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

E. Kang et al.

Received and published: 26 September 2007

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.

Full Screen / Esc

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Interactive Discussion

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1 - *The previous referees have nicely summarized the goals of this work. This new concept eventually should be published. The current paper suffers from trying to include too much information, while glossing over several important points that must be addressed for this concept to be truly useful. Also, the present version of the paper is not well written; it is, in places, poorly organized and rambling. Section 3.4 is not really needed, and Section 3.5 is premature. The performance of the technique needs to be firmly established in the laboratory before it can be applied to ambient data. I suggest that these two sections and their associated table and figure be removed. (Figure 3 is also not necessary.) The following points need to be addressed.*

We are pleased that all the other referees think that the manuscript is “clearly written”, “well written”, and a “thorough discussion”. We would be happy to re-examine the places in which the manuscript appears to be “not well written” if the referee would be willing to let us know where those places are. We want this introduction of the PAM concept to be as clear as possible to as many readers as possible. We thank the referee’s for their efforts that help us make it better.

We understand that the manuscript may be a bit overwhelming, but we feel that it is important to provide as much information as possible so that the reader can judge the potential of the PAM concept.

We agree to remove Figure 3. But we disagree to remove Section 3.4 and 3.5. The reasons given next are repeated for anonymous referee 5, whose comments may have sparked these comments from this referee.

In Section 3.4, 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_s. 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. It is also potentially an interesting difference from the results of Robinson et al. (2007) and speculation of Volkamer et al. (2006).

In Section 3.5, the first field test was performed to see if how the PAM chamber could work in uncontrolled ambient air. In this test, the PAM chamber produced noticeable secondary aerosol formation in ambient air and the PAM chamber tracked 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 paper.

The referee suggests that the PAM concept should be completely characterized before field studies are attempted. Our extensive experience with the development of new field instruments is that the interplay between the laboratory development and field tests is a requirement for success. Complete laboratory characterization does not guarantee a successful field measurement. The process is highly iterative, starting with laboratory work followed by field trials, carrying out new laboratory tests guided by the results of the field trials, etc. Our primary goal with this paper is to lay out the necessary ground work that will allow others to apply the technique in new ways and continue to move the science forward. Section 3.5 clearly demonstrates that the PAM concept may have potential for atmospheric measurements. We believe that this demonstration is important and should remain in the paper.

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. The figure clearly shows no transient behavior for atmospheric measurements. That is very interesting and needs further investigation.

2 - What is the effect on the chemistry of the 185 nm and 254 nm radiation? Photodegradation of VOC reaction products may occur at these wavelengths while not at those > 300 nm. The authors do establish that this radiation is not affecting α -pinene chemistry; this may not be the case for other systems in which products are more Photo-labile.

The effect of the photo-degradation of VOC reaction products can be explained by the SOA yield reduction in UV radiated condition by Presto et al., (2005a). Also, Kamens and Jaoui (2001) described the formation of more-volatile products such as decomposition of aldehydes under the natural sunlight.

In our PAM chamber, however, we observed similar SOA yield in the dark, dry chamber and in the UV-irradiated dry chamber (See Section 3.2.5, Page 9943). In our UV-irradiated dry chamber, we measured 10 to 15 pptv of OH, because trace amount of water molecules in dry air was oxidized to OH under very intense UV light. Therefore, the loss of produced SOA by UV radiation in the PAM chamber might be compensated by the additional SOA formation by OH. Our PAM chamber is operated in extremely high amount of the oxidants O₃ and OH; thus the contribution of UV radiation may be less significant than the effect of oxidant amount. But this effect will be studied in a future as suggested by the following modifications to the manuscript.

Page 9942, line 17:“ Extremely high UV actinic flux could possibly alter the SOA yields

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and the gas and particle product composition (Presto et al., 2005a; Kamens and Jaoui 2001).”

3 - *What is the sources of OH and HO2 under dry conditions? Wouldn't one expect virtually no production of these radicals at RH less than 1%? This led to problems in the results in Section 3.2.5.*

We used a couple of Drierite cylinders to dry out humid air before adding to the chamber in the air-purifying system. But, these Drierites could not remove 100% of water molecules. Even 1% of measured relative humidity contains 2.5×10^{17} molecules cm^{-3} of H_2O . In the high UV radiation, this amount of water vapor can produce OH and HO_2 . It may be the reason of why we did not see the SOA yield reduction in the UV-radiated chamber with dry air (dry air means $<1\%$ of relative humidity measured). We will study about this UV radiation effect in a future. We modified the manuscript as follows.

Page 9943, line 17: “The difference between the two observations could be explained by the existence of 10 to 15 pptv of OH in the UV-irradiated, dry PAM chamber. This amount of OH was produced from the photolysis of a trace amount of H_2O that was in the dry air that entered the PAM chamber.”

