

## ***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** - Page 9926, last line. *It is inappropriate to use Seinfeld and Pandis as a blanket citation for such things. The papers showing things like the health effects of aerosols should be cited directly.*

We replace the citation “(Seinfeld and Pandis, 1998)” as following.  
Page 9926, line 26: “(Krewski et al., 2000; Lall et al., 2004)”.

**2** - Page 9934, *the uncertainty of the TEOM is quite large compared to the scale of the measurements being made. Should a different measurement for aerosol mass be used? Or has one?*

The goal of this study is to test the PAM chamber with the widely used real-time aerosol mass measurement method. The TEOM precision is actually 3 to 5  $\mu\text{g m}^{-3}$  for a 4-min average that we use. In the laboratory tests, the aerosol mass measured by the TEOM was generally higher than 15  $\mu\text{g m}^{-3}$ , which is at least 3 times higher than the TEOM precision. The mass concentrations measured to get the yields shown in Table 1 were between 40 and 500  $\mu\text{g m}^{-3}$ , well above the TEOM precision limit. In addition to precision issues, the TEOM zero does drift as temperature and relative humidity change; this drifting can affect the absolute numbers. However, because the UV light is turned on and then off, the PAM signal can be separated from the drifting zero signal. The TEOM precision is good enough that the ambient PAM measurement is clearly seen when the UV light is turned on and then off (Figure 12).

The PAM chamber can be mated to a wide variety of aerosol particle sampling instruments. In addition to the TEOM, we had brief access to an AMS and to particle

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sizing instruments. The aerosol mass measured by the TEOM and the AMS showed same value to within 10%. Once, we tested the SMPS and CPC with a constant particle density  $1.4 \text{ g/cm}^3$  for  $\alpha$ -pinene runs, and the aerosol mass concentration was similar to the TEOM result.

**3** - *Page 9934, why was an additional port not incorporated into the instrument to allow for measurement of OH and HO<sub>2</sub> during the actual experiments. Now, these values must be assumed based on a limited subset of previous experiments.*

It is neither practical nor desirable to keep GTHOS which measures OH and HO<sub>2</sub> connected to the PAM chamber for all experiments. GTHOS is fairly large, so we could not deploy the TEOM and the GTHOS simultaneously. It is also in constant demand for field and laboratory studies. However, repeated experiments over several days showed that the amount of OH and HO<sub>2</sub> in the chamber were functions only of the amount of UV light and the humidity. The point that we make in the paper (bottom of page 9934 and top of page 9935) is that the HO<sub>x</sub> losses are totally dominated by HO<sub>x</sub> chemistry. To test this idea, we added 30 ppbv of SO<sub>2</sub> or 400 ppbv of CO; we saw no change in the OH or HO<sub>2</sub> measured by GTHOS. We modeled the PAM chamber chemistry and saw that even 100 ppbv of  $\alpha$ -pinene can reduce HO<sub>x</sub> for only 10-20 s before it is reacted away; the rest of the time, in the chamber, OH and HO<sub>2</sub> amounts are unchanged. In addition, the OH measured by GTHOS at the bottom of the PAM chamber agreed well with the OH calculated by measuring a decrease in the SO<sub>2</sub> before and after the UV light was turned on.

**4** - *Page 9934, with respect to Figure 2. What is going on with the points at approximately 35% RH? They all seem to look like fliers from the trends of the rest of the data as a function of RH. Also, the text states that the O<sub>3</sub> level could be reach up to 30 ppmv, yet the figure y-axis exceeds this value. Does the unexpected behavior at the*

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*35% RH point mean that they can not say with any certainty what the oxidant level in the PAM chamber is?*

They are the legend. We have removed the legend and added an explanation of the symbols in the figure caption.

*5 - Page 9935, the values used as typical seem somewhat large. Does this affect their comparison to the PAM chamber values?*

These values for OH and HO<sub>2</sub> are typical for sunny days in Nashville, New York, City, Houston, and Mexico City, according to measurements that we have made in these locations (Ren et al., 2005). Clearly OH and HO<sub>2</sub> are less when the sunlight is low, such as when it is cloudy or winter. In addition, the HO<sub>2</sub>/OH, and OH/O<sub>3</sub> ratios can also be quite different over the course of a day. The point is that the ratios of oxidants in the PAM chamber are the same as typical values observed in the atmosphere. Thus, if these oxidants dominate the conversion of precursor gases to particle matter, then our highly oxidizing environment in the PAM chamber will have the same chemistry as for the low oxidant levels in the atmosphere, but it will occur much faster.

*6 -Page 9937, I find Figure 3 unnecessary.*

We agree with the reviewer and have removed Figure 3.

