Response to comments by Referee #1 on “Humidity-dependent phase state of SOA particles from biogenic and anthropogenic precursors”

We have previously submitted the reply to the most critical comments of the reviewer #1. Many of the comments of the rev. #1 are related to the issues discussed already in our previous response. Thus here we won’t come back with those, but reply to some other points brought up by the reviewer.

Ref. comment, page 3:

“…No attempt is made to explore whether changes in bounce as a function of RH are correlated with how much water is absorbed…”

> We didn’t have HTDMA in our use in the measurement campaign, thus we are dependent on the previous publications related to hygroscopic growth of SOA in low humidity values. Unfortunately many of the published data on the hygroscopic growth of SOA particles are for RH values higher than those used in our study. There are also papers presenting growth factors at low RH values (RH<65 %) for various SOA systems, but very few of those report the O:C ratio of the particles. And, as reported e.g. by Jimenez et al. and Massoli et al., the hygroscopic growth of the particles depends on the O:C ratio of the SOA system. Thus making a comprehensive correlation of bounce and amount of water in the particles is not possible based only on the literature.

Page 4:

“Is it true that a bounce fraction of 0.1 means liquid?”

> Considering the measurement uncertainty of the method we can conclude that particles having bounce value of 0.2 or smaller are “liquid-like”. By the term “liquid-like” we mean substances having low viscosity values. Generally the substances having viscosity of ~100 Pas or smaller are considered as liquids. As discussed in our manuscript, currently we can’t give exact viscosity limits for particles showing high bounce (>0.6) and low bounce (<0.2). Our future work is related to this subject.

Ref: “The two particle components (SA and SOA) could be, and most likely are morphologically separated” + comments on page 8-9

> Based on e.g. study of Song et al., 2012 the phase separation of inorganic-organic materials depends on the solubility of the organic fraction. In the case of the longifolene SOA, which was the studied system in SA+SOA experiments, it is possible that the particles are phase

separated. In any case, there are no reasons to assume that SA would form an outer shell on the particles. We have mentioned the possibility of the phase separation in the revised manuscript.

Page 8:

“What is a liquid like particle?”

By liquid-like particles we mean particles having low viscosity. As stated in the manuscript, currently we can’t give exact viscosity values for particles having certain bounce characteristics.

“The presence of oligomers can play a very important role in SOA properties. Would one even expect SOA to undergo glass transition? With a large fraction of oligomers in SOA, would it not be better to think of it as being composed of longer chain cross-linked polymers?”

The comment by the referee seems to imply that oligomerisation and glass formation are two unrelated ALTERNATIVE interpretations for the observed behavior of SOA particles. It should be pointed out, however, that oligomerisation, polymerisation and cross-linking do make statements about the primary chemical structure of the related material, while glass formation relates to the physical state (more specifically to the phase state) of the material.

For example, small molecules, oligomers, polymers, and cross-linked polymers can all undergo a glass transition and form amorphous solids. But upon uptake of small solute molecules do linear polymers and cross-linked polymers behave differently: linear polymers may liquefy entirely upon solute uptake, while cross-linked polymers may transform into a semi-solid state such as a gel.

Coming back to the original question raised by the referee: What is the effect of oligomers and cross-linking upon glass transition? There is clear evidence from different types of materials that oligomerisation and polymerisation do lead to an increase of the glass transition temperature of a chemical compound, and even semi-empirical formulations exist (e.g., the Fox-Flory relation) that describe the molar mass dependence of Tg (Fox and Flory, 1950; Rietsch et al., 1976; Koop et al 2011). Moreover, there is also mounting evidence that cross-linking of polymers also leads to an increase in Tg when compared to the same linear polymer, independently of whether the polymers are cross-linked in a linear or even branched fashion (Nielsen, 1969; Rietsch et al., 1976), owing to a reduced segmental motion of the individual monomeric chain units (Fried, 2007).

