

*In the present manuscript the equilibrium size of aerosol particles in the presence of semivolatile organic compounds is studied. It is shown that co-condensation of semivolatile (organic) substances with water could potentially increase the particle size and affect the ability of particles to act as cloud condensation nuclei. It is also discussed that due to partitioning of semivolatiles the current methods to measure aerosol hygroscopicity might be erroneous in some conditions. The manuscript includes interesting results and the results are mostly presented in a concise way. The topic is highly relevant within the scope of ACP. I have only few, mainly minor comments that should be addressed before accepting for publication.*

*You did not give the conditions represented in Figure 1 clearly enough. What is the amount of organics and how does it compare with different atmospheric conditions? What is the number concentration of particles? Without those it is difficult to estimate how realistic conditions you are using, so a more detailed description is needed. The same for the results presented in Figure 2. Is the number concentration of particles changing with changing size keeping the total mass constant? - the reader can have an idea that the effect of organics is larger than the effect of ammonium nitrate and chloride on CCN potential. This might be the case but some support is needed. Maybe you could also have a figure showing the amount of organics in the particles as a function of saturation ratio compared to the amount of sulphate and thus give some idea how close to the activation point organics are actually condensed from the gas phase. It would be nice to see similar results with the model solving the condensation dynamics, but I guess it is outside the topic of this manuscript.*

**Response.** We apologise for the lack of clarity here. The reviewer is correct in that the number concentration of particles would determine the amount of condensed material. As we are not solving the condensation dynamics between different sized particles, it is difficult to predict the true potential effect on cloud activation. This will form the focus of a future study. The condensed mass in figure 1, an aerosol comprised of 30% core material at 0%RH, would equate to a number concentration of ~600/cc. If we were able to solve the equilibrium across different sizes for higher concentrations, the amount of condensed material per particle would decrease. Conversely at lower concentrations the amount would increase. The cerise area displayed in figure 1 would then either converge toward the grey areas representing Kohler theory or diverge away. We have added two arrows to figure 1 to highlight this. The reviewer has also raised a very important point in that not only size and composition remain uncoupled, but so does size, composition and **number**. We suggest the title of the paper now becomes: **'Tight coupling of particle size, number and composition in atmospheric cloud droplet activation'**. As a comparison with the work of Kulmala et al (1993) we have added another line on figure 1 to show the potential effects of Ammonia/Nitric acid co-condensation under the same conditions (concentrations of particles and condensing gas). The core is assumed to be that of ammonium sulphate and thus corresponds to the lower boundary of the cerise area. In this case it shows the potential effect is comparable if not slightly greater than the reported effect of ammonia/nitric acid co-equilibration. For the organic fraction this will change with volatility profile as we try to demonstrate with figure 2. Following the addition of arrows to Figure 1, we have also added similar arrows to figure 2. We also now suggest adding the following text to the discussion of figure 1 on line 26 page 25159: *'The actual amount of soluble material condensing per particle will depend on the size distribution and number concentration. In this example, the multicolored arrows indicate the direction the coloured areas would follow on increasing and decreasing the concentration of particles. The shape of the size distribution, concentration, volatility profile and amount of condensable material will dictate this final result, a solution of the condensation dynamics the focus of future work.'* Following the discussion of figure 2, a similar line will be placed at line 14 page: *'The block arrows indicate the effect changing the particulate concentration would have on the amount of additional condensed soluble material per particle through co-condensation, thus critical saturation ratio.'*

One novel aspect of this paper is the ability to account for an unlimited number of semi-volatiles in the equilibrium calculation of critical saturation ratios, which hasn't been presented before this work. In addition, the paper still provides important considerations when measuring single particle hygroscopicity of organic aerosol, and the potential role of co-condensation in currently reported discrepancies, as we discuss in the manuscript. Given the above discussions we suggest the following text is added at the end of section 1: *'In these simulations we have not solved equilibrium between different sized particles or accounted for the concentration of particles as a function of size. Nonetheless, following the previous studies of Kulmala et al (1993), the results in figure 1 highlight the inherent limitations of using traditional Köhler theory in the presence of semi-volatile organic compounds, including the difficulties in determining single particle hygroscopicity through laboratory studies as discussed in the following section. This would suggest that size, number and composition remain inherently coupled whenever semi-volatile compounds are present at reasonable atmospheric concentrations. To assess the true potential effect on cloud activation, thus cloud droplet number concentrations, the condensation dynamics has to be solved with appropriate aerosol size distributions. This is the basis of ongoing investigation.'* We also suggest the following modification to the abstract, line 15, page 25156: *'owing to inextricable linkage between the aerosol composition, a particles size and concentration under ambient conditions.'*

*Page 25164, line 7: Is 150kJ/mol a typical value for enthalpy or how did you choose that?*

**Response:** This value was taken from the study of Cappa and Jimenez et al (2010) and is a typical value. The potential effect of a decrease in temperature is shown in figure A1.