*7 - Page 9938, is it really true that other SOA precursors react more rapidly with OH than alpha-pinene? I thought that aromatics reacted more slowly.*

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The following list shows the reaction rate constant for precursor gases what we used here. Other VOC<sub>s</sub> react slower than  $\alpha$ -pinene, but even the aromatics still react faster than SO<sub>2</sub>. We observed all nine hydrocarbons were depleted in the UV light on condition by GC-FID measurement, and this is described in Line 21 in Page 9938.

SO<sub>2</sub>:  $k_{OH} \times 10^{-12} = 1$ ,  $k_{O_3} \times 10^{-22} = 2$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
 $\alpha$ -pinene:  $k_{OH} \times 10^{-12} = 50$ ,  $k_{O_3} \times 10^{-22} = 800000$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
 $\beta$ -pinene:  $k_{OH} \times 10^{-12} = 70$ ,  $k_{O_3} \times 10^{-22} = 200000$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
 $\Delta^3$ -carene:  $k_{OH} \times 10^{-12} = 90$ ,  $k_{O_3} \times 10^{-22} = 380000$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
cyclohexene:  $k_{OH} \times 10^{-12} = 60$ ,  $k_{O_3} \times 10^{-22} = 760000$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
m-xylene:  $k_{OH} \times 10^{-12} = 24$ ,  $k_{O_3} \times 10^{-22} = 29$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
p-xylene:  $k_{OH} \times 10^{-12} = 13$ ,  $k_{O_3} \times 10^{-22} = 13$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
1,3,5-TMB:  $k_{OH} \times 10^{-12} = 60$ ,  $k_{O_3} \times 10^{-22} = 29$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
toluene:  $k_{OH} \times 10^{-12} = 6$ ,  $k_{O_3} \times 10^{-22} = 5$ , (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
ethylbenzene:  $k_{OH} \times 10^{-12} = 7$ ,  $k_{O_3} \times 10^{-22} =$  not available, (molecule<sup>-1</sup>cm<sup>3</sup>s<sup>-1</sup>)  
(from NIST chemical kinetics, <http://www.nist.gov/srd/chemkin.htm>)

We modified the sentence.

Page 9938, line 20: “Essentially all SOA precursor gases react at least 3 times faster with OH than SO<sub>2</sub> does, so that these hydrocarbons should be completely oxidized in the PAM chamber.”

**8** - *Page 9939, what is going on here with the results showing an initial maximum followed by a lower plateau in the aerosol mass concentration? This has not been observed with these precursors in the literature. Because this paper is focused on the PAM measurement and its initial application, this observation needs to be explained to a much greater degree. The authors speculate that reactions of SVOC mass in the gas phase cause repartitioning. What if the oxidation of these SVOCs leads to less*

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*volatile products? Then their explanation is clearly incorrect.*

The observed initial maximum is a transient phenomenon in the PAM chamber that we are trying to understand. It is not seen with SO<sub>2</sub> but only with the large amounts of the pure organics or the mixture of  $\alpha$ -pinene, m-xylene, and p-xylene. Nor is it observed in our atmospheric measurements (please see Figure 12). We have some nice data that we have just begun to analyze, but these observations are not yet understood. We will need to do some modeling to test our ideas.

However, we do not believe that we must be able to explain this transient peak before we can publish this paper. The similarity of the SOA yields between the PAM chamber and the environmental chambers and the one mass spectrum (which we will discuss below) shows that the PAM technique has potential.

We revise the paragraph at the bottom of page 9939 as follows.

Page 9939, 3rd paragraph: "This behavior is a transient phenomenon that is observed only in the PAM with the pure organics and a mixture of 3 organics when we turn on the UV light to initiate the oxidation. When we ran the chamber with the UV light on continuously for a stable oxidant level, and added precursor gas later, we did not observe the peak mass and the following stable mass. Interestingly, it is not observed in the atmosphere, as shown later in the paper (Figure 12). That it is not observed in the large environmental chambers suggests that it is due to the extremely rapid initial particle formation in the PAM chamber. We cannot yet explain this behavior. However, it had no effect on the observed stable SOA properties that are discussed in this paper. We will examine this behavior and the roles that OH and HO<sub>2</sub> play in more detail in another manuscript. For the feasibility study in this manuscript, we will use the SOA mass observed after stabilization in the equation for aerosol mass yield Eq. (7)."

**9** - Page 9940, their finding that continued reaction between ozone and alpha-pinene reaction products does not occur is not surprising given that the parent VOC only has one internal double bond, which should be oxidized completely in the first reaction. This is discussed in Ng et al. with respect to first- vs. second-generation products contributing to SOA.

