**Atmospheric
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Discussions**

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Comment

Interactive comment on "Evolving mass spectra of the oxidized component of organic aerosol: results from aerosol mass spectrometer analyses of aged diesel emissions" *by* A. M. Sage et al.

A. M. Sage et al.

The authors sincerely thank both reviewers for their helpful and insightful comments. We have attempted to address the concerns of each below. Reviewer comments are shown in *italics*; author responses in plain text.

1   Response to Dr. Allan's review

The authors do not go into any detail concerning the types of oxidation reactions they think are occurring other than that they are UV initiated. While these are not

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constrained, the reader should be told of what sort of reactions that could be expected in this system, be they through OH, O_3 or NO_x chemistry.

We expect that the SOA formation that we are observing results from the reactions of saturated hydrocarbons with OH radicals under high-NO_x conditions. We have added a description of this chemistry and a discussion of our understanding of its compatibility with our observations to Section 3.2 of the text.

There are a number of issues associated with the SMPS volume comparison. Firstly, there will be a discrepancy brought about by the fact that the AMS does not detect elemental carbon whereas the SMPS will. Secondly, why was a density of 1 g cm-3 assumed? Density measurements of both POA and SOA exist in the literature and are shown to be different (e.g. Slowik et al, Aerosol Sci. Technol., 38, 1206-1222, 2004; Cross et al, Aerosol Sci. Technol., 41, 343-359, 2007). Thirdly, the assumption that the fresh primary particles are spherical is difficult to make, given that soot particles are generally found to be fractal. Finally, the authors should comment on whether they consider electrophoresis to be an important loss mechanism, given that combustion particles are generally charged. If a neutraliser was used on the delivery system, this should be stated.

We concur that the absolute accuracy of our comparison with the SMPS volume measurements is limited by uncertainties in a number of particle characteristics, including those mentioned. These uncertainties have been addressed at some length in a companion publication (Weitkamp et al., 2007).[1] Given both these uncertainties and the analytical limitation of unit-resolution on the Q-AMS, the purpose of comparing results from the two instruments is primarily to show that there is qualitative agreement, and

[1]Weitkamp, E. A, Sage, A. M., Pierce, J. R., Donahue, N. M., and Robinson, A. L.: Organic aerosol formation from photochemical oxidation of diesel exhaust in a smog chamber, *Environ. Sci. Technol.*, 41: 6969-6975, 2007.

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thus that the mentioned uncertainties and limitations do not quantitatively overwhelm the results we are presenting. That being said, Dr. Allan brings up a number of valid points about the comparison, which deserve to be addressed.

Firstly, in comparing AMS and SMPS data, we have accounted for the fact that the AMS does not measure elemental carbon (EC) and the SMPS does. We did this by subtracting our best estimate of the EC from the reported SMPS mass. Our estimate was based on previous EC measurements carried out on the same engine under similar operating conditions. We assume that, after wall-loss corrections, the EC mass in the chamber will remain constant.

Secondly, the density of these particles is unquestionably different from 1 g cm^{-3}. In addition to the citations mentioned, our own comparisons of the particle size distributions measured with SMPS and AMS suggest that the initial effective particle density increases by 20-30% during the first half hour of an experiment when SOA is rapidly formed. We attribute this increase to the formation of an SOA coating on the initially fractal-like primary diesel particles. However, given that we have made a number of assumptions in our analysis already, we believe that assuming specific densities for POA and SOA when we are uncertain of the split between the two would only further complicate the interpretation of our results. A density of 1 g cm^{-3} was assumed because we do not know the density of these particles, and we assume it will be changing. We acknowledge that the SMPS data we are presenting are essentially the measured volume and not the mass, but we have expressed them in mass concentration units (ug/m3) to facilitate understanding. The observed increase in particle density (or change of shape) is not accounted for in our wall-loss model and means that we may be underestimating SOA produced in the initial stages of the experiment by 20-30%. Because one of the issues we wish to address in these experiments is the potential for significant SOA production from previously unconsidered precursors, we felt it prudent to present the most conservative estimate of the amount of SOA formed.

Thirdly, we also acknowledge that the fresh diesel particles are probably not spheri-

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cal, as has been shown by EM images, but assuming sphericity again maximizes the primary estimate (if they are fractal the SMPS will be overestimating their mass), and gives the most conservative estimate of the SOA yield. However, the correlation between AMS mass and SMPS volume remained tight throughout all of the experiments described here, so the combined uncertainties in density and shape factor do not influence the trends that make up the core of this paper.

