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Comment

## ***Interactive comment on “Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events” by J. R. Pierce et al.***

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### **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 SOC's contribute significantly to the

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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 careful discussion this study merits publication in Atmos. Chem. Phys. after addressing some minor remarks given further below.

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## 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 ( $\text{RO}_2$ ) 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. Extrapolating 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 significantly 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 volatility 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.

\* 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 somewhere  $\text{CO}_2$ .

\* p. 14506: I don't understand the reasoning of setting  $C^*$  to 1 microgram/ $\text{m}^3$ . A sentence more than *'but the conclusions are similar to  $C^* = 0.1 \mu\text{g m}^{-3}$  cases, so it is not included...'* would improve the readers understanding of the authors arguments.

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What is similar, what is different? What is your measure to define the best set of parameters?

\* 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.

\* 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?

\* 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.

\* p. 14514, 2nd para. (comment only): The accommodation 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.

\* 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 occurrence of reactions of similar types that determine the values perhaps not the volatility since the anthro-

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pogenic VOCs in urban areas are generally about half of the size of biogenic ones with a much higher volatility.

\* 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 highlighted by the authors nicely.

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

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 organo sulfate or what ever, which does evaporate at elevated temperatures. Unfortunately the chemical species do not act independently.

Comment on the estimated volatility range of 0.001-0.01 /m<sup>3</sup> or lower: Assuming 0.01 /m<sup>3</sup> would result in a saturation concentration of about 3x10<sup>7</sup> molecules per ccm. Compared to a total molecule number concentration of 2.5x10<sup>19</sup> molecules/ccm this yields a volume mixing ratio of about 1 ppt and a vapour pressure of 10<sup>-7</sup> Pa. Even the dicarboxylic acid of two monoterpenes, i.e. pinic acid is in the order of five magnitudes higher in volatility ( $\approx 0.06$  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 ( $p_{sat} = \text{ca. } 10^{10} \text{ molecules/cm}^3$ ). Please comment on that.

### Technical comments:

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

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\* p. 14506, l. 12: Give a reference for organic aerosol constituent density of 1400 kg/m<sup>3</sup>! Know about the Jenkin approach (Jenkin, 2004) but isn't there anything better?

\* p. 14509, l. 6: Omit - between 'mono' and 'disperse'.

\* p. 14513, l. 18: Put () around 'd' when addressing Figure 4d as done for 'b'.

## 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.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 14495, 2011.

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