

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.

Anonymous Referee #1

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This paper reports an interesting chamber study on the photooxidation of diesel engine exhaust. The evolution of the AMS mass spectra of the SOA products was examined in detail. This paper was very well written and its results fit well to the scope of ACP. I recommend publication after several comments.

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

The Q-AMS used in this study does not have adequate mass resolution to determine the elemental composition of an ion. Besides CO₂⁺, C₃H₈⁺ also has a nominal m/z of 44. Similarly, the condensed phase m/z 28 signal detected can be contributed by

C₂H₄⁺, 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 C₃H₅O⁺ (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.

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.

However, the analyses done in this paper are nevertheless useful and the phenomenology interesting. But it 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. A warning message on the limitations of the two component algorithm is posted together with cautionary statements on some of the situations that the codes should not be used.

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

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Line 11, page10073, replace CHO+ with CH3O+

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 don’t contain oxygen, such as C2H6N+, C3H8+, 13CC2H7+.

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.

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.

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

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