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Interactive comment on "Connecting the solubility and CCN activation of complex organic aerosols: a theoretical study using the Solubility Basis Set (SBS)" *by* I. Riipinen et al.

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We thank this Reviewer for the thoughtful read of our manuscript and the insightful comments – which we think will help us improve the revised version of the work. Our point-by-point responses to the Reviewer's comments are below. The direct quotes from the Reviewer are in *italics* and our responses in normal font.

(1) I am very unsure of, and uncomfortable with, the use of the terminology Basis Set in the context of the current study. It makes no sense in terms of the common usage in theoretical and computational chemistry, nor that in linear algebra. Its usage in terms of

the well-established VBS was also difficult to understand and its adoption in the current work by analogy to the VBS requires explanation. As stated, the current manuscript considers "a continuous distribution of solubilities" in classes one decade apart. This provides a suitable reference scale on an appropriate axis, but I do not see where there is any reference "set" (of functions, of compounds, of properties, of vectors etc...) that can be used to make sense of the impacts of particle component solubility. This is particularly important in the context of the non-independence of the presented component description in terms of solubility and the extended volatility description where the second dimensions considers the degree of oxygenation (in terms of O:C or oxidation state), see below.

We understand the point of the reviewer and indeed the different dimensions of the “basis sets” are not expected to be independent of each other. We have therefore primarily used the term ”solubility distribution” instead of ”solubility basis set (SBS)” throughout the revised manuscript, except for the point in which the analogy to the widely-used VBS approach is discussed.

(2) To expand on this point, given the relationship between aqueous solubility of organic molecules and their polarity (and hence practically, their oxygen-containing functionality), the solubility consideration in the current paper is clearly not independent of the 2-D VBS of Donahue et al., 2011 or the Carbon number - oxidation state representation of Kroll et al., 2011. Whilst both approaches are mentioned in the current work, the relationship between the approaches is insufficiently discussed. It appears that the current work concerns itself with the cloud droplet activation behaviour of OA components, whereas the "VBS" approaches are more concerned with formation and transformation of the OA. However, the relationship between degree of oxygenation and hygroscopicity has been widely investigated, both in terms of the VBS and otherwise (e.g. in terms of AMS m/z 44 in the paper introducing the 2D-VBS). Introduction of yet another approach without contextualisation appears to add to the confusion, rather than to its clarification.

It is expected that the mixture solubility distribution will depend on both polarity and thus O:C ratio (Donahue et al., 2011; Kroll et al., 2011) as well as the molar mass (Shiraiwa et al., 2014) of the mixture constituents. To illustrate this, we have added a figure depicting an example solubility distribution for a representative case of α-pinene SOA (Chen et al., 2011), where the solubilities have been estimated using the SPARC (see e.g. Wania et al., 2014 and references therein) prediction tool. Also the mean molecular mass and O:C ratio for each solubility bin are presented. A brief discussion of the expected dependence of the solubility on these different molecular properties has been added along with the description of the new figure to the revised manuscript.

(3) Line 7 p28530 it is stated that "This assumption is justified to a first order by the different equilibration time scales of the droplets with respect to water vapour and the organic vapours in typical atmospheric conditions" when referring to the lack of consideration of partitioning of organics between the gaseous and either aqueous or non-aqueous phases in the current study. This is a bold statement. The activation is driven by the increase in water saturation ratio by cooling (updraught in a cloud, radiative or advective in a fog). The (low) rate of change of saturation ratio caused by this will lead to the mass flux of water. Since the number of water molecules is high, it is frequently assumed that the number of collisions leads much more rapid condensation of water vapour than of other components. However, the rate of change of saturation ratio of organic molecules can be very much higher (owing to both temperature, but equally or more importantly photochemical reaction). Since the vapour pressure of the organic can be many orders of magnitude lower than water, a strong diffusion gradient between the gas phase and the particle surface can be very rapidly established. There are very many potential oxygenated organic compounds that can all be rapidly produced in response to strong emission and photochemical changes. It is far from clear to me that the addition of soluble mass to a particle in moving towards cloud base can be ignored to a first order approximation (and hence that the solubility distribution of components at lower RH will be the same as the solubility distribution of components close to activation). The Topping et al. Nature Geoscience paper (doi:10.1038/ngeo1809) should

be referenced in this regard. Again, the blurred relationship between volatility treated in the "VBS" approaches and solubility treated here is related to this. It appears conceptually peculiar to silo treatments of partitioning and water uptake into the separate approaches; the moist atmosphere is a single entity in which both processes simultaneously occur.

We agree that this is an important assumption and that it deserves additional discussion. It is also true that for a comprehensive picture of the CCN activation, all the relevant dynamic processes for all the involved species (and their gas phase concentrations) need to be explicitly considered. This requires, however, a much more complex modeling framework and detailed information about the connections between volatility and water solubility of the different organic compounds that is not currently available. For the scope of this work we felt that it is important to focus on the solubility effects on the CCN activation process, without adding the uncertainty related to e.g. the gas-phase concentrations of the organic species and atmospheric dynamics. This is clearly a first step and investigations with a cloud parcel model including all the relevant dynamic processes will be carried out in a future study. We think that this approach is justified, as this is the first study investigating the sensitivity of the CCN activation processes to a wide selection of solubility distributions. In the revised manuscript we have added a reference to Topping et al. (2012) and replaced the statement of the justification of this assumption with a more nuanced discussion of the corresponding issues mentioned by the reviewer.

