

Response to referee's comments for "A parameterisation for the activation of cloud drops including the effects of semi-volatile organics"

The referee's comments to be addressed are given as bullet points in black text with our replies following in red text.

A. Laaksonen (referee)

- Nitric acid should behave quite similarly as the organics with similar volatility and effective Henry's law **We will respond to this and the following comment together;** ... in many cases nitric acid does not partition completely to the growing droplets before S_{max} is reached, and the organics in the two or three most volatile bins of the volatility distribution (see Topping et al, Nature Geoscience 2013) are more volatile and have smaller Henry's law constants than nitric acid" **It must be appreciated that the majority of organics do not have similar volatility and effective Henry's law coefficient to nitric acid (see supplementary material in Topping et al, Nature geoscience, 2013) and also that, when studying the potential role of non-ideality, the Topping et al. (2013) paper showed calculations up to $RH=0.9999$ only – not S_{max} . Our calculations with nitric acid also suggest that nitric acid does not partition completely – under lower RH conditions it is more volatile than the bins we are considering here and is only similar or less volatile than our most volatile bins above the RH plotted in Topping et al. (2013) The reason that the organics do not behave "quite similarly" to nitric acid, when placed in a dynamic parcel simulation is that the organics continually condense to the growing droplets controlled by a constant, pure component, vapour pressure diluted in the increasing volume of water. The driver for nitric acid condensation, on the other hand, increases with increasing liquid water volume beyond the simple dilution of the pure component. This happens just when the dynamics of the simulation start leading to a departure from equilibrium. More nitric acid, therefore, remains uncondensed at S_{max} than would remain if the vapour pressures were constant leading up to S_{max} . This is illustrated in Figure S1, which shows the equivalent volatility for HNO_3 over different solutions converted to a C^* value (right panel) based on results from E-AIM for the equilibrium vapour pressure of HNO_3 above multiple inorganic compositions (left panel).**

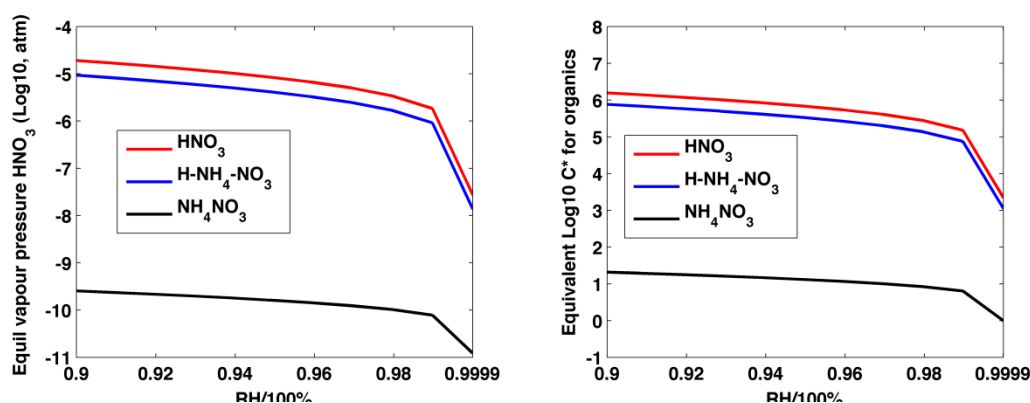


Figure S1 – Equilibrium vapour pressure of HNO_3 above multiple solutions using E-AIM (left panel) and equivalent $\text{Log}_{10}C^*$ of HNO_3 exhibiting the same equilibrium vapour pressures (right panel).

