Response to comments by Referee #2 on "Humidity-dependent phase state of SOA particles from biogenic and anthropogenic precursors"

The authors thank Referee #2 for the positive comments and constructive points raised in the review. The points brought up are discussed below:

"Overall, the methods used to generate the particles raises the question if and to what degree these results can be applied to the real atmosphere or how the implications from these experiments would hold true for "real-world" aerosols. The generation of oxidized compounds using the PAM technique leads to a high degree of oxidation of organic compounds but does barely resemble the life cycle of an aerosol particle in the real atmosphere. Aging of particles or air masses in the atmosphere involves several processes like the dial cycle, temperature changes, air mass transport, cloud processing and oxidation. Unlike in the PAM, *OH is not the only oxidant. Furthermore, different oxidants lead to different products and path ways of atmospheric oxidation. Also, in the atmosphere organic aerosols are produced from thousands of precursors and not from only a limited number."

> As the reviewer is no doubt aware, a significant issue with conventional smog chamber techniques is that they are limited to simulating equivalent atmospheric oxidation timescales of ~1 day. This prevents the formation of highly oxygenated SOA that is characteristic of aged atmospheric aerosol (e.g. Ng et al.,2010). While the PAM technique has its own limitations, one of which was mentioned by the reviewer, it does not suffer the same limitation as smog chambers in regard to integrated oxidant exposure. In fact, the PAM technique has been demonstrated to produce SOA with atmospherically-relevant mass spectra and elemental ratios (A.T. Lambe et al. 2011; A.T. Lambe et al. 2012).
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> While the reviewer's point is fair (regarding the laboratory simulation of diurnal cycle, temperature changes, air mass transport, and in-cloud processing), this is an issue that is not unique to the PAM technique, as smog chamber techniques do not explicitly simulate these processes either. No laboratory technique is a perfect simulation of the atmosphere. The reviewer is correct that OH is not the only atmospheric oxidant. However, it is almost certainly the most important oxidant in regards to atmospheric SOA formation and aging. We note that the OH radical production scheme used in this work ($O_3 + h\nu \rightarrow O(^1D) + O_2$ followed by $O(^1D) + H_2O \rightarrow 2OH$) is also the primary source of atmospheric OH.
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> The reviewer makes the point that "different oxidants lead to different products and pathways of atmospheric oxidation". The distribution of oxidation products is governed, at least in part, by the relative ratios of hydroperoxy (HO_2) radicals, peroxy (RO_2) radicals, and

NO_x, all of which lead to alkoxy (RO) radical formation and/or stable end products which can then be further oxidized by OH. Relative humidity can also influence product disributions in some cases (e.g. T. Nguyen et al., 2011; Y. Zhou et al., 2011). With the exception of NO_x, all of these species are used or produced in the PAM reactor. We have also recently demonstrated that the chemical composition of alkane SOA produced in the PAM reactor is comparable to SOA produced downwind of the Deepwater Horizon off-shore oil site during the Gulf Oil spill in June 2010 (A.T. Lambe et al., 2012).

The final point raised by the reviewer is that "atmospheric organic aerosols are produced from thousands of precursors and not only from a limited number". Unfortunately, using thousands of precursors in a laboratory experiment is impossible. Laboratory SOA studies (not just those conducted in the PAM reactor) almost always use a simplified subset of precursors to design a feasible experiment, and then relate those measurements to atmospheric aerosols as best as possible given the inherent limitations in laboratory studies. The subset of precursors used in this work represent the range of known secondary aerosol precursors in the atmosphere (e.g. terpenes, aromatics, alkanes, SO_2) and should therefore provide valuable and relevant insight even if they do not exactly replicate the complex mixture of ambient SOA precursors.

To address this comment in the manuscript, we have added the following text:

Page 4452, line 5: "Previous studies haveshown that the PAM reactor can produce SOA at a level of oxidation that is atmospherically-relevant (Massoli et al., 2010; Lambe et al., 2011b, 2012) but unattainable by conventional smog chamber techniques that are limited to ~1 day of equivalent atmospheric oxidation (e.g. Ng et al. (2010))."

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

Ng, N. L., Canagaratna, M. R., Zhang, Q., Jimenez, J. L., Tian, J., Ulbrich, I. M., Kroll, J. H., Docherty, K. S., Chhabra, P. S., Bahreini, R., Murphy, S. M., Seinfeld, J. H., Hildebrandt, L., Donahue, N. M., DeCarlo, P. F., Lanz, V. A., Prvt, A. S. H., Dinar, E., Rudich, Y., and Worsnop, D. R.: Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry, Atmos. Chem. Phys., 2010; 10, 4625–4641.

A. T. Lambe, T. B. Onasch, P. Massoli, D. R. Croasdale, J. P. Wright, A. T. Ahern, L. R. Williams, D. R. Worsnop, W. H. Brune, and P. Davidovits. Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA). *Atmospheric Chemistry and Physics.* 2011; 11, 8913-8928.