Finally, there was no neutralizer in the delivery system, and the particles generated are likely to carry significant charge. We have accounted for this charging in the wall loss estimation model (APE) (Pierce et al., 2007).[2] Electrostatic effects are specifically dealt with in the "size-dependent wall loss" case. The application of this model to these data is discussed in Weitkamp et al. (2007).[1]

There is no discussion on the collection efficiency assumed during the analysis of the AMS results. While this does not affect the conclusions of the paper, the authors should explain why it does not.

The particles in this experiment were within the transmission window of the AMS lens assembly, and we therefore do not expect any collection difficulties associated with particle size. Changes in vaporization efficiency (i.e. "bounce") and consequently in detection efficiency may occur as particle morphology changes. However, as long as SOA is condensing onto existing mass, the need to consider these differences is eliminated by normalizing the MS recorded at time t by the total organic mass at that time. A clarifying statement has been added to Section 2.1 of the text.

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[2]Pierce, J. R., Engelhart, G. J., Weitkamp, E. A, Pathak, R. K., Pandis, S. N., Donahue, N. M., Robinson, A. L., and Adams, P. J.: Constraining particle evolution from wall losses, coagulation, and condensation-evaporation in smog- chamber experiments: optimal estimation based on size distribution measurements, submitted, 2007.

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While this would not affect the qualitative conclusions of the paper, a problem exists in how the wall losses affect the relative concentrations of the different stages of SOA. Compared to the SOA produced early in the experiment, the later SOA products will condense onto fewer particles, so therefore the amount of mass per particle per mole of condensable material will be greater, making the more oxidised SOA artificially more prominent.

We have considered the various wall-loss possibilities extensively. Many lines of evidence (including common sense) convince us that particles deposited on the chamber walls remain part of the condensation - evaporation equilibrium governing particle behavior in the chamber. Particles deposited to the chamber walls do not lose contact with the vapors, therefore we believe that they should remain in equilibrium with the gas phase. If this is true, we expect the composition of the material on the walls to match the composition of the material still suspended in the chamber. We have explored this issue in spiking experiments that are described in Weitkamp et al.[1] The same basic experiment was conducted as is described here, but the chamber was spiked with substantial amounts of toluene. The results of these experiments indicated that the toluene remains in equilibrium with the organic mass on the walls.

10070: The method by which the gas-phase N_2 was subtracted should be described in greater detail. In most fragmentation table implementations, the m/z 28 peak is taken as a reference point for all gas phase signals. Was a constant value simply subtracted from the data matrix, or was the air referenced to a different peak in the mass spectrum?

Although we did correct our organic MS to include particle mass appearing at m/z=28, we did not correct the entire air MS to exclude it. We corrected the air time series by scaling it to periods during which particle-free air was sampled through a HEPA

filter, as described in the text, and we used this corrected time series in accounting for multiplier decay. We also explicitly corrected the gas-phase signal at m/z=18 based on our understanding of the relative humidity in the chamber during these experiments.

Due to the natural isotopic abundance of ^{15}N, N$_2$ makes a contribution not only at m/z=28, but also at m/z=29 and 30. Additionally, Ar is calculated in the fragmentation table from the gas-phase N$_2$ signal appearing at m/z=28. We have not corrected the air signal at these masses. Therefore, the contribution from air at these masses may be overestimated by as much as 15%, where the difference should be attributed to the organic MS. At its maximum, however, compensating for this overestimation only leads to a 1% change in the total organic mass, therefore it is a minor correction.

10071: A potential flaw in the assumption that the mass spectrum of POA is constant is if a fraction of the initial POA is semivolatile and in equilibrium with the gas phase. This would be effectively converted to SOA through gas phase reactions over the course of the experiment. The assumption has to be made that either the particulate semivolatile fraction is so small as to not affect the mass spectra or that the changes are not manifested in the relative peak sizes due to the fragmentation properties of aliphatic chains.

We have conducted control experiments in the absence of irradiation to look at changes in the MS as a function of suspended particle mass in the chamber. Over the course of a 10-hour experiment during which the mass loading in the chamber changed by two orders of magnitude (from approximately 1000 μg m^{-3} to approximately 10 μg m^{-3}, the cumulative change in the MS was 13%. This compares with changes induced during photochemistry experiments of 63%. The changes that were observed in the MS during this control experiment did have the affect of making the MS look more oxidized–increasing the fraction of the mass at m/z = 44, and decreasing that at 57. The experiments discussed here were less than half the length of this control experiment, and so would be subject to considerably less re-partitioning of the

primary organic material. Additionally, the formation of SOA during the experiments acts to slow the rate at which the suspended mass concentration changes, which will further limit re-partitioning. On the whole, we expect re-partitioning to cumulatively change the primary MS considered here by less than 5% over the course of an experiment. This re-partitioning would introduce a systematic overestimation of both the fraction of material that is secondary and the extent of oxidation of that secondary material. However, the relative rate of change in the primary MS due to repartitioning in the control experiment is minimal compared to the rate of change in the total MS that we observe due to oxidation chemistry in other experiments. Explicit treatment of this partitioning will not significantly change either our qualitative or quantitative results.