(4) I'm a little confused in how the approach described here to calculate the equilibration of components between the insoluble core and the surrounding aqueous shell relates to previous approaches to deal with phase separation in complex mixtures in atmospheric aerosol (notably that presented by Topping et al., 2013, doi:10.1039/C3FD00047H, which should be referenced). The solubility in the non-aqueous and aqueous phases must implicitly account for non-ideality (and e.g. degree of dissociation of weak acids and bases) and hence must be considered an effective

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solubility in the mixture. In the aqueous phase, this effective solubility may or may not be relatively simply related to the infinite dilution solubility of the component. In any case, it will very likely be relative humidity dependent. As such, the effective solubility distribution in the two phases will be RH dependent and this will (potentially significantly) affect the shape of the Kohler curves and the results illustrated in Figure 3. Coupled to the equilibration between the gas phase and the two condensed phases, it might be expected that this effect is substantial. In figure 8 a simple sensitivity to an assumed activity relationship is explored (using equation 5). Such calculations can be carried out for simple real mixtures where the activity coefficient data (albeit on a mole fraction scale) are available (and complex mixtures where the activity coefficients can be predicted). This sensitivity is assumed to constrain the real behaviour (very likely correct). It would be useful to know whether the real behaviour more normally follows one or the other of these limiting cases. Even in the absence of confirmatory experimental data, such calculations are possible.

We have added the reference to Topping et al. (2013) and the corresponding discussion. We have also cited the work of Cappa et al. (2008) with some discussion on the potential non-ideality of multicomponent mixtures of dicarboxylic acids. Unfortunately, there is very little experimental information available about atmospheric organic compound activity coefficients in the aqueous or multicomponent organic phases. Data is available for individual organic compounds, but it is not clear how useful these data would be to estimate the mixture behavior. Our simplified ideality assumption for the aqueous phase activities below the saturation concentrations is a reasonable starting point. The corresponding solubilities discussed here should be interpreted, as the reviewer suggests, as “effective” solubilities. A brief discussion has been added to address this point in the revised manuscript.

(5) It is stated on line 15 of 28532 that "... all the equations presented below can be rederived in a relatively straightforward manner taking into account a potential difference between the mole and the mass fractions in the organic phase". This is correct, but

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the reference scale difference for the activity coefficients (mass or mole fraction) must be emphasised. This must be made explicit - it is the same problem as encountered in the VBS and is more important here, since the molecular weight distribution and degree of functionalisation will significantly affect effective solubility and hence phase partitioning.

This is correct. We have added a sentence to the revised manuscript emphasizing the fact that we have studied the special case where the mole and mass fraction scales are the same, but that these should be distinguished for realistic atmospheric mixtures.

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(6) Some reference to the expected individual component effective solubility range for atmospheric components would be helpful. The very heavy functionalisation (of multi-functional peroxides, peroxyacids etc...) expected and required to attain observed O:C ratios with a measured molecular weight distribution of organics provides some surprisingly high solubilities. Along with the very low solubilities of slightly functionalised high molecular weight primary compounds, this will lead to a very wide distribution of solubilities as shown in Figure 2. Are there any data available to say whether the real atmosphere is likely to be closer to one or another of the chosen distributions? If not, what are the difficulties and are there suggested routes forward?

To link our approach better to realistic atmospheric organic mixtures, we have now constructed the solubility distribution for an example composition of secondary organic aerosol (SOA) mixture derived from α-pinene oxidation (see Chen et al., 2011 for details of the gas-phase composition and conditions corresponding to this distribution). It should be noted though that this is only one example, and the organic aerosol formed under different conditions or derived from other precursors can have vastly different solubilities, nevertheless being equally well represented by the solubility distribution approach. The results from our manuscript can then further be used to assess the requirements (e.g., range of solubilities, resolution) of a solubility distribution measurement approach to represent the CCN activation of these mixtures. We have added discussion on the link of the study to realistic atmospheric organic mixtures, along with adding a new figure depicting an estimated realistic solubility distribution to the revised manuscript.

(7) I am not sure that the 2 sentences in the abstract from line 17 to 21 and 21 to 24 are not contradictory. Please check. Can the stated material in the first sentence be assumed completely soluble and is this material not just a subset of the material considered within the distribution mentioned in the second sentence and hence requiring understanding of the details of its distribution in solubility? In any case, the arguments considered together in such close proximity before the reader has accessed the rest of the paper are too complicated for easy interpretation.

Indeed these two statements can cause some confusion. We have revised the statements to read:

”Depending on what was assumed about the organic phase activity, material with solubilities larger than 0.1-100 g L-1 could be treated as completely soluble in the CCN activation process over atmospherically relevant particle diameters and supersaturations. Our results indicate that understanding the details of the solubility distribution is thus probably necessary only in the range of 0.1 to 100 g L-1, while resolution outside this solubility range will not add much knowledge to understanding the CCN activation of the mixture.”

(8) On p28526, 3 prior assumptions are described that are considered in the paper. The kappa consideration is not the only single parameter representation of hygroscopicity (e.g. Wex et al., 2007, doi:10.1029/2006GL028260), nor the first (e.g. Rissler et al., ACP, 2004). These treatments should be acknowledged.

Thank you for pointing this out, we have corrected this in the revised manuscript.

(9) It isn't clear how the presence of inorganics effects results in this paper. It is likely

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that there will be an inorganic fraction under most expected atmospheric conditions and this should be mentioned in the discussion.

This is an important point as the present work addresses explicitly only organic particles. The work can be extended to include inorganic salt adding one more variable for consideration (the organic mass fraction in the particle). However, accurate considerations on the mixture activity and potential phase-separation effects will become much more complex, requiring detailed experimental data as well as advanced thermodynamic models – being thus a very interesting topic for a future study. We will add a brief discussion on this to the revised version of the manuscript.

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