. The important size range was up to 10-15 nm in diameter.

Most recently we have made additional lab studies and we are still aiming to get those published in the near future. Those lab studies display the essential need for organics in nucleation to grow by radical assisted reactions. Extraopolating this to plant chamber studies and atmospheric conditions it was possible to explain the observed nucleation and growth. The point I want to make here is the importance of the radical assisted reactions, which would sgnificantly lower the volatility of condensing substances when treating the SOC as a lump sum. May this explain the low volatility probably obtained? This low volatility is a very nice result and I'd like to congratulate the authors for achieving this.

Please consider the volatlity of major biogenic VOC oxidation products and the time needed to decrease volatility. During this time the compounds can be taken up by particles too. Thus this is a time limited process to achieve the small volatilities calculated.

This is a very good point. In our recent paper (Donahue et al., 2011, GRL in press) we address this exact issue and come to the conclusion that a significant fraction but typically not all could indeed be explained by the most probable gas phase reaction pathways that lower the volatility of the organic molecules. Our results thus are not contradictory to the scenario that some particulate phase chemistry – or an unknown gas phase reaction that decreases the volatility considerably within one oxidation step – is needed to explain the presence of these low volatility compounds, although they do not directly confirm the hypothesis on the particulate phase chemistry either. In our simulations we circumvent the problem of treating the VOC emissions and their complex gas phase chemistry by taking the total condensational flux of organics from the AMS data. To direct the reader to the discussion on the capability of gas phase chemistry to produce the low-volatility material we observe, we have added a reference to Donahue et al. (2011).

Donahue, N.M., Trump, E.R., Pierce, J.R., and Riipinen, I.: Theoretical Constraints on Pure Vapor-Pressure Driven Condensation of Organics to Ultrafine Particles, in press Geophys. Res Lett, 2011.

** p. 14506, l. 12: Why do you choose exactly 200 g/mol? Monoterpene oxidation products are primarily below 184 g/mole with the primary carbonyl compounds even less. Ongoing atmospheric chemistry should crack the molecules down to somewhen CO2 .*

This was a ballpark estimate based on assuming that if vapor pressures were decreasing, functionalization was occurring more than fragmentation. Upon further inspection, our results are not sensitive to our assumption of molecular weight since volatilities and diffusivities are specified independently.

** p. 14506: I don't understand the reasoning of setting C* to 1 microgram/m3. A sentence more than 'but the conclusions are similar to C* = 0.1 µg m−3 cases, so it is not included...' would improve the readers understanding of the authors arguments. What is similar, what is different? What is your measure to define the best set of parameters?*

We have changed the sentence to be more specific: SOA with $C^{*}=10^{0}$ µg m^{-3} would largely be in the aerosol phase for our cases (because ambient SOA concentrations were generally around or above 1 µg m^{-3}), but the conclusions are similar to $C^{*}= 10^{-1}$ µg m^{-3} cases (freshly nucleated aerosol showed little to no growth since nearly all new OA mass went to the accumulation mode), so it is not included.

** p. 14507: Although well listed and named there is one aspect ignored: What about cross-effects of the six points listed? They are supposed to act not independently. I think they are varied partly adjoined, which is correct but not clearly stated.*

In our analysis, we try every combination of parameters, which amounts to several hundred permutations (with a simulation for each of the 9 days for each permutation). We added the sentence: "We test every permutation of the above parameters to look at cross-parameter effects.".

** Where are the organics and their ambient values taken from? Their emissions and ambient concentrations are a highly complex issue varying notably for different compounds with a multitude of serious challenges to overcome in the measurements. Did the authors have measurements to constrain their VOC input, which potentially condenses or are values chosen because of earlier measurements at similar conditions?*

Our organics are added to the gas phase based on the rates of change of organic aerosol mass (dM/dt) measured by the AMS. Since our test equilibrium vapor concentrations are always much smaller than the total organic aerosol mass concentrations, nearly all of the organics added to the gas phase go to the aerosol phase. Thus we match the correct condensation of total organic aerosol mass.

Using this technique, we avoid using VOC precursors and worrying about the details of chemistry.

This is described in the text: "Organic material is initially formed in the gas phase (particle-phase chemistry discussed later) using the change in aerosol organic mass concentrations measured by the

AMS with time. Since all SOA formed has a volatility of 10^{-1} μg m^{-3} or less and total organic concentrations are generally much larger than 10^{-1} μg m^{-3}, nearly all of the freshly formed organic vapors will condense to the aerosol phase to form SOA mass."

We have added the sentence to this: "Thus, we are able to tightly constrain our total SOA mass formation without the uncertainties associated with VOC emissions and chemical yields."