10076: The CO_2 peak at 44 is not a common feature in conventional electron impact mass spectrometry. It is thought that with the AMS, this peak almost entirely originates from the pyrolysis of species on the vaporiser surface.

This has been noted in the revised text.

10078/10092: If the m/z=28 data on figure 3 is unreliable, it should not be included on the figure.

The data are now believed to be reliable and have been retained.

10078/10080: There is a possibility that the 44 contribution to the POA spectrum is from SOA formation that occurs before lights-on, through unwanted oxidants either in the delivery system or chamber. The authors should discuss whether they think this is a possibility or not.

We routinely see m/z=44 features in fresh diesel emissions. As we expect the SOA chemistry in this system to be initiated by H-atom abstraction by photochemically-generated OH, we do not believe that significant SOA formation will occur prior to illumination. In an experiment with a one-hour delay between exhaust injection and lights-on, we see only a slight increase in the fractional contribution of m/z=44 prior to lights-on, but a sharp kink upwards after. We cannot definitively say that this early, dark "oxidation" is not of chemical origin, but we strongly suspect that is related to the repartitioning of primary material that is discussed above. If it is chemical, the conditions are only mildly oxidizing.

10084: It would be of great benefit to the paper if the authors were to discuss what future experimental work would be needed to quantitatively constrain the phenomena reported here and further investigate the mechanisms.

Suggestions for future work have been added to the Conclusions section.

In terms of language use, the word "one" is used at several points in the text to refer to the numerical quantity, but this can be ambiguous. This should be replaced either with the numeric "1"; or the word "unity".

This change has been made.

10090: The graphs in figure 1 are a little difficult to read. The authors should consider moving some of the descriptions of the different lines onto the plot in the form of a legend.

This change has been made.

2 Response to Review 2

It will be useful to provide more information on the photochemical conditions, e.g., actinic flux, NOx, O3 and OH concentrations, etc.

OH concentrations of $3 \pm 1 \times 10^6$ molecules cm^{-3} in the chamber were calculated from the observed decay of toluene. NO$_x$ concentrations were not measured but were assumed to be high. These conditions are discussed in detail in the companion publication[1] and have been added to the experimental summary in the first paragraph of the Methods section. Actinic flux and ozone concentrations were not measured during these experiments. As discussed above, we expect that the observed oxidation is due primarily to OH and NO$_3$ chemistry, so we don't believe that ozone and flux measurements would provide additional insight.

The Q-AMS used in this study does not have adequate mass resolution to determine the elemental composition of an ion. Besides CO_2^+, $C_3H_8^+$ also has a nominal m/z of 44. Similarly, the condensed phase m/z 28 signal detected can be contributed by $C_2H_4^+$, not just by CO^+. These hydrocarbon ions are especially relevant to diesel exhaust particles. They are also consistent with the observations of significant m/z=44 and 28 signals in the spectra of fresh diesel particles and the decrease of m/z 28 signal in SOA during photooxidation (Figure 2 page 10070). On the other hand, oxygenated OA may produce $C_3H_5O^+$ (nominal m/z = 57). If the SOA species photochemically generated indeed produce this ion, the SOA fraction may be underestimated to some degree by the m/z=57-based subtraction method. A high-resolution AMS will be

needed to verify these possibilities, but it is necessary to discuss them in the paper.

We agree that unit mass resolution of the Q-AMS is not adequate to unambigously identify these ions. The $C_2H_4^+$ and $C_3H_8^+$ ions make minor, but observed contributions at m/z=28 and 44 in the standard electron impact (EI) mass spectra (MS) of aliphatic hydrocarbons. Our observed primary MS (denoted MS_{POA} in the text and hereafter) contains contributions at m/z = 28 and 44. Regardless of its specific identification, we have treated this signal as primary in our calculations.

More importantly, we cannot exclude the suggested possibility that the $C_3H_5O^+$ fragment contributes to the signal appearing at m/z=57 in our MS, or the possibility that the $C_4H_9^+$ fragment can result from EI ionization of oxidized organics.