*Appendix A: It is said that iteratively solving the equilibrium equations for every single component enables construction of a new Köhler curve, thus cloud activation predictions. Could you then say which particles would activate to cloud droplets at some supersaturation with realistic aerosol size distribution? I guess not. As far as I see Köhler theory cannot actually be used to predict CCN properties of aerosol in the presence of semi volatiles and different sized aerosol particles. It just gives the lowest possible critical saturation when only single type and monodisperse aerosol exist in the system with the known amount of semivolatiles. In the page 25162, lines 23-24 you acknowledge this, but this would hold only in the case of single particle size and not during "cloud activation" that is usually understood to be something actually happening in the atmosphere.*

**Response:** Yes this is correct. As mentioned previously, cloud droplet number predictions require a solution to the condensation dynamics, which is the subject of ongoing investigation. We suggest replacing 'cloud activation predictions' with 'activation potential predictions'. As stated in response to the earlier comment, the results displayed still highlight a 'potential' effect, the true effect likely to depend on multiple factors such as updraft velocity and assumed aerosol size distribution.

*Little bit more discussion in the main text should be included on what would happen in the case of aerosol size distributions when the difficulty is not only the partitioning of semivolatiles between the gas and particle phase, but also partitioning between different sized particles. Then the equilibrium partitioning would not give the maximum effect on the cloud droplet formation as due to Kelvin effect big particles would grow even bigger.*

**Response:** Please see the response to the first question in which we suggest the addition of text to clarify this. We would also like to clarify that traditional Köhler theory is still used to reconcile single particulate hygroscopicity as measured using HTDMAs. As we highlight in the manuscript, traditional Köhler theory cannot be used confidently in the presence of semi-volatile organics. As compilation of hygroscopicity data from such instruments is used to

assess the role of composition on cloud activation, the other focus of this paper is to suggest the reported discrepancies could be caused by this effect and further work is required to assess the 'true' effect of composition on hygroscopicity and CCN activation potential.

*" $P_{i0}$  represents the partial pressure of  $i$  above a flat solution containing only a sub-cooled form of itself" is quite complicated way of describing saturation vapor pressure. Should "flat solution" be "flat solution surface". Also can solution be composed of single component only?*

**Response:** This is the thermodynamically correct description of pure component saturation vapour pressure: the partial pressure of a compound above a flat single component system comprising only itself in a sub-cooled state. We suggest replacing the existing text with this new description for clarity.

*There are several references at the end that are not used in the manuscript: Albrecht 1989, Facchini et al 1999, Solomon et al. 2007, Twomey 1977, Warner 1968, Wex et al. 2009.*

