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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Dependence of SOA oxidation on organic aerosol mass concentration and OH exposure: experimental PAM chamber studies" *by* E. Kang et al.

Anonymous Referee #2

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General Comments

This manuscript is a crucial follow up to the previous research by Kang et al. (2007) that initially outlined the Potential Aerosol Mass (PAM) concept. To further characterize this technique, the chemical composition of SOA formed in the PAM chamber from the gas-phase oxidation of a few precursor organics under extremely high OH and ozone concentrations was studied in detail here and compared with SOA formed in other laboratory studies and ambient OA. This work is an important contribution to the research on atmospheric aging of OA. The topic of this manuscript is appropriate for publication in ACP, and results were presented in a concise manner and clearly

explained. Therefore, I recommend this manuscript for publication in ACP after the comments here and by other referees have been sufficiently addressed.

Specific Comments

This paper mostly focuses on the analysis of m/z 44 and 43 fractions of the AMS mass spectra, which are important OA mass fragments to study, but for this type of laboratory based study seems somewhat restrictive. The analysis can be extended to also study changes in the overall mass spectra. How do the mass spectra evolve over the course of a single experiment and with OA mass and OH exposure? How do the spectra compare with chamber SOA and ambient PMF/PCA factors such as HOA, SV-OOA and LV-OOA factors? These comparisons are discussed only qualitatively in the paper and could easily be more quantitatively correlated. Offline characterization of the chemical composition and molecular weights of species in OA would also be highly complementary to this work, as it would shed some light on the importance of oligomerization reactions in this study, which cannot be determined with AMS measurements, compared to offline analyses of chamber SOA.

Given the possible temperature dependence of SOA yield due to partitioning of semivolatile organics, it is unclear why a correction for OA mass measured by the TEOM measurements at 30 C is not needed. This point is mentioned briefly in Kang et al., 2007, but is not explained in this work. The AMS and TEOM measurements are in good agreement in this work, where an AMS transmission efficiency of 100% is assumed. Yet recent studies such as Salcedo et al. (2006) and Virtanen et al. (2010) have shown that SOA particles are likely in amorphous solid state and therefore have an AMS transmission efficiency less than 100% due to particle bouncing. How do you reconcile your observations with these studies? Would the particle bounce effect impact TEOM results in a similar fashion to AMS measurements but still allow good agreement between the two techniques? Were these techniques compared with some size distribution measurements such as SMPS to check whether particle bounce was an issue?

Have the OH concentrations been directly measured in the PAM chamber with GTHOS during an oxidation experiment to confirm that the OH concentrations were consistent with modeled values for the high VOC concentrations over the course of an experiment? Volatile and semivolatile oxidation products may also react with OH radicals to reduce its overall concentration during an oxidation experiment. Have the OH reactions with these oxidation products also been taken into account in the model?

It would be useful to discuss the role of multigenerational oxidation chemistry and its impact on OA formed in the PAM chamber compared to other chamber and flow tube studies. In particular, how many oxidation generations do the volatile organics and SOA particles undergo with respect to OH oxidation under different OH exposures? Does the number of oxidation generations change significantly with increase in precursor VOC concentrations (i.e. experiments in Sec 3.2), and can this in part explain reduction in F44 with OA mass? Do particle-phase organics undergo enough oxidation generations to impact the chemical composition of OA through heterogeneous oxidation compared to gas phase oxidation?

Is it possible that the reduced OA mass with OH exposure (decrease of OA mass from transient maximum to stable concentration in Fig. 6) may not be due to fragmentation induced by heterogeneous oxidation as suggested, but other reasons, such as: a) photolysis induced fragmentation of gas-phase and/or particle-phase oxidation products, b) changes in transmission/collection efficiency in AMS/TEOM due to changes in particle phase/shape or c) wall loss? A reduction in particle size (size distribution measurements) would more clearly show whether the particles are in fact volatilizing. The observed OA mass loss in this work with OH exposure could more quantitatively be compared to observed mass/volume loss (particle size change) due to OH oxidation in other laboratory studies such as Kroll et al. (2009) and George and Abbatt (2010). Is the observed mass loss in this work quantitatively consistent with these studies? Can these observations be reconciled with Kang et al., 2007 (i.e. Fig. 6) where SOA yield from the photooxidation of a-pinene did not decrease with OH exposure?

