

Interactive comment on “Introducing the concept of Potential Aerosol Mass (PAM)” by E. Kang et al.

E. Kang et al.

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General comments

We are pleased that all the referees think that this work should be published after we address their concerns. We agree with many of their suggestions and have modified the manuscript to meet many of their suggestions. The greatest change is the inclusion of a section on the comparison of a SOA mass spectrum generated in the PAM chamber to one generated in a large environmental chamber. Since Dr. Darin Toohey, University of Colorado, provided the AMS and worked with us on interpreting the results, we would like to include him as a co-author.

We respond to the comments of each referee separately. Their comments are included in italics, followed by our responses. Since some of the referees have some of the same comments, we repeat our responses.

Specific comments

1 - *This approach is truly very innovative and might help to elucidate the SOA formation in new ways. In some sense it is similar to the POCP (photochemical ozone creation potential) rather than the total OH reactivity as pointed out by one of the other reviewers. I think that the paper is long enough and includes a thorough discussion. I hope that the chemical characterisation using aerosol mass spectrometers will follow soon to get a more complete picture of the potential of this technique. If there are some measurements available, the authors might like to comment on the results already in this manuscript but refer to a future publication showing this in more detail. I think that this is a very interesting contribution and surely should be published. I would like to see a more detailed discussion on the main points below*

We include a new section 3.6 Comparison of mass spectra from m-xylene to introduce the chemical characterization of SOA formed in the PAM chamber using the aerosol mass spectrometer. The mass spectra of SOA from m-xylene photo-oxidation in the PAM chamber were similar to the mass spectra previously observed in a large environmental chamber. This example supports the hypothesis that the highly oxidizing environment in the PAM chamber mimics oxidation that occurs in large environmental chambers designed to probe atmospheric processes.

Main points:

1- *p.9929 “ should occur as they do in the atmosphere” This should be stated a bit more carefully. The night-time chemistry including NO₃ oxidation will not be modeled by the chamber. Another issue are possible reactions in the condensed phase that might take a bit longer than the PAM chamber can simulate. Oligomerisation reactions have shown to be important (Kalberer et al., 2004, Science, 303, 1659-1662). The time evolution of this oligomerisation process is detailed in Gross et al. (2006, Anal.*

Chem., 78, 2130-2137). In this context the use of both commercially available aerosol mass spectrometers should be used for the chemical characterisation of the PAM chamber in future.

Yes. Secondary aerosol formation process in the PAM chamber is designed to present photo-oxidation in the daytime atmosphere. This is clarified in the revised text. We will study the oligomerization in the PAM chamber in a future study. The aerosol mass spectrometer used in this study was not designed to look at oligomers. We have carried out a preliminary comparison of size distributions measured by the AMS with those measured by optical scattering techniques (e.g. the UHSAS), which indicate the organic particles are of relatively low-density, unlike what we would expect from oligomers. However, chemical characterization of PAM aerosols with more sophisticated instruments designed to measure oligomers is highly desirable, and subject to an entirely new study that we hope to carry out in collaboration with others who have suitable instruments. These collaborations will help us to learn more about the chemistry and microphysics in the PAM chamber and to compare behavior observed there to behavior that is observed in large, environmental chambers and the atmosphere. The PAM chamber is relatively easy to either replicate or to transport to other laboratories to do these studies. We are particularly eager to examine this oligomer issue with the PAM chamber. We modified the manuscript as follows.

Page 9929, line 6: “For this approach to simulate the photo-oxidation in the atmosphere, all of the processes, including oxidation of precursor gas, nucleation, and gas and particle partitioning, should occur as they do in the atmosphere, except that instead of taking hours, the processes should be complete in a few minutes.”

2 - P9930 As I understand, the air including the particles is exposed to the lights emitting at 185nm and 254 nm. I am wondering if the processing concerning photolysis

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of e.g. aldehydes can be considered to reflect what is happening in the atmosphere. How much processing is happening due to photolysis compared to OH and ozone chemistry if one thinks for example about aldehydes in both the gas and aerosol phase.