A. T. Lambe, T. B. Onasch, J. Franklin, D. R. Croasdale, J. P. Wright, A. T. Martin, P. Massoli, J. H. Kroll, M. R. Canagaratna, D. R. Wornsop, and P. Davidovits. Transitions from functionalization to fragmentation reactions of secondary organic aerosol (SOA) generated from the laboratory OH oxidation of alkane precursors. Environmental Science and Technology. 2012; In Press.

“Another small point of criticism is the representation of the mass spectrometry results. Although these are not the main focus of the manuscript a large part of the findings is based on the O/C ratios obtained by the AMS; however a clear description on how these results were obtained as well as quality assurance for the instrument are simply omitted. Where there any changes applied to the fragmentation table of the AMS analysis? While under ambient conditions the fragmentation table requires only small adjustments, for laboratory measurements the situation is quite different, especially if organic compounds are involved. Often it can lead to artifacts and misinterpretation of results. The same applies to the sulfate measurements. Sulfate will dissociate and form sulfuric acid during the thermal desorption process; therefore, water is one of the most important fragments. Any source of water, but especially changes in relative humidity, particulate water or water from organics might lead to a bias. Were the results corrected for such artifacts? Also, what are the uncertainties of the AMS measurements and O/C ratios?”

> The reviewer is correct in saying that the adjustments required to the fragmentation table of the AMS analysis are different for laboratory and ambient measurements, and that water can represent a non-negligible contribution. For these measurements, we adjusted the fragmentation table based on the mass spectrum of PAM particle free air. Adjustments were made for the gas phase contribution (frag_air, including frag_O16). The water contribution (as frag_RH) was corrected for as well. The other frag waves were not treated in a different way (no specific adjustments for SO4, NO3, NH4).
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> The reviewer is also correct in that errors for the AMS elemental ratios should be reported. Typically, the absolute error in O/C and H/C are based on Aiken et al., (2007,2008), and they are stated as 31% and 10%, respectively (these values are upper limits and they are based on laboratory measurements). In our case, the variability of the measurements can be captured by the precision error (standard deviation) which for these laboratory conditions was less than 5%. A statement has been added to the section 2.4. The errors for the O/C and H/C ratios have been added to Table I (as standard deviation of the measurements).

“P4449 L24-26 “Organic matter (OM) forms up to 90\% of observed aerosol particulate mass, and secondary organic aerosol (SOA) represents up to half of the organic fraction (Jimenez et al., 2009; Hallquist et al., 2009) on the global scale.”

In this reviewers opinion this statement is wrong or at least misleading. While there might be circumstances where organic matter can contribute up to 90% of the particulate aerosol mass, these occasions are rather limited to very few places. The composition of the atmospheric aerosol is by far dominated by inorganic compounds, although organics sometimes dominate the non-refractory sub-micron size range.”

> The reviewer is right. The statement has been modified as follows:
>
> " In many locations, organic matter (OM) forms up to 90% of observed submicron aerosol particulate mass, and secondary organic aerosol (SOA) represents up to half of the organic fine fraction (Jimenez et al., 2009; Hallquist et al., 2009).”

P4450 L1-3 “SOA particles are generally associated with a direct cooling effect as they scatter the incoming solar light and they participate in cloud formation by acting as cloud condensation nuclei, CCN (IPCC, 2007, ch.2).“

I would change this statement. Secondary organic aerosol particles are definitely not the most important sources for CCN. In the current understanding, organic aerosols are believed to influence cloud formation by rather suppressing the CCN activity of a particle.

> We agree with the reviewer. The radiative effect of SOA is highly uncertain and wavelength dependent. Many studies showed that SOA can absorb light quite efficiently in the UV, so the radiative forcing is not necessarily understood and it might not always be cooling effect. We decided to remove the statement.

P4452 L2-5 “The reactor is capable of simulating atmospheric oxidation timescales of days to weeks with actual residence times of minutes.”

Why is it important or atmospherically relevant to simulate oxidation timescales of weeks? The average lifetime of an aerosol is believed to be around eight days. Is there any measurement/source that suggest an aerosol particle could actually undergo oxidation for such a long timescale without being removed?

> “Atmospheric oxidation timescales” referred to in this paper are only intended as approximate equivalents to laboratory OH exposures, simply because the wide range of potential atmospheric OH concentrations makes for a high level of uncertainty in any extrapolation. A specific OH exposure time in the laboratory can correspond to a wide range of equivalent atmospheric oxidation timescales.
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> For example, the maximum OH exposure used in this study is ~$2*10^{12}$ molec cm^{-3} s.
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> - If we instead assume an average ambient OH concentration of $1*10^{6}$ molec cm^{-3} (e.g. remote pristine environment), the equivalent atmospheric age increases to 23 days.
> - If we instead assume an average ambient OH concentration of $3*10^{6}$ molec cm^{-3} (polluted environment, and/or period of higher photochemical activity), the equivalent atmospheric age is 8 days--exactly the average age referred to by the reviewer.
>
> Obviously, these alterations by themselves do not make an OH exposure of $2*10^{12}$ molec cm^{-3} s more or less atmospherically relevant. In this case, we assumed an average [OH] = $1.5*10^{6}$ molec cm^{-3} based on the work of Mao et al. (2009). But we advise against the outright dismissal of PAM conditions as “atmospherically irrelevant” based solely on a certain number of “OH days” at some assumed ambient [OH]. This conversion is uncertain by at least a factor of 2.
>
> The more precise comparison would be to relate laboratory OH exposures to ambient OH exposures, rather than laboratory OH exposures to ambient “OH days”. Unfortunately, because ambient OH concentrations are highly variable and not routinely measured, we are somewhat limited in this regard.