We agree with the referee that the yield from the reaction of ozone and  $\alpha$ -pinene does not change with additional ozone. However, because we are trying to demonstrate the feasibility of the PAM concept, we are showing that oxidation in the PAM chamber is occurring as expected.

We add the following sentence after line 15 on page 9940.

Page 9940, line 15, add: "Additional ozone is not expected to reduce the SOA yield from  $\alpha$ -pinene because it has only one double carbon bond (Ng et al., 2006). This result demonstrates that the extreme oxidation in the PAM chamber is occurring as expected for this reaction."

**10** - Page 9941, the authors should use a better source for reaction rate coefficients than the MCM website (see earlier comment about use of Seinfeld and Pandis as a reference). In addition, the authors do not know a priori that the increase of yield associated with OH is due unequivocally to alpha-pinene/OH reactions. Could it not also be that OH oxidizes the reaction products of alpha-pinene/O<sub>3</sub>?

We use the NIST chemical kinetics database for reaction rate coefficients.

**11** - Page 9942, I would caution the authors to say that RH does not affect SOA formation from the ozonolysis of alpha-pinene. It does not appear to affect it in this

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case because of the lack of a seed aerosol (see Cocker et al. papers from 2001).

We do not understand the reviewer's point because we are comparing our result to Cocker et al.'s result for the no-seed, humidified condition. We modify our sentence as follows.

Page 9942, line 12: "This result is consistent with a previous study of  $\alpha$ -pinene ozonolysis, in which increasing the relative humidity from 0 to 40% in the seed-free condition increased the SOA mass only 10%, including the water mass in the aerosol particles (Cocker III et al., 2001)."

**12** - *Page 9943, is there a difference in wavelengths between the PAM and the Presto studies that could be leading to these discrepancies?*

The reviewer makes a good point. Presto et al. (2005a) used black lights (General Electric model 10526 black lights) that have a broad spectral peak between 350 and 400 nm, with no lines at 254 nm or 185 nm, whereas we used ozone-producing UV lights (BHK Inc. Grid lamps) for which the two strongest spectral emissions are at 254 nm and 185 nm. We would think that the more energetic 185 nm and 254 nm light would be more effective at photoreactions, but perhaps the absorption cross section is larger at 350 nm. We clarify this difference by adding a paragraph after line 21, page 9943 as follows.

Page 9943, line 21. Add: "The difference between our result and that of Presto et al. (2005a) may also be due to the difference between our UV lamps, which have strong emissions at 185 nm and 254 nm, and their black lights, which have a broad spectral emission between 350 nm and 400 nm and no emissions at 185 nm and 254 nm. While it might be thought that the more energetic emissions at 185 nm and 254 nm



would be more effective than the 350-400 nm emissions from the black lights, we do not know the absorption cross sections for the photo-reactions that would reduce the SOA yield.”

**13** - *Page 9947, the seed used by Ng et al. was neutral, so there should be no seed effect as hypothesized by the authors.*

Even though Ng et al. (2007) used neutral seed, not acidic seed, the absence of seed particles in their earlier work caused the SOA yield reduction by “the induction period” in which precursor hydrocarbon reacted but no aerosol formed (Ng et al., 2007; Kroll et al., 2007).

**14** - *Pages 9948 and 9949, “the room air addition studies” do not provide much useful information to this work. Sections 3.4 and 3.5 should be removed from this paper. All section 3.4 does is verify the hypothesis of Odum et al. regarding how one can calculate SOA yields of mixtures from the data from individual VOC experiments. Section 3.5 describes the first field deployment. I believe that the first PAM paper should focus on the concept and laboratory study/validation. Future papers should focus on field use.*

We agree to take out the room air data, but disagree with the reviewer that the Section 3.4 and 3.5 should be removed.

Section 3.4: In this paper, we are trying to compare data from the PAM chamber to that from the large environmental chambers in as many different ways as we can. Section 3.4 shows that the highly oxidizing condition in the PAM chamber works for the mixture of VOC<sub>s</sub>. That we verify the Odum et al., (1997)’s hypothesis says that the

highly oxidizing environment in the PAM chamber is acting as expected. This result is an important confirmation of the PAM concept.

Section 3.5: In Section 3.5, the first field test was performed to see if how the PAM chamber could work in uncontrolled ambient air. As a result, the PAM chamber in ambient air could produce noticeable secondary aerosol formation and the PAM could track the fast change of precursor gas. The ultimate goal of the PAM concept is to use the PAM chamber in the monitoring sites and in the intensive field campaigns, so the qualitative examination of that if the PAM chamber could work in the field is the important feasibility test in this manuscript. Retaining this section and the figure is important for another reason; it demonstrates that the transient behavior that we observe in the laboratory with pure organics or small mixtures is not observed in the atmosphere. Figure 12 answers the reviewer's concern that the transient behavior with pure gases that this phenomenon needs to be explained to a much greater degree before this paper can be published. The figure clearly shows no transient behavior for atmospheric measurements. That is very interesting and needs further investigation.