However, higher resolution spectra would not change the basic result of our analysis: the MS of the secondary aerosol becomes progressively more oxidized with time. Our residual analysis method assumes that a constant MS_{POA} is a component of any MS recorded during these experiments. The *magnitude* of this contribution is calculated here by assuming that the entire signal at *some* peak (in this case m/z = 57) can be attributed to the primary material, but qualitatively, the magnitude is of secondary interest. Our focus is the fact that the total MS becomes increasingly oxidized in time, and since the primary material is believed to be at most minimally processed, the secondary material must account for the observed changes in the MS.

Quantitatively, if secondary organic aerosol produces signal at m/z = 57, then we are over-subtracting the MS_{POA}, and the calculated residual spectra ($MS_{residual}$) in Figs. 2 and 3 appear more oxidized (in terms of the fraction of the total mass appearing at m/z = 44) than they should. However, the "correct" subtraction would not produce results substantially different than those reported here, because independent apportionment of the observed aerosol mass between primary and secondary (see Fig. 1) corresponds relatively well to the split calculated from the residual analysis method.

We have added clarifying statements to Section 2.3 of the text that address the analytical limitations of the Q-AMS and the uncertainties implicit in apportioning m/z = 57 entirely to primary material.

Another major comment I have concerns the application of the 2-component CPCA method (Zhang et al., 2005a) to these chamber results. Note that an important assumption underlying this technique is that every mass spectrum in a given measurement matrix can be represented as the linear combination of two mass spectra that are constant. This technique will not give sound results in a situation where more than two distinct components clearly make an impact in the data, or if the component mass spectra change significantly over time. Since the SOA products clearly became more oxidized and their mass spectra change significantly over the course of these experiments, in principal these chamber data are not suitable to be fitted with a two component linear model. 8230;[I]t will be important that the limitations of the analysis methods are clearly stated and explained. In addition, if the CPCA analyses were done with the AMS Organic Analysis software posted at http://www.asrc.cestm.albany.edu/qz/, it will be helpful to cite the link.

Literature applications of the 2-component CPCA method strongly suggest that the derived HOA and OOA spectra represent POA and SOA. In our chamber experiments, we expect only contributions from these two components as well. However, as the reviewer points out, our SOA products clearly become more oxidized in time, bringing into question the validity of trying to represent this SOA with a single constant OOA component.

It is exactly this conundrum that we wish to highlight with these data. In general, SOA cannot be described by a single, constant component. The chemical composition of SOA evolves in time. The cases where the 2-component solution will be successful are those for which the dominant influences on the organic aerosol composition are fresh

emissions and highly processed SOA. This SOA has reached an asymptotic limit: it is "fully" oxidized and can be accurately described by a single, highly-oxidized OOA spectrum.

What these data, and recent applications of multicomponent analysis techniques show is that these 2-component cases do not capture the initial chemistry responsible for early SOA formation. We demonstrate this by using the 2-component CPCA on the divided dataset. When applied in a piecewise fashion to our data, the CPCA method shows a progressive evolution of the oxidized organic material. The 2-component solution becomes increasingly like the ambient HOA and OOA factors with time.

In section 3.3, we have clarified in the text that the purpose of our application of the 2-component CPCA method is not to identify definitive HOA and OOA components, but to demonstrate that intelligent application of a quantitatively-validated analysis technique confirms the results of our residual analysis method and that these results are not contradictory to ambient observations.

We have also added the reference to the open-source CPCA software, and thank the reviewer for pointing out this oversight.

Line 2, page 10071, what is the range of percentage estimated to be gas phase CO2 at m/z 44?

Nearly 100% of the signal is in the condensed-phase PToF peaks during the experiments.

Line 11, page10073, replace CHO^+ with CH_3O^+.

This change has been made.

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Line 9, page 10076, calling m/z=44 "the canonical indicator"; is a bit too strong. Suggest replacing it with something like "usually an indicator"; because signals detected at m/z 44 can come from ions that contain oxygen, such as $C_2H_6N^+$, $C_3H_8^+$, $^{13}CC_2H_7^+$.

This change has been made.

Line 23, page 10078, what "inlet"; is it referred to? It does not seem to be the AMS or SMPS inlets as the chamber temperature was well controlled.

"Inlet" in this case refers to the port in the chamber through which exhaust from the generator was added. The text has been revised to make this clearer.

It will be useful to show in Figure 5d the ratios of error to organic mass as well. This will provide a better picture of how good the fits are.

The signal-to-noise ratio in these experiments was high, and the error was less than 1% of the organic mass throughout the experiment. Graphically, it would appear as a flat line across the bottom of Fig. 5d, therefore it was not added to the figure.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 10065, 2007.