As we report in the supplementary material of Topping et al (2013), if using Henry's law constants (K_h) as a point of reference, the effective solubility constants of components can be calculated. The vapours contributing most to the co-condensation (those with the greatest increases in additional condensed mass with increasing RH) are those in volatility bins corresponding to $-1 < \text{log}_{10}C^* < 3$. Donahue et al (2011) presented the correlation between measured C^* values with typical oxygenated functionality and carbon number. For example, $\text{Log}_{10}C^*$ between -1 to ~3 is covered by multiple acids and diacids with carbon numbers

ranging from 3 to 12. From our ideal simulations presented in that paper, compounds in these bins will have an effective solubility around $4 \times 10^5 < K_h < 4 \times 10^7 \text{ M atm}^{-1}$. According to the extensive compilation of Henry's law constants by Sander (1999), mono and dicarboxylic acids have Henry's law constants between 10^2 and $10^{18} \text{ M atm}^{-1}$. For example, malic acid, with a predicted vapour pressure of 10^{-9} atm (hence $\log C_{\text{star}} \sim 1$) has K_h of $2.0 \times 10^{13} \text{ M atm}^{-1}$. Similarly, citric acid (vapour pressure of 10^{-12} atm , $\log C_{\text{star}}$ of -4) has a value of $3.0 \times 10^{18} \text{ M atm}^{-1}$, tartaric acid (vapour pressure 10^{-12} atm , $\log C_{\text{star}}$ -2) has a K_h value of $1.0 \times 10^{18} \text{ M atm}^{-1}$. Glyceraldehyde, with a higher vapour pressure of 10^{-5} atm ($\log C_{\text{star}}$ of 5, above the range of volatility used in our model) has K_h of $3.0 \times 10^{11} \text{ M atm}^{-1}$ and erythritol (vapour pressure 10^{-10} , $\log C_{\text{star}}$ 0) has a value of $2.0 \times 10^{16} \text{ M atm}^{-1}$. Higher volatility compounds whose contribution to co-condensation are largely excluded in the model runs in the current study ($\log_{10} C_{\text{star}} \geq 4$) include alcohols, ketones and aldehydes with K_h values of the order 10^2 - 10^5 , $\sim 10^1$ and 10^1 - 10^6 M atm^{-1} respectively. Those compounds with K_h values reported as less than or equal to 10^3 M atm^{-1} include alkanes, alkenes, alkynes and ketones, none of which are generally expected to contribute significantly to condensed phase organic mass and all of which have vapour pressures that make their saturation concentration $\log C_{\text{star}}$ much greater than 3 and hence not important for our parcel model simulations.

- The present parametrisation appears to reproduce the parcel model simulation results very well, but the simulations have only been carried out for a limited range of conditions. **We address this in your later comment about extra simulations below.**
- Also, I would like to be convinced that the success of the parametrisation is not due to cancellation of errors related to including both very low volatility species and very high volatility species which behave very differently at cloud activation but are lumped together in the parametrisation. **it is not clear what errors are being referred to. We will demonstrate the parameterisation over a wider parameter range, as requested in your later point below, which will demonstrate its validity, with the caveat that it is beyond the scope of this paper to address non-ideality, which is partly investigated in Topping et al (2013). To do in its entirety this would require consideration of individual component concentrations for a given set of VOC conditions with non-ideality**
- The parametrisation is based on the assumption that all of the gas-phased organics partition to the aerosol phase at cloud base (BTW, does this mean the location of 100% RH or that of the maximum supersaturation?). **Anecdotally it means that if we assume all gas phase organics are in the aerosol and calculate the activation we get a good agreement with the parcel model; hence, the relevant place that this is applied in the parameterisation is at S_{max} . It is important that the Topping et al (2013 Nature Geoscience) paper showed condensed organics at $\text{RH}=0.9999$, so more organics will be condensed at S_{max} than that shown by Topping et al (2013); however, we re-iterate that the parcel model simulations assume solution ideality.**
- The authors justify the assumption of complete partitioning to droplets by the calculation shown in Topping et al (Fig. 2 there), but that was done for a size distribution with a very large median diameter, 150nm, while the median diameter in the present manuscript is only 60nm. I strongly suspect that the partitioning to the droplet phase is clearly less for the 60nm size distribution regardless of the number concentration. **Fig 1a in our paper mostly shows that our assumption of organics in the same volatility range as the Topping et al (2013) paper completely condensing is a good one for low updraft speeds. Where it isn't a good approximation is for faster updraft speeds with low drop concentrations; however, as we state in the manuscript, it does not matter since nearly all aerosol particles act as CCN in this regime regardless of semi-volatile co-condensation, because of a 'saturation of activation' effect.**
- Secondly, I am not completely convinced by the justification given for the constant shift of the size distribution (i.e. constant arithmetic SD) due to condensation of the organics. Fig. 2 shows what happens at an RH of 95% where only the most involatile organics condense

