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Atmospheric
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Interactive comment on “Reversible and irreversible processing of biogenic olefins on acidic aerosols” *by* J. Liggio and S.-M. Li

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Response to general comments:

We appreciate the careful consideration of this manuscript by the reviewer, and the useful comments which were made. These comments are addressed below.

We agree that the acidities used in this study may be somewhat high; however we feel that this does not negate the relevance of this work. We do not believe one can absolutely say that areas of biogenic activity would not have highly acidic aerosols. Even background SO2 can nucleate to form aerosols or condense onto existing aerosols, resulting in high acidity. Another possibility is through in-cloud production of sulphate that can lead to high acidity in aerosols once clouds evaporate. This can in principle happen over a forested region, and has been observed (Riipinen et al., 2007). Although particle growth may be dominated by biogenic SOA in these regions, the original nucleated aerosols may be rather acidic as a result of sulphuric acid nucleation. This may in fact be the case in most areas. As yet unpublished data (Shao-Meng Li, personal communication) from forested regions of Nova Scotia and Ontario, Canada also clearly show that highly acidic aerosols do indeed exist over these areas from time to time.

We agree that nucleated aerosols can be neutralized to some degree after the fact. This however depends on how much NH3 is available, which over forested areas is usually quite low. How much acid catalyzed growth occurs may be related to how long it takes for such particles to become fully neutralized. Depending on the conditions, it may take a significant amount of time to completely neutralize these aerosols especially if NH3 is low. If reactions as reported in this paper are fast enough then a significant amount may still accumulate. Furthermore, it is also possible, and perhaps probable that additional sulphuric acid may condense on fully neutralized particles of varying size. It is unknown what the acidity of this freshly condensed layer might be but may be similar to pure sulphuric acid aerosols. In addition, in cloud SO2 oxidation and evaporation of cloud droplets can also result in a very low pH. This may be somewhat important given that in cloud sulphate formation can account for a significant fraction of ambient sulphate, for example, typically considered to be about one third in eastern North America based on models. We do not believe that one can make a generalization regarding the acidity of aerosols given the dynamic nature of the atmosphere, the very few ambient acidity measurements and the uncertainties related to nucleation/H2SO4 condensation on aerosols. The relevance of the presented process is better determined through a modeling study which could be the topic of future papers.

Indeed polymeric material has been identified in ambient particles on several occasions (Kalberer et al., 2006; Zappoli et al.,1999; Denkenberger et al., 2007); however determining the origin of the polymer is not always possible based on mass spectra alone. Similar olefinic polymers, of both biogenic and anthropogenic origin may be a part of what has already been observed in abundant ambient organic aerosol mass spectra. On the other hand, terpene-like polymers have in fact been identified in ambient surface films and attributed to heterogeneous reactions (Lam et al., 2005). Our study in fact corroborates this evidence.

Attempting to use ambient AMS data to justify the existence of this process may not be entirely possible. Realistically, statistical approaches cannot completely deconvolute the spectra into the multitude of components which we know must actually exist in the atmosphere. This is especially true for those methods which use the variance of the original data to determine the components, since many different compounds/processes can vary in the same manner and yet be lumped into the same component. Thus, it may be likely that the spectra observed in this study are contained within the OOA or HOA components. We agree that m/z 44 is dominant in OOA and less so in our spectra, but this is of no consequence unless one is convinced that the OOA is composed of a very large fraction of polymeric material. We do not believe this to be the case. We agree that the estimate of 2.7 ug/m3 may be somewhat high, but it is dependent upon a number of factors such as acidity, reaction time, surface area, BVOC type, and concentration. Thus, the ideal conditions for this process may only occur for a short period of time such as a burst of nucleation, which may not be fully resolved by the HOA/OOA approach, especially if these particles are below the size cut of the AMS. During such a short time period this process may be important. The value of 2.7 ug/m3 was intended to be an upper limit, but could be significantly less depending on the above factors. We have taken this into account and reduced the estimate of the upper limit (see response below).

The upper limit to the formed mass was calculated from the highest uptake observed for sesquiterpenes (Exp. 15). Using the associated accommodation coefficient a pseudo first order heterogeneous rate constant (khet) was calculated as khet = (alpha $<$c$>$ S)/4 where S represents a typical total surface area for a biogenic area. The formation rate is then k multiplied by the gas-phase concentration. Consequently, khet is highly dependent on S, which was adapted from a model surface distribution for rural areas (790 um2 cm-3) (Seinfeld and Pandis, 1998). In hindsight, this value is likely rather high, and not applicable to a forested area. A better value is obtained from actual measurements over forested regions. We have now chosen to use a value of 230 um2 cm-3 (mean) over a forested region in Canada (Hoff et al., 1996); however significantly lower surface areas for other forested regions has been observed (Koponen et al., 1999; Zhou et al., 2002). Using this value significantly reduced the upper estimate. Furthermore, we have included an uncertainty range to these estimates based on the calculated uncertainties of the uptake coefficients. We have also reduced the available reaction time to 30 minutes (from 1 hour) to correspond with the time required for most of the uptake observed in these experiments.