**Response:** This has been corrected.

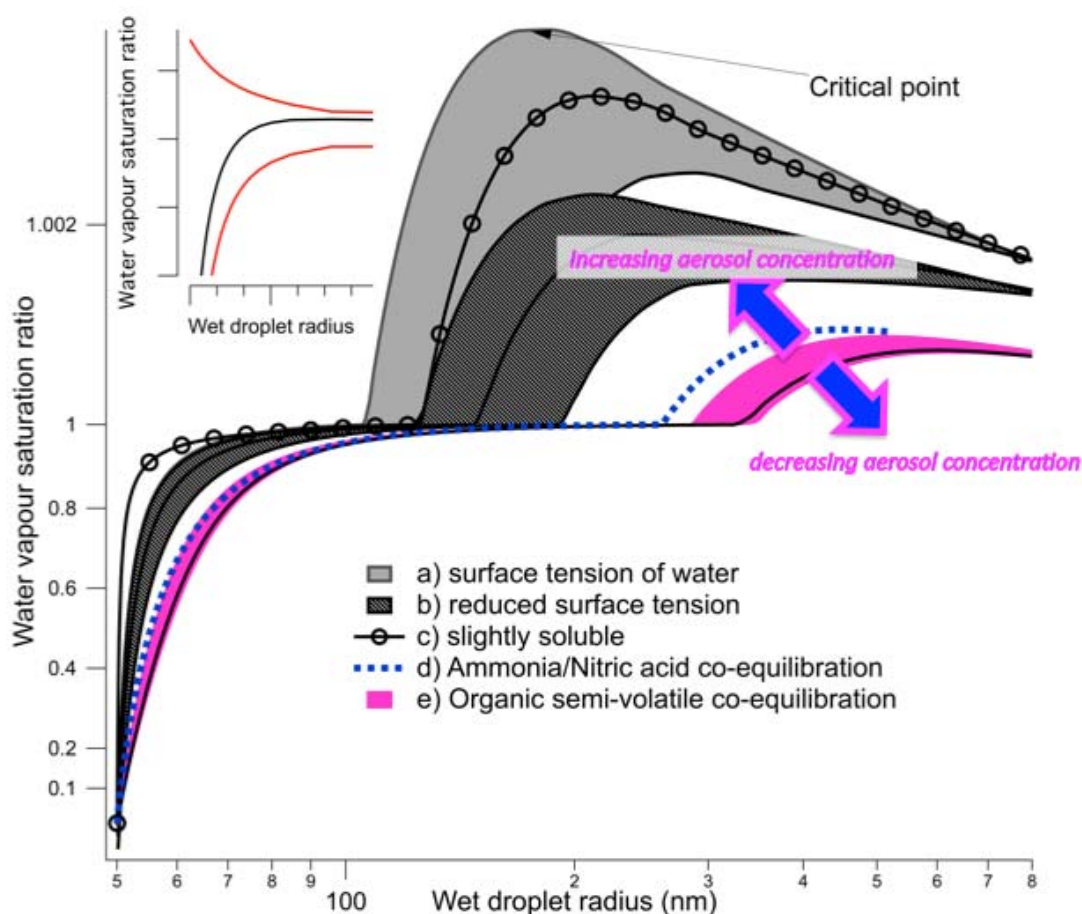


Figure 1. Three representations of Köhler theory for a 50nm dry particle, comparing traditional Köhler theory without (grey shaded area) and with (hatched surface area) an (unrealistically large) influence of surface active material assuming the surface active molecules do not reduce the Raoult effect, and our new formulation which allows the co-condensation of any number of compounds (coloured area). Above a saturation ratio of 1 the axis scale has been changed to more clearly display the critical point. Each area is constructed by changing the properties of a core (comprising 30% of the condensed mass at 0%RH) from insoluble organic compound with molecular weight of 320  $\text{gmol}^{-1}$  to  $(\text{NH}_4)_2\text{SO}_4$ , with the solid line through each area representing a soluble compound with molecular weight of 320  $\text{gmol}^{-1}$  (in each case, moving from the insoluble compound to  $(\text{NH}_4)_2\text{SO}_4$  decreases the critical saturation ratio,  $S_{\text{crit}}$ ). Circle markers represent the assumption of a slightly soluble shell using

conventional Köhler theory. The dashed blue line represents co-equilibration of Ammonia and Nitric acid for brief comparison to the work of Kulmala et al (1993). In this instance the equilibrium constants were taken from Seinfeld and Pandis (1998) and the core assumed to be  $(\text{NH}_4)_2\text{SO}_4$  to obtain the lowest  $S_{\text{crit}}$ . Equilibration of multiple semi-volatile components results in by far the largest decrease in critical supersaturation and increase in cloud droplet forming behaviour, by increasing the soluble mass as the RH increases, towards activation. The actual amount of soluble material condensing per particle will depend on the size distribution and number concentration. As all simulations at 0%RH correspond to a number concentration of  $\sim 600/\text{cc}$  in this example, the multicolored arrows indicate the direction the coloured areas would follow on increasing and decreasing the concentration of particles. The shape of the size distribution, concentration, volatility profile and amount of condensable material will dictate this final result, a solution of the condensation dynamics the focus of future work. The small inset at the top left of the figure is a simple schematic displaying the contribution of the Raoult (bottom red line) and Kelvin terms (top red line) to the resulting Köhler curve (black line). The Kelvin term asymptotically approaches infinity as the size tends to zero.