The UV radiation effect is described in Section 3.2.5. The SOA yield can be varied by the UV radiation, and Kamens and Jaoui (2001) and Presto et al., (2005a) demonstrated particulate aldehydes were decomposed to gas phase by the photolysis resulting in the SOA yield reduction. We did not have the time to examine this issue thoroughly for this manuscript, but plan to do it as future work. In our current PAM chamber setting, we did not have precise control over UV that is necessary to do this study. However, since OH is a product of both UV and humidity, the next system will have the capability to produce the same amount of OH by simultaneously varying UV and humidity in order to keep OH fixed while looking for UV effects. In addition, we can examine effects of UV at 254 nm by inserting windows in front of the lamps that block the 185 nm light that makes OH and allows 254 nm light to irradiate the chamber. We modified the manuscript as follows.

Page 9943, line 21: “This balance seems unlikely but will be tested by varying the humidity and thus OH for a fixed UV flux, to fix OH by varying humidity and UV simultaneously and by adding a window in front of the UV lamps to block the OH-producing 185-nm radiation while passing the 254-nm radiation into the PAM chamber.”

3- p. 9938: *small wall loss of SO₂: SO₂ is not a very sticky component. If I think about some oxygenated VOCs or the VOCs of intermediate volatility as suggested by Robinson et al. (2007, Science, 315, 1259-1262) the losses might really be important. I suggest that the authors might mention that future experiments comparing heated with unheated inlets might be beneficial.*

We agree that oxygenated VOC_s or VOC_s of intermediate volatility could be lost on our inlet. However, this problem is common to everyone trying to measure these potentially important compounds. We are talking to the experts in these measurements and taking their advice for which materials to try and how to test them. We assume that such semi-volatile compounds would eventually come into equilibrium with the walls. Thus, one strategy is to maintain the temperature of the sampling lines very close to the ambient temperature. We agree that comparing heated and unheated inlets would be an excellent test. We modified the manuscript as follows.

Page 9938, line 9. “This small wall loss for SO₂ suggests that other gases can be brought through the chamber with at most a small loss, but careful tests of inlet materials and heated and unheated inlets will be needed to minimize the loss of oxygenated VOC_s and semi-volatile VOC_s in the inlet lines and PAM chamber.”

Minor points:

2- p. 9927 Concerning high fraction of SOA, I would include the paper of Lanz et al. (Atmos. Chem. Phys., 7, 1503-1522, 2007)

We include Lanz et al. (2007). We modified the manuscript as follows.

Page 9927, line 7: “(Murphy et al., 1998; Huebert et al., 2004; Drewnick et al., 2004b; Salcedo et al., 2006; Lanz et al., 2007)”

3- p. 9931: NO_x : Fraction of NO and NO₂?!

We used diluted NO gas in nitrogen as a NO_x source. In the UV-irradiated PAM chamber, the extreme amounts of HO₂ and O₃ force almost all of the NO_x to NO₂, which rapidly reacts with OH to form HNO₃.

4- *p. 9934 comparison of TEOM and aerosol mass spectrometer. What was the assumed collection efficiency (with rather high uncertainty) to provide the comparison of 10%?*

A collection efficiency of 1.0 was assumed for the AMS, as the particles were expected (and demonstrated by detection of $m/z = 18$) to be fairly wet. The 'high uncertainty' for collection efficiencies of the AMS to which the reviewer refers pertains to ambient particles, where it has been found that collection efficiencies varies with relative humidity, presumably due to non-sphericity or particle bounce (e.g. see Canagaratna et al. (Mass Spectroscopy Review, 26, 185-222, 2007)). Consistent with this interpretation, it is interesting to note here that the mass loadings determined by the AMS and TEOM agreed very well for all experiments reported here, which were at high relative humidities, and were we to apply the 0.5 collection efficiency employed commonly by the AMS community, the AMS mass would be double that measured by the TEOM. Thus, we conclude that under the conditions employed by the PAM reactor, the particles are wet and spherical. Future proposed work with the AMS and UHSAS will address the possibility that the AMS collection efficiency varies with relative humidity in the PAM chamber, as has been observed for ambient particles.

