

Interactive comment on “Chemical aging of single and multicomponent biomass burning aerosol surrogate-particles by OH: implications for cloud condensation nucleus activity” by J. H. Slade et al.

Anonymous Referee #1

Received and published: 27 March 2015

The manuscript entitled, “Chemical aging of single and multicomponent biomass burning aerosol surrogate-particles by OH: . . .” by Slade et al., addresses an important topic on how CCN activity evolves with composition (produced by a heterogeneous reaction with OH radicals). In particular the authors study model biomass aerosols in pure form and also in mixtures with inorganic species. The data is analyzed by the kappa parameterization of Kohler theory. The main conclusions are that when aerosol contains water soluble organic material or inorganic species chemical aging does not have a significant impact on hygroscopicity. However, there are a number of substantial issues that the authors need address to support these main conclusions, otherwise

C1158

these conclusions require significant revision.

Major Comments:

1. The current measurement approach introduces significant ambiguity into the data analysis and therefore the overall interpretation of the data presented in the paper. The authors use a polydisperse particle size distribution for the OH aging experiments, which is in principle ok and done extensively in the community. However, for CCN measurements significant uncertainty is introduced when measuring hygroscopicity by scanning particle size in a chemical aging experiment. This is due to the fact that the oxidation lifetime (and thus chemical composition of the aerosol) is a function of particle size. For a distribution of sizes, smaller particles will be much more oxidized than larger ones at the same OH exposure. This is simply due to the difference in surface to volume ratio (assuming the uptake coefficient is independent of particle size, which is a reasonable assumption here). So by scanning the particle size at a fixed supersaturation, hygroscopicity is determined using a set of particles that are not compositionally identical (smaller particles are more oxidized than larger ones). Therefore drawing any robust conclusions from such an approach can be quite ambiguous. A slightly better approach is to scan the supersaturation for the whole size distribution, which still leads to some ambiguity as described below. The best approach is to size select the particles (monodisperse) before the reaction (so all particles sizes exiting the reactor are compositionally identical) and then scan the supersaturation for hygroscopicity determination. Furthermore, using monodisperse particles enables clear measurements of volatilization. This was the approach adopted by George et al., [Atmospheric Environment, 43, (2009)] and Harmon et al. [Phys. Chem. Chem. Phys., 15, 9679 (2013)] in their CCN studies of chemically aged aerosol. Furthermore, if chemical erosion occurs at a given oxidation lifetime, which was observed for levoglucosan by Kessler et al. [Environmental Science & Technology, 44(18 (2010))], then one would expect even a more pronounced differences in composition as a function of size at a fixed OH, which would be obscured using a polydisperse distribution and size selecting after the reac-

C1159

tor. One of the main conclusions in the paper is that chemical aging has no significant impact on OA hygroscopicity of water soluble species simply cannot be supported or refuted using the measurement technique described here and the associated ambiguities between particle size and composition (CCN depends critically upon both) cited above.

2. The authors interpret their data exclusively within the Kappa framework. As implemented, the authors assume in Equations 2 and 3 that surface tension is that of pure water (this should be stated manuscript stated explicitly in the manuscript). There are a number of studies [e.g. George et al., *Atmospheric Environment*, 43, (2009), Schwier et al., *Atmospheric Environment*, 54, (2012), Noziere *Nature Comm.* 5, (2014), Harmon et al. *Phys. Chem. Chem. Phys.*, 15, 9679 (2013), etc.] that show that surface partitioning of organics can play a role in CCN activity, even organics that would be normally considered water soluble. Some discussion is needed about the potential role of surface tension depression, and how neglecting its effects might alter or not the main conclusions of the paper. In particular George et al. and Harmon et al. both study the effects of chemical aging on CCN activity and both studies report evidence for surface tension reduction as well as the role of fully soluble and slightly soluble reaction products of relevance for the present study. Also on page 6785 line 3 the authors compare kappa for oxidized levoglucosan with several carboxylic standards measured by others. The authors should also include a discussion of surface tension here since there is recent evidence reported by Ruehl et al. [*J. Phys. Chem. A*, DOI: 10.1021/jp502844g (2014)] that the hygroscopicity of the same set of diacids coated on ammonium sulfate particles is more complex and not controlled by bulk solubility alone but involves surface processes not captured in the kappa formulation.

3. The authors say that they measure Kappa (e.g. p. 6784 line 11), which is strictly incorrect since Kappa is derived (with some assumptions) from the measurements of critical diameter. Given that the experimental observable is critical diameter vs. OH exposure this data should be included in the manuscript and added explicitly to figures

C1160

5, 6, and 7. This will give the community easy access to the “raw” data.

3. Some of the authors previously published a very nice study on the how the reactive uptake depends upon RH, water diffusion coefficient etc. for both levoglucosan and MNC. What is the RH for the aging experiments reported here? Changes in reactive uptake of OH can signal changes in the chemistry, so some context of this prior work on the chemistry of aging should be included. The authors present no clear relationship between the evolution of kappa and the extent of reaction (depends upon the uptake coefficient, which is function of RH). It is not clear in the current manuscript that the reason for this is simply a small uptake coefficient and therefore a small extent of reaction so that the particle remains mostly levoglucosan over the range of exposures accessed in the experiment.

4. Since particle size plays a key role in hygroscopicity, the authors need to report how the average particle size changes (or doesn't) as a function of OH exposure (chemical erosion).

5. The authors should explain why drying the particles out to RH < 5% after reaction but before the CCN measurements is done. Could this drying step not impact the phase state of the particle and thus unnecessarily complicate observing the connection between aging and CCN properties produced by oxidation?

6. The results for the coating experiments shown in Figure 8 are very difficult to follow. The discussion of the coating method is also quite confusing on page 6791. The authors should clarify why Figure 8a and 8b are time dependent since the key relationship is between kappa and Vorg, which is not time dependent. Are the coatings applied thermally and are they not stable over time? Some details in the experiment section are clearly needed for the reader to better understand how the data is obtained in figure 8.