4 - *How does one know that SOA formation is really complete given the short residence time? SOA formation can occur as a result of second-generation reactions. Do these have enough time in the tube?*

There are several indicators which were demonstrated in the manuscript.

1. The sulfate aerosol yield from SO_2 agrees with theoretical expectations at different

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Discussion Paper

relative humidities. SO_2 reacts slower with OH than essentially all SOA-forming VOC_s . So, if SO_2 is completely reacted, any VOC that reacts as fast or faster will also be reacted away.

2. If there are slower reacting secondary products, then they would need to be much slower reacting to not react in the PAM chamber. Our typical procedure was to establish a flow of the air and VOC_s and then turn the UV lamps on. Thus, the VOC_s that are exiting the chamber within seconds of the UV lamps going on have had much less exposure to OH than the VOC_s that are entering the chamber when the UV lamps were turned on. Both the measurement of VOC_s by the GC and modeling of the PAM chamber oxidation chemistry show that all the initial precursor VOC_s are reacted away within 10-20 s. Thus, any second-generation reactions would need to be about 10 times slower in order to not be completed during residence in the PAM chamber. This scenario seems quite unlikely and is not consistent our observations.

3. The SOA yields in the PAM chamber are generally similar to are slightly larger than the reference SOA yield range in the large environmental chambers (Table 1).

4. No VOC_s remained after the UV radiation in the PAM chamber (Complete consumption of precursor organic gases). (Page 9938, line 23).

5. The SOA mass did not increase further as we increased the exposure time \times [OH].

6. The SOA mass spectra produced in the PAM chamber is similar to that produced in the large environmental chambers, at least for m-xylene. (We will add the section about the chemical characterization of SOA from m-xylene in the PAM chamber).

Moreover, the comparison of the oxidation time-scale by OH in the atmosphere and in the PAM chamber supports the SOA formation can be completed in the PAM chamber.

The oxidation time-scales in the atmosphere and in the PAM chamber are roughly calculated with the amount of OH and the exposure time. For instance, the amount of OH and the exposure time in the PAM chamber is roughly 200 pptv and 180 s,

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respectively. If the atmosphere has about 0.2 pptv of OH, 50 hours are needed to complete the same oxidation in the PAM chamber. Therefore, about 3 days of the atmospheric time-scale is reproduced in the PAM chamber in about 3 min.

5 - *In judging the NO_x regime, the important ratio is that of HO_x to NO (page 9946). The authors need to carefully compare the conditions in their system with those in large chambers.*

Similar VOC/NO_x ratios in the PAM chamber and in large environmental chambers are the same in some respects and different in others. Exploring these similarities and differences between the PAM chamber and the work of Ng et al. (2007) may elucidate the reasons that their yields for m-xylene in a relatively low NO_x condition are 3-4 times ours in a truly low NO_x condition. It will be difficult for us to match the exact conditions of the large environmental chambers; but it is not yet clear at all that matching them exactly is either desirable or necessary.

If the oxidation of precursor VOC_s is driven by reactions with OH, HO₂, and O₃, then the PAM chamber mimics the atmospheric reactions, but at a much faster rate. Thus, the relative rates of NO_x and VOC oxidation will be the same in the PAM chamber and the atmosphere. However, if a reaction of a VOC product with NO is an important pathway that competes with the reaction of that same VOC product with OH or HO₂ in the atmosphere, it will not be competitive in the PAM chamber. The oxidation by OH or HO₂ will overwhelm the reaction by NO, which will be heavily suppressed. Similar reasoning suggests that HO₂+RO₂ reactions will be sped up proportionally to other oxidation pathways involving OH, HO₂ or O₃, but RO₂+RO₂ reactions that might be important in the atmosphere will not be important in the PAM chamber.

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The question is “How important are these VOC+NO and RO₂+RO₂ channels in the production of SOA?” This is a serious research question that an alternate approach like PAM can contribute to. If for example, it is hypothesized that a particular RO₂+RO₂ reaction is essential for SOA formation from a particular precursor VOC, then comparing the SOA yield and the chemical composition from the PAM chamber and a large environmental chamber will test that hypothesis.

That most of the SOA yields and the m-xylene chemical composition appear to be in good agreement with results from environmental chambers suggests that RO₂+RO₂ or VOC product + NO are playing a secondary role in the SOA formation for those precursor gases.

Even though NO_x cannot provide potentially relevant competing oxidation pathways to HO_x and O₃ in the PAM chamber, it can still play an important role as nitric acid. And if the VOC oxidation pathways leading to SOA are truly dominated by OH, HO₂, and O₃, then the PAM chamber may accurately mimic the atmosphere. Testing this possibility will require much more research.