We do not believe that this process is a significant sink for such gas-phase compounds. The gas-phase lifetime due to heterogeneous reaction derived for every experiment are far too long compared to that of ozone + sesquiterpenes reactions in particular, which are on the order of 1 minute. The shortest lifetime due to heterogeneous reactions was observed during one experiment for b-Caryophyllene (Exp 15, ˜ 20 minutes); all others are significantly longer than this. We therefore have removed the relevant statement from the manuscript. A full accounting of all sinks and sources etc, would require a detailed modeling study and is beyond the scope of this paper.

Response to specific comments:

p. 11977, line 10 (or Table 1):

We have included the seed solution concentrations

p. 11981, line 7; p. 11984, line 22; and elsewhere:

(see response to specific comments of reviewer #1)

We agree that CE would normally be an issue. However, as mentioned in the text, all the masses are normalized to the AMS derived particle number, resulting in a mass per

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particle. This means that any intrinsic CE problems are not important. The decrease in sulphate observed by Bahreini et al 2005 was likely due to CE issues as the mass was not normalized as far as we know.

p. 11981, Eq. 1:

We agree that it may be possible to form product p2 from p. We have added this possibility to equation 1. Regardless, this does not affect the conclusions drawn from this paper.

p. 11981, line 16:

Under some circumstances increasing the RH may not rapidly affect the particle acidity, however this was very likely not the case for these experiments. Measurements of the particle diameter clearly show a significant increase in size immediately after increasing the RH, caused by the addition of water to the particle. Given the somewhat non-polar nature of the polymers it is highly unlikely that this significant water uptake would have occurred unless it was taken up into the inorganic fraction to a great extent. Also, the thickness of the organic coating in these experiments would have to be very small given the size of the original seed and the amount of uptake. There would no doubt be sufficient time for liquid phase diffusion to the acid core in the several hours of these experiments if indeed that is what occurred. The increase in diameter noted above has been added to Figure 3, with additional text in the manuscript explaining it.

p. 11986, line 13:

CTSP can refer to the aerosol mass which can participate in absorptive and adsorptive partitioning. We have assumed TSP to be both the inorganic and organic fraction of the particle. It is unclear at this point if one or both fractions participate, and so we have included both. We agree in a theoretical calculation of Kp, it is necessary to understand the nature of the absorptive/adsorptive material (among other things). However, this is an experimental determination, and thus a total TSP should be sufficient.

p. 11992, line 9 (and Table 1):

We agree that simple pH is not the best estimate of acidity in every case (see response to reviewer #2). We have recalculated the pH using H3O+ activities which are a better estimate. The new calculations have been included in Table 1.

p. 11992, line 15:

Irreversibility of reactions is what we state to have implications in the ambient atmosphere. This is not related to how much of the acidity is reduced; it would occur whether it was reduced or not. How important this process is, depends on a number of factors, part of which is acidity. The potential for acidic particles has been discussed in the response to general comments above.

p. 11992, line 21:

While it is true that little correlation between particle acidity and organic loading has been observed, assuming that oligomers/polymers do not exist based on the lack of a correlation can be dangerous. Firstly, only part of SOA may be formed by this process. Thus, any correlations are likely easily washed out by other compounds/processes. Furthermore, total organic loading (perhaps even WSOC) is likely not a measure of all of the SOA, and thus may not be correlated with acidity at all. In addition, if polymers were formed early on in the particle lifetime, then even after subsequent neutralization, aerosols would still contain this material, and correlations with acidity would be less useful. In fact, this is the point of the paper, in that even neutral aerosols can contain polymeric material depending on its history, and each secondary particle almost always starts its life being acidic in the atmosphere. We do not believe that a lack of correlation with acidity negates the relevance of this work at all.

p. 11992, line 27:

We agree that pre-existing primary organics may slow the oligomerization rates, although currently there is no evidence to suggest this. This statement in the work of

Kalberer et al 2004, was a hypothesis which at this point has not been entirely tested. In fact, it may be that the non-polar nature of preexisting primary aerosols more efficiently takes up the parent terpene which is also non-polar (followed by reaction). We do not know what effect this would have, but it does not affect the conclusions of this paper.

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