5- *p.9934 I would not state that ozone is independent of RH. The dependence is rather significant.*

Yes. Ozone is also dependent on relative humidity because more water molecules absorb more UV light. However, this dependence is less than the dependence of either OH or HO₂. However, the reviewer is correct. We modified the manuscript as follows.

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Page 9934, line 22: “Ozone decreases about a factor of 2 with increasing relative humidity, unlike OH which increases over a factor of 10.”

6- p. 9935: *Main loss of OH is the reaction by HO₂: Is this also true for really high NO₂ or VOC concentrations*

This statement is true for almost all of the chamber. Modeling studies show that even large amounts of NO₂ or α -pinene – as much as 100 ppbv or more – are completely consumed in the first 10-20 s after the air enters the chamber. Measurements of α -pinene in the PAM chamber with a GC confirm this modeling result. At that point, the HO_x production is able to completely replenish the HO_x, which then is limited by HO₂+HO₂ and OH+HO₂ reactions and comes into steady state. Interestingly, for typical atmospheric levels of VOC_s and NO_x, HO_x is hardly affected and depends essentially only on the HO_x production rate and HO_x loss processes.

7- p. 9945 *NO_x was added : please specify in which form (NO or NO₂ or both (in which percentage)?)*

We added NO gas for NO_x source. And, NO is converted to NO₂ rapidly by HO₂.

8- p. 9946 *[VOC]/ [NO_x] (ppbC/ppb) < 15 : One should be careful with such interpretation of this ratio regarding NO_x or VOC sensitivity of the ozone production as this is strongly dependent on the VOC. please add a sentence.*

We use the definition for the low-NO_x condition – ([VOC]/[NO_x] (ppbC/ppb) > 15) –

that is cited from Presto et al. (2005b). The NO_x dependence in the low or high NO_x condition was studied for α -pinene and m-xylene by Presto et al. (2005b) and by Song et al. (2005). We assumed that this low NO_x condition work for the VOC_s what we tested in the PAM chamber. Also, the low NO_x condition with $[\text{VOC}]/[\text{NO}_x]$ (ppbC/ppb) > 15 was determined experimentally for SOA yield test. This concept of low NO_x is quite different from the NO_x of VOC sensitivity for ozone production.

9- *p 9949 Volkamer should read Volkamer. I suggest to include the paper of Robinson et al. in this discussion. The higher yield might not be due to mixture of very volatile VOCs but by these intermediate volatility organic compounds.*

Yes. The reason of the higher yield is suggested to be the co-condensation of gaseous oxidation product. In the photo-oxidation of hydrocarbon mixture, various kinds of oxidized gaseous product from semi-volatile organic carbons or intermediate-volatile organic carbons may result higher SOA mass. We modified the manuscript as follows.

Page 9949, line 17:“(Volkamer et al., 2006)”

Page9951, line 1, add new paragraph: “This agreement is also inconsistent with Robinson et al. (2007). They tested diluted diesel exhaust and observed higher SOA mass than expected from a model that used known SOA yields from VOC_s . They suggest that many IVOC (Intermediate-Volatility Organic Carbons) were in the diesel exhaust, resulting in the higher SOA mass than expected. It may be that some simple mixtures, such as the ones used by Odum et al. (1997), and us, contain fewer and less IVOC_s .”

10- *in general (maybe it was mentioned ..): What material was the inlet made of. There should be a trade-off of maybe losing particles versus losing sticky gases.*

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Gases are brought into the Teflon PAM chamber with Teflon tubing; Stainless steel is used to sample the SOA with the TEOM at the bottom of the PAM chamber. If we want to sample both pre-existing particles and PAM, then we will need to find a way to do this. The metal tubing loses VOC_s and oxygenated VOC_s; the Teflon tubing loses particles. It may be that we will need to run two inlets and alternate their use. We are in the midst of testing specially coated stainless steel and Teflon for the inlet at a field site.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9925, 2007.

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