6 - *The lack of agreement of the aromatic SOA yields with those of Ng et al. (2007) is troubling. The presence of seed aerosol cannot explain this discrepancy. Are the NOx conditions really the same? (See comment above)*

We do not find the lack of agreement of the aromatic SOA yields with those of Ng et al. (2007) to be troubling; we find them to be scientifically interesting. There is clearly a difference, but it seems to us that we should report our findings, even if they conflict with those of Ng et al. (2007), and then in subsequent research and papers should try to resolve those differences. At present, we do not have a solid explanation for the

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differences.

The major differences between Ng et al. (2007) and ours are the OH source and the presence of seed aerosol. Their OH source is the photolysis of H₂O₂ and they used neutral seed aerosol. They used extreme levels of H₂O₂ to generate their OH radicals, estimated at 3-5 ppmv. Could these extreme levels of H₂O₂ play a role in elevating the SOA yield? This should be investigated.

Kroll et al., (2007) observed the lower SOA yield in no seed condition than in neutral seed condition. They concluded that an induction period delayed aerosol formation in no seed condition. They observed SOA yield reduction from 18% to 44% for m-xylene and toluene photo-oxidation experiments in the no seed condition. So the presence of seed aerosol may explain a part of this SOA yield disagreement, but we agree with the referee that it is unlikely to be responsible for all of the difference.

In this manuscript, we use results from environmental chambers as the benchmark for the results from the PAM chamber. However, given the many studies that we have done in a short time, it would be quite surprising if there were no differences between the results from the PAM chamber and from the large environmental chambers. It is perhaps more surprising that there are so few and that the SOA yields and the few mass spectra we have are so similar, despite differences in conditions.

7 - In α -pinene + O₃, why is it necessary to add up to 12 ppm of O₃ to achieve maximum yield? Do we really understand the mechanism occurring in the system?

If we assume that the rate coefficient for α -pinene + O₃ is roughly $8 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$, then for 12 ppmv of O₃ with a reaction time of 200 s, 99 % of α -pinene should be

reacted away. Thus, the data suggest that the first step, the reaction of α -pinene with O_3 , limits the rate of SOA formation and that it does take that much O_3 to react away the α -pinene in the 200 s residence time in the PAM chamber.

8 - *Section 3.2.3. Why is the α -pinene SOA yield 5 times higher in light vs. dark. Known OH yields do not seem to be able to explain this.*

In Figure 6, one of the experiments we were doing here is showing that relative humidity is not affecting the SOA yields, at least for RH up to 60%. For this experiment, we were able to generate only 5 ppmv of O_3 in the dark. So we held the amount of O_3 generated with the UV light in the PAM chamber to 5 ppmv. From Figure 6 and the discussion to the question above, it is clear that the amount of O_3 was insufficient to react away all the α -pinene to SOA. Thus, figures 5 and 6 are consistent; the SOA yield is only 10% for these conditions because some α -pinene remains. However, the amount of OH generated with the UV lamps and RH >20% is more than enough to react away all the α -pinene. Our measured SOA yield for α -pinene is 40% for T 22 °C, only 20% higher than the SOA yield of Lee et al. (2006). Several factors affect the SOA yield, and M_o is one of them. So, this result is well explained.

9 - *In summary, this is an intriguing new idea, but the work, as presented here, is premature. The authors have tried to do too much, yet have left fundamental issues in atmospheric chemistry unanswered.*

We agree with the referee that this is an intriguing idea. All the more reason to publish this manuscript so that the atmospheric sciences community can decide what they think. All the more reason to publish this manuscript so that others can try to duplicate our results.

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

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One advantage of the PAM concept is that it is relatively inexpensive and relatively easy to duplicate. We are very interested in the rapid spread of this concept to see if it has the merit that our initial studies have indicated. This will not happen if we must attack all the “fundamental issues in atmospheric chemistry” that the referee thinks we must before publication. We might add that a large number of publications about SOA formation that have and are currently being published do not answer “fundamental issues in atmospheric chemistry”; they point to aspects, they provide intriguing observations and speculations; they are moving the science forward by a combination of new observations, new hypotheses, and further testing.

This PAM concept can contribute to both the fundamental understanding and the atmospheric measurements. This manuscript introduces this new concept to the atmospheric science community, shows the potential by comparing to previous observations in large environmental chambers, and welcomes the community to see what the potential might be. Only through this scientific process involving more than our laboratory will the community be able to assess the true value of the PAM concept. The other referees have all signaled a need to publish this manuscript with some revisions that we believe we have addressed; we believe it should go forward.

[Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9925, 2007.](#)

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