To address this comment in the paper, we have revised the text as follows (changes bolded):

Page 4453, line 3: “Typical OH exposures ranged from 2.7×10^{11} to 2.2×10^{12} molec cm^{-3} s. These values are equivalent to 2 to 17 days of atmospheric oxidation assuming an average atmospheric ∗OH concentration of 1.5 ×10^{6} molec cm^{-3} (Mao et al., 2009). However, we note that this equivalent “atmospheric age” may be a factor of 2 or more uncertain depending on the assumed ambient OH concentration.”

P4453 L12-13 “Gas-phase SOA precursors used in these experiments were a-pinene, longifolene, isoprene, naphthalene and n-heptadecane.“

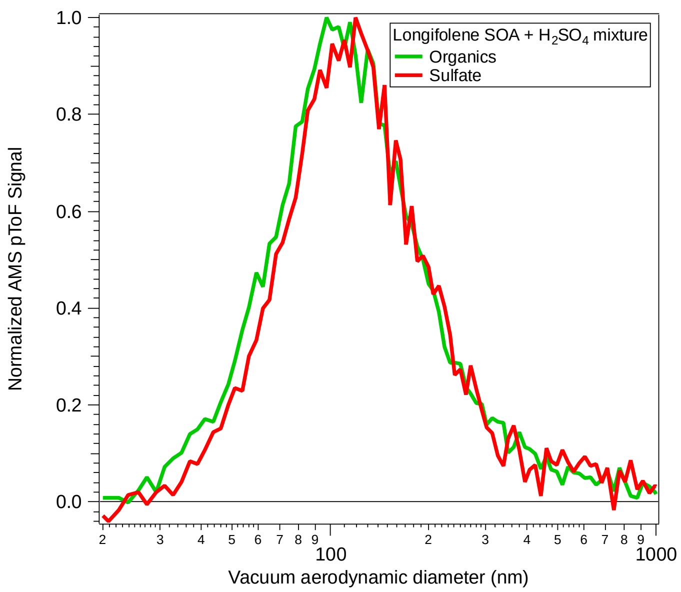
I suggest removing this sentence. The information is redundant within this paragraph.

Redundant sentence removed from the manuscript.

P4457 L22-23 “AMS particle time-of-flight measurements confirmed that the SOA and sulphuric acid were internally mixed in all cases.”

Please clarify. Did you investigate single particle spectra, or simply assume internal mixture from the particle-time-of-flight distributions? What if the particles had a sulfate core and an organic coating? Wouldn’t the PToF distributions still suggest internal mixture?

We did not investigate single particle spectra. As the reviewer surmised, we assumed internal mixtures from the particle time-of-flight distributions. Included in our response is a figure showing representative particle time-of-flight traces for organics and sulfate, normalized to the maximum signal of each species:



As is evident, the size distributions of organics and sulfate are the same within uncertainties. This suggests internal mixing. However, as the reviewer points out, we cannot infer anything about phase (in)homogeneity of the mixed particles. The organics and sulfate could either form a single phase or multiple phases (e.g. sulfate core and organic coating), and we would not be able to discern the difference from pToF data.

To address this comment in the paper, we have revised the text as follows (changes bolded):

p. 4457, lines 22-23: “AMS particle time-of-flight measurements confirmed that the SOA and sulfuric acid were internally mixed in all cases, It should be noted, that in the case of the multicomponent inorganic-organic particles it is possible the two phases are separated.”

If the reviewer and/or editor feels inclusion of the pToF figure is warranted, we would be happy to oblige.

P4457 L 27-28 “The ammonia is presumably from trace concentrations from the PAM system and makes up 11–14% of the total mass.”

The ammonia can originate from many origins including the tubing, or it can be an artifact of the AMS analysis and the fragmentation table. Without the mentioning of detection limits or quality assurance from the AMS analysis this number could well be within the noise of the instrument. What was the total mass measured by the AMS? This information could give the reader more confidence in the AMS results.

As the referee suggests, The uncertainty for ammonia is large, even after fragmentation table adjustments. The combined uncertainties in both collection efficiency (CE) and relative ionization efficiency (RIE) typically leads a 30% uncertainty (see Bahreini et al., 2009). Therefore, the 11-14% variation that we observed was within instrumental noise. The mass of the ammonia is however included in the total aerosol mass in the calculation of the SO_4^{-} fraction of the aerosol. This clarification is added to the manuscript.

Table 1

O/C and H/C values are presented with two digits precision; however no uncertainty or errors are presented. Are the differences significant (for example, for isoprene)?

Please add this information.

The standard deviation for O/C and H/C are added to table 1.

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