The F44 and F43 values from OA produced in the PAM chamber were directly compared to the SOA particles in Jimenez et al. (2009) and George and Abbatt (2010). It should be noted that both these studies produced a-pinene SOA from ozonolysis and passed the SOA particles through activated charcoal denuders to remove volatile (and potentially semivolatile) organics before exposure to OH radicals in the flow tubes. Could these differences in SOA production – and lack of volatile organics in these studies partially explain differences in chemical composition of SOA as well as their chemical evolution with OH exposure?

In Ng et al. (2010), Figure 9 shows the evolution of F44 with organic mass concentration of SOA over the course of a chamber experiment, where photooxidation of a-pinene and m-xylene look quite different. Were the changes in F44 of a-pinene SOA over a single PAM oxidation experiment comparable to m-xylene shown in Fig. 6 of this work, and if so, please discuss why this is not consistent with results in Ng et al. (2010).

Minor Points

Pg. 24054 Line 26: “cardiovascular and respiratory systems” would be more appropriate than “cardiovascular system”

Pg. 24055 Line 6-7: Nel (2005) and Forster et al. (2007) references should be cited on previous page when discussing aerosol climate and health effects. Jimenez et al. (2009) and Ng et a. (2010) papers do not focus on SOA particles, per se. More appropriate references here to reflect the breadth of SOA research are the recent SOA reviews, e.g. Kroll and Seinfeld (2008), Hallquist et al. (2009).

Pg 24056 Line 11: With exception of the Jimenez et al. (2009) reference, placing the other references here are somewhat misleading as they do not focus on SOA aging and hygroscopicity.

Pg 24056 Line 19: Shilling et al. (2009) might not be appropriate reference here as they did not study SOA aging in particular, unless by “aging” you are also including atmospheric dilution. Shilling et al. (2009) would be more appropriately cited after sentence in Line 25-26 when discussing partitioning and dilution.

Pg. 24056 Line 16-17: Explain what is meant by the phrase “probably because the aging much less than in the atmosphere”? Do you mean aging timescale is shorter? Or the experiments do not include all aging mechanisms such as dilution and cloud processing? Also, what is specifically meant by ‘this limitation’?

Pg. 24057-24058: Second and third paragraphs under Section 2 do not pertain to experimental methods and would be better in the introduction when discussing different OA oxidation types OOA, HOA etc. Typical values for O/C ratios would be useful to state in the second paragraph instead qualitative statements such as “SV-OOA. . . has a low ratio of oxygen to carbon (O:C)”.

Pg. 24064: Section 3.1.3 is unnecessary. The point about F44 and F43 values differing with fragmentation table modifications can be emphasized in the previous subsection.

Pg 24067 Lines 16-17: “Oxidation pathways seem to be divided to fragmentation and oligomerization. . .” please also add “functionalization”. Also, conclusions cannot be made on importance of oligomerization from this work.

24069 Line 3: “oxidation saturates” Please clarify this point. Do you mean that under high OH exposures OH adsorbs to particle surface and takes up all surface sites via Langmuir-Hinshelwood mechanism or that reaction kinetics of OH with surface organic species do not slow down with increasing OH exposure?

Table 1: Could you state the SOA yield for each experiment? Are OH exposures the corrected values?

Figure 2: Can these mass spectra be compared with reference chamber SOA spectra for SOA produced under similar conditions to those in this study, for example plot reference spectra on the respective plots and/or state correlation coefficients in the text?

Figure 4. Why do F44 values have such large errors at low OA masses?

Figure 5: Please show a second x axis for atmospheric OH aging time equivalent to the OH exposure assuming an atmospherically relevant average daily OH concentration.

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