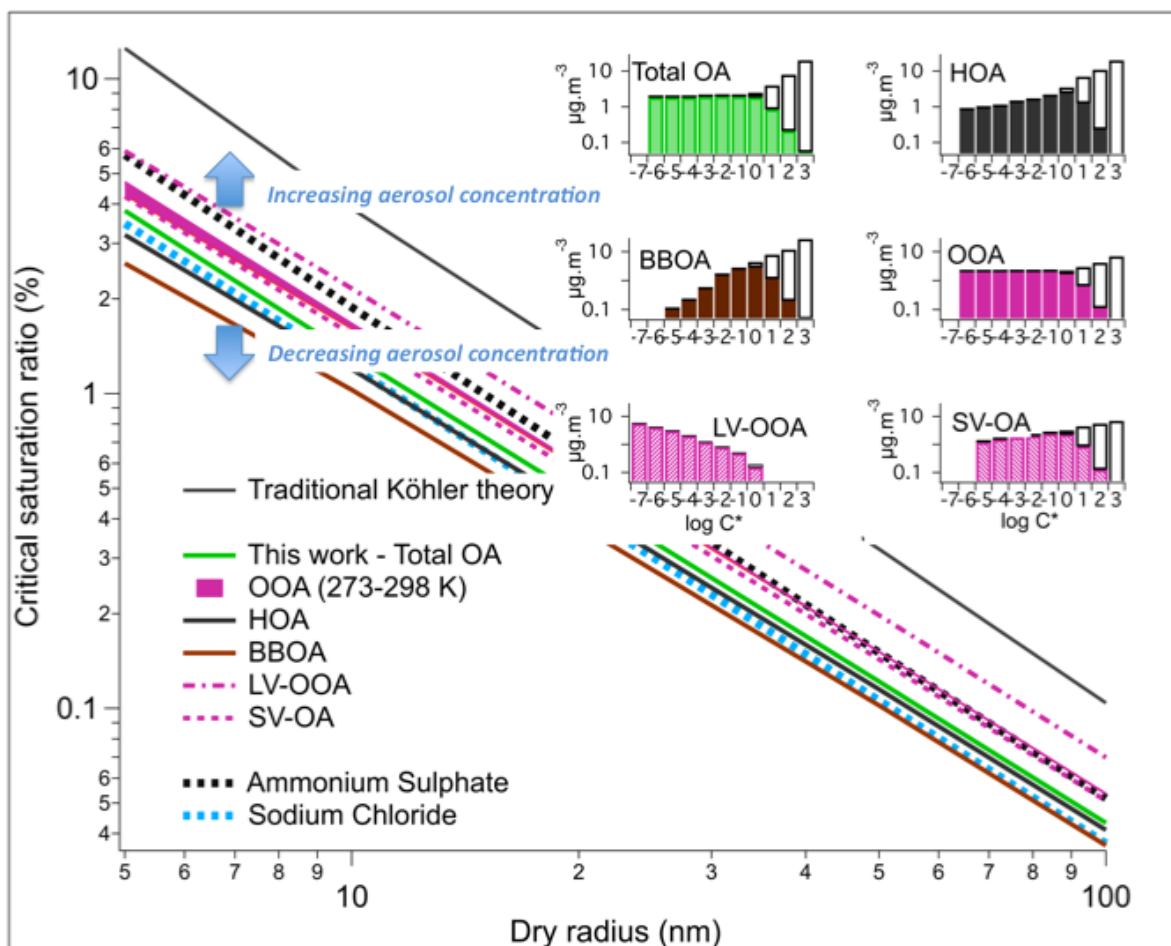


Figure 2.  $S_{\text{crit}}$  as a function of dry radius (nm) for multiple semi-volatile fractions taken from Cappa and Jimenez (2010), shown in the insert panel. ‘Total OA’ represents the entire semi-volatile fraction, the ‘Traditional Kohler theory’ lines representing traditional Kohler theory predictions for the same aerosol type. Additional representations are as follows: HOA- Hydrocarbon like, OOA- Oxygenated, BBOA- Biomass burning, LV-OOA – low volatility, SV-OOA Semi-volatile organic aerosol. For reference the  $S_{\text{crit}}$  for NaCl,  $(\text{NH}_4)_2\text{SO}_4$  are given as blue and black dashed lines. The actual amount of soluble material condensing per particle will depend on the size distribution and number concentration. To demonstrate this, the solid

blue arrows indicate the direction the predicted critical saturation ratios, after accounting for co-condensation, would follow on increasing and decreasing the concentration of particles. The shape of the size distribution, concentration, volatility profile and amount of condensable material will dictate this final result, a solution of the condensation dynamics the focus of future work.

References: Kulmala, M., Laaksonen A., Korhonen P., Vesala T., Ahonen T., and Barrett J.C.: The effect of atmospheric nitric acid vapor on cloud condensation nucleus activation, *J. Geophys. Res.*, 98, 22949–22958, 1993. 25157