Page 5:

“The use of 10^{12} OH molecules/cm^3, which is about a million times (!) higher than OH concentrations in the ambient atmosphere, raises some interesting questions. In the real atmosphere, once a molecule is oxidized, it is a million times more likely to condense than react again with OH than in the reaction chamber used here. Does that not mean that it has a much higher chance to undergo a number of oxidation stages before it is lost to the condensed phase?“

To clarify one point raised in this comment by the reviewer, the maximum OH exposure (OH concentration times average residence time) used in the PAM is $2.2*10^{12}$ molec cm^{-3} s. At an average residence time of 100 sec (p. 4452, line 9), this corresponds to a maximum OH concentration of $2.2*10^{10}$ molec cm^{-3}, not 10^{12} molec cm^{-3}.

The reviewer is correct that gas-phase chemistry in the PAM reactor is accelerated relative to processes that may occur in the condensed phase, such as heterogenous oxidation and oligomerization reactions. This is certainly a valid and important concern, and was the focus of a recent study by Renbaum and Smith (2011). In this paper, flow tube experiments were performed to assess whether oxidant concentration and exposure time are interchangeable parameters, and if conserving the product of the two parameters (i.e. integrated oxidant exposure) allows extrapolation to atmospheric conditions. Renbaum and Smith studied the uptake kinetics of OH and Cl radicals on 2-ocyldodecanoic acid (2-ODA) organic aerosols at exposure times of 2 and 66 sec. Based on their results, they conclude:

"No difference is observed in the reaction kinetics of 2-ODA aerosols with OH or Cl when the decay profiles are constructed by changing the radical concentration [...] or the reaction time [...] as long as the [radical] precursor (O_3 or Cl_2) concentration is the same in both cases. Thus, it is appropriate to consider the radical concentration and reaction time as interchangeable parameters with the product of the two, the exposure (=[OH]·t or [Cl]·t), being conserved. Consequently, it seems reasonable to extrapolate results from laboratory aerosol flow tube studies, in which reactions are studied with high radical concentrations on the timescales of seconds to minutes, to atmospheric processes, which involve much lower radical concentrations and occur over several days to a few weeks."

To address this comment in the manuscript, we have added the following text to the manuscript (changes bolded):

Page 4453, line 3: "While OH concentrations in these experiments (approximately 2.7×10^{9} to 2.2×10^{10} molec cm^{-3}) are higher than ambient OH concentrations, the integrated OH exposures are similar. Previous work suggests that, to first order, extrapolation of flow tube reactor conditions (high [OH], short exposure times) to atmospheric conditions (low [OH], long exposure times) is reasonable (Renbaum and Smith, 2011)".

We have also added the following citation to the list of references:

Renbaum, L. H. and Smith, G. D.: Artifacts in measuring aerosol uptake kinetics: the roles of time, concentration and adsorption, Atmos. Chem. Phys., 11, 6881–6693, http://dx.doi.org/10.5194/acp-11-6881-2011doi:10.5194/acp-11-6881-2011, 2011.

"What does "more solid" mean?"

Semi-solid / solid amorphous materials have very wide viscosity values. The viscosity of the semisolids varies from ~10^{2} Pas up to 10^{12} Pas. Material having viscosity > 10^{12} Pas can be considered as "glass" (e.g. Koop et al., 2011). Thus "more solid" refers to the (amorphous) material having higher viscosity than some other (amorphous) material.

The referee also discuss about the effect of oligomerization to particle phase and SOA water content at a given RH (in page 8). We agree with the referee, that oligomers most likely affect the particle phase and also might affect the humidity behavior of the particles. We have actually discussed about the effect of the molar mass of the compounds on particle phase in chapter “4. Discussion”

“Figure 8 I missing error bars. Starting the slope analysis at 50% RH is an arbitrary choice. The data do not support the idea that there is a magical transition point at 50% RH that is applicable to all cases…”

- We will add the error bars into Fig. 8
- We are not claiming that RH 50% is a “magical” transition point of phase transitions. As pointed out by the referee, the RH 50% is quite an arbitrary choice made here to quantify the behavior we see in the measurements. It is important to note, that the result of the analysis / conclusions wouldn’t change if we changed the RH value in question.

References

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