** p. 14510, l. 2: A variation of surface tension with respect to its not well-known value is feasible and an excellent point made. But what do the authors think about a surface tension of 0 N/m? Basically this would mean a reactive uptake, since the Kelvin effect does not play a role anymore.*

The inclusion of the 0 N/m surface-tension test was to allow us to isolate the effect of surface tension from the other varied factors. When we introduce the surface tension assumptions we now say, "The surface tension of the aerosol. We test values of, 0, 0.025 and 0.05 N m^{-1}. While the surface tension cannot be 0 N m^{-1}, we include this case for the purpose of isolating the surface tension effect from other effects." We also re-iterate this point at the end of Section 3.1.1.

** p. 14514, 2nd para. (comment only): The accomodation coefficient is actually a fitting parameter. Thus, if a potential decline is found with particle size, there might be an additional effect such as a chemical one, too. For instance the surface composition of the larger particles is different from the smaller and does not favour attachment or reaction as for the smaller particle.*

We have added the sentence: "Other factors, such as differences in surface composition may also affect the accommodation/uptake coefficient as a function of size."

** p. 14515: Regarding the volatility range mentioned especially the varying results for different days it needs to be taken into account that the volatility reduces only during oxidation, which is primarily a function of OH. Therefore different daily pattern of OH with different VOCs emitted by the boreal forest will certainly yield different results. Interesting in this context is the comment on Mexico City. Completely different VOCs are present in Mexico as compared to the boreal forest zone but resulting in a similar outcome! In my personal point of view this might indicate the occurence of reactions of similar types that determine the values perhaps not the volatility since the anthropogenic VOCs in urban areas are generally about half of the size of biogenic ones with a much higher volatility.*

Yes, this definitely seems possible and it would be an interesting topic for a future study.

** p. 14516: Aerosol reactions: The size dependent chemical composition is very important in this context. Most likely different heterogeneous reactions are going on at different size ranges. This is being highlightened by the authors nicely.*

Thanks

p. 14517: The volatility required for significant uptake of organics assumes condensational uptake only, but no reactive one (see above). Please comment on that.

In our analysis we are assuming that the transition to lower volatility happens instantly as the gas-phase species reach the ultrafine particles. This essentially is assuming reactive uptake.

p. 14519: Final paragraph of the discussion section: The complete evaporation of sulphuric acid and ammonium sulfate assumes no chemical reaction and the formation of an organosufate or what ever, which does evaporate at elevated temperatures. Unfortunately the chemical species do not act independently.

We have changed the text to read: "Previous work estimates that all aerosol sulfuric acid and ammonium sulfate in the ultrafine particles should be evaporated within 1 second in the VDMPS at 280 °C (Ehn et al., 2007). However, interactions between inorganic and organic species (e.g. aminium sulfate) may cause changes in the evaporation temperature."

Comment on the estimated volatility range of 0.001-0.01 /m3 or lower: Assuming 0.01 /m3 would result in a saturation concentration of about 3x107 molecules per ccm. Compared to a total molecule number concentration of 2.5x1019 molecules/ccm this yields a volume mixing ratio of about 1 ppt and a vapour pressure of 10−7 Pa. Even the di- carboxylic acid of two monoterpenes, i.e. pinic acid is in the order of five magnitudes higher in volatility (≈ 0.06 Pa)[Bilde and Pandis, 2001]. There are certainly additional compounds which are supposed to lower the volatility such as hydroxy-hydroperoxides and highly oxidised species. But to shift the volatility down remarkably is by far no easy task to perform especially when considering the present knowledge about identified compounds. May this be an indication for a reactive uptake such as for sulphuric acid (psat = ca. 1010 molecules/cm3). Please comment on that.

This is an excellent point: It is indeed puzzling that the volatilities that we find are so much lower than any saturation vapour pressures of known biogenic organic molecules reported in literature. As pointed out by our approximate analysis in the manuscript, on potential explanation for this observation is reactive uptake. However, an unknown gas phase reaction that produces very low volatility products with a single reactive step cannot be ruled out based on our data set.

Technical comments:

** p. 14499, l. 6: Omit . after '(IVOCs)' and before '(Donahue et al., 2009)'. C6408*

Done

** p. 14506, l. 12: Give a reference for organic aerosol constituent density of 1400 kg/m3! Know about the Jenkin approach (Jenkin, 2004) but isn't there anything better?*

Like with molecular weight, this was a ballpark estimate and our results are not greatly sensitive to this. We have added mention to this in the text.

** p. 14509, l. 6: Omit - between 'mono' and 'disperse'. * p. 14513, l. 18: Put () around 'd' when addressing Figure 4d as done for 'b'.*

Done

References:

Bonn, B. et al., Atmos. Chem. Phys. Diss., 6, 13165–13224, 2006. Bilde, M., and S. N. Pandis, Environ. Sci. Technol., 35, 3344-3349. Donahue, N. M., A. L. Robinson and S. N. Pandis, Atmos. Environ., 43, 94–106, 2009. Jenkin, M.E., Atmos. Chem. Phys., 4, 1741-1757, 2004.