**15** - *Page 9954, the authors, in my opinion, absolutely must present the chemical characterization data of laboratory-generated aerosol in this paper. Because this paper is the first to describe PAM, the instrument needs to be validated completely, including chemically. This is by far the biggest weakness of the manuscript and needs to be addressed prior to publication on ACP. With the deletion of sections 3.4 and 3.5, the authors can add this material without making an overly long paper.*

We agree with the reviewer that a comparison of mass spectra taken in the PAM chamber and in a large environmental chamber adds considerable weight to our hypothesis that highly oxidizing environment in the PAM chamber can mimic atmospheric oxidation processes as represented by large environmental chambers. We do not have a lot of aerosol mass spectra, especially for conditions that are similar to the

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conditions of the published aerosol mass spectra. We do have one comparison that is fairly convincing. We include the following comparison spectrum and words as the new Section 3.6. We will save some space by removing Figure 3.

However, if we are going to include this mass spectrum, we will need to increase our author list to include Darin Toohey of the University of Colorado. He lent us his AMS and participated in the experiments involving the AMS that were done last February. The additional figure for the Section 3.6 will be submitted in an additional author's comment separately.

“Section 3.6 Comparison of mass spectra from m-xylene.

A critical test of the PAM concept is the comparison of the chemical composition of SOA particles formed in the PAM chamber to the chemical composition of SOA particles formed in large environmental chambers. The percent contribution to the total organic aerosol signal for m/z between 15 and 100 is a good indicator of the chemical composition (Jimenez et al., 2003; Bahreini et al., 2005; Alfarra et al., 2006; Canagaratna et al., 2007).

Aerosol mass spectra were measured in the PAM chamber with a Quadruple Aerosol Mass Spectrometer (Q-AMS) from Aerodyne Research Inc. (Jayne et al., 2000). The AMS inlet was inserted into the PAM chamber near the inlet for the TEOM so that total mass and mass spectra were measured simultaneously. Experiments were performed for three SOA precursor gases –  $\alpha$ -pinene, m-xylene, and p-xylene – at different amounts of precursor gases and oxidants.

To compare the mass spectra taken in the PAM chamber to those taken in large environmental chambers, the amounts of precursor gas should be similar in the two experiments. The PAM chamber experiment with 163 ppbv of m-xylene is quite similar to the amount used for a published mass spectrum of 143 ppbv of m-xylene (Bahreini et al., 2005). The percentage contribution to the total organic mass signal for the two

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studies is shown in the Figure (*newly included*). At each  $m/z$ , the smaller percentage is plotted in front of the larger. The similarity of the mass spectra indicates that the chemical composition of the particles produced in the PAM chamber is similar to the chemical composition of particles produced in the large environmental chamber. Differences exist, however, particularly in the ratio of  $m/z$  43, which represents less oxidized organics, to  $m/z$  44, which represents more oxidized organics (Zhang et al., 2005; Alfara et al., 2006). The ratio from the PAM chamber is about 1.0, while the ratio from Bahreini et al. (2005) is 0.8. This difference should not be surprising. The degree of oxidation depends on the total exposure to oxidants and on the initial precursor gas amount, which affects to total SOA mass. The smaller the precursor gas amount, the more oxidized the SOA particle will be for a given exposure to oxidants. The lower  $m$ -xylene amount in the Bahreini et al. (2005) experiment means that the SOA particles should be more aged and have a lower  $m/z$  34 to  $m/z$  44 ratio than the SOA particles in the PAM chamber, as is observed. Taking the differences in precursor gas amount into account explains most of the differences in the  $m/z$  43 to  $m/z$  44 ratio that were observed.”

**16** - *Page 9954, the end of the conclusion seems like a sales pitch and can probably be reduced.*

We assume that the reviewer is talking about the last two paragraphs, since the other paragraphs generally summarize the results described in the paper. However, we feel strongly that the last two paragraphs stay. It is important for the readers to begin thinking about how the PAM concept might be applied to their research. It is our intent to form a community of users of this concept.

**17**- *In Figure 11, yield fitted curves should go through the origin.*

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The curve is fixed.

**18** *Technical corrections*

- *The caption on Figure 4 refers to measured and expected sulfate aerosol, while the data show measured sulfate and SO<sub>2</sub>.*

We have corrected the legend in Figure 4 to be consistent with the manuscript.

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