(species which have clearly lower volatility than nitric acid). I would like to see the shift of the size distribution at cloud base. **This is a valid concern and we can easily provide this for the revised paper, the result is the same as shown in figure.**

- Regarding the low volatility organics with $\log_{10}(C^*)$ between -6 and -2 (or -1). As can be seen from Figs. 1 a) and b), these substances condense rapidly (about half of the organics are depleted within a few tens of seconds when there is sufficient aerosol surface area present) at RH's clearly below 100%. In fact, these low volatility substances are capable of condensing at RH's much less than 95%, and I believe that in reality (and also in large scale models having advanced partitioning or condensation schemes for organics), it is very rare that they remain in the gas phase when RH has increased to 95% (or even 90% for that matter) as is assumed in the present work. **We agree, and this is what the model shows. As we state in our recent paper (Topping et al 2013), co condensation does not require any of the very low volatility components of $\log_{10}C^* < -1$ ever to be in the organic vapour pool. They will always be in the condensed organic pool. It is worthwhile to note however that, when initialising the parcel model simulations with fixed inorganic:organic mass ratios in the 'dry' size distribution, the total mass in lower volatility bins does affect the condensed amount in higher volatility bins.**
- This is because the condensable organics are produced photochemically at sunny conditions when there is sufficient OH to oxidize the less volatile species, and by the time the RH has increased to 95%, the conditions are usually pretty cloudy. I therefore think that these low volatility species should not be included in the parcel model simulations at all. **Again we agree with the reviewer on the behavior of these lower volatility bins as a function of RH. As stated previously, they are actually important to include in initialising the parcel model simulations as for a given prescribed organic: inorganic mass ratio and size distribution, the total amount of organic material, and thus condensable vapours, is affected by the shape of the volatility distribution. These bins were therefore important in defining how much condensable material was available in the higher volatility ranges, as discussed in the supplementary material of Topping et al (2013).**
- I also think that the comparisons between the parcel model simulations should be done for a broader range of conditions than shown in the manuscript in order to make a convincing case of the goodness of the parametrisation. The median diameter and the SD of the aerosol size distribution should be varied sufficiently, and at least some of the comparisons should be repeated at a lower temperature. **We can certainly do some extra simulations. For example we can run with different median diameter and a run with a different standard deviation. Temperature does not have a large effect in that moving to lower temperatures results in even more of the organic in the aerosol phase. We will include this in the revised manuscript.**
- It would also be interesting to know what the effect of possible insoluble core material in the aerosol is. **There are certainly plenty of effects to investigate, and we plan to. We suggest that this aspect be included in a separate publication as including it here would detract from the main message.**
- The authors should make plots from parcel model runs that clearly show what fractions of the three most volatile bins condense before cloud base at different temperatures and updraft velocities, and with different aerosol size distributions. If important effects are seen, these effects should be included in the parametrisation. **The plots are possible as the data are there. It is not clear what you mean by 'important effects' since the most important point is whether we manage to reproduce the parcel model in terms of activated fraction, which is our aim for this paper.**
- As noted above, the nitric acid effect on cloud activation is very similar to that produced by semivolatile organics. The literature should therefore be cited (especially papers in which parcel model simulations have been carried out). **We are happy to cite papers on nitric acid, thanks for the suggestion.**
- It appears that the present parametrisation is at least somewhat similar to that used by Xu and Penner, and it would be interesting to see discussion about the similarities/differences of

the two parametrisations. we are happy to discuss this point; however, there do not appear to be many similarities between our work and the work of Xu and Penner.

References

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