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Atmospheric Chemistry and Physics Discussions

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.

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General comments

This paper reports the results from smog chamber experiments where the emissions of an engine were introduced directly into the chamber and the aerosol exposed to ultra-violet light. The aerosol produced from this system was analysed using an Aerodyne Aerosol Mass Spectrometer and Scanning Mobility Particle Sizer to study the physical and chemical evolution of the particles and were able to track the addition of secondary organic mass onto the pre-existing particles. They were able to show that the chemical nature of the secondary material produced changed over time, manifested in the mass

spectra reported by the AMS and speculated that given enough time, a mass spectrum resembling those routinely seen in remote polluted environments would be evident.

This is an especially relevant publication because there is a currently a major gap in our understanding of the processes that govern secondary organic aerosol formation. Current models, using data derived from chamber studies investigating simpler systems involving constrained precursors and oxidants, tend to under-predict the amount of SOA produced by around an order of magnitude. These experiments have also yet to reproduce AMS mass spectra that are commonly observed in the ambient atmosphere.

This experiment offers the tantalising prospect that it is indeed possible to generate the SOA seen in the ambient in controlled laboratory conditions. It also highlights the fact that there are several stages in the generation of the SOA, involving a spectrum of precursors that must undergo different amounts of oxidation before they will form condensable material. The main weakness of the paper is that while providing some interesting insights, they are very general and do not in themselves further our abilities to tackle the problems. More specifically, the work does not on its own shed any light on the oxidation mechanisms themselves. It also does not show how this technique could be applied to provide any quantitative constraints for chemical models. This paper would benefit greatly if the authors could comment on how this work could be taken forward with these objectives in mind (see below).

The paper is generally well-written and clearly structured and the figures are mainly well-presented. However, it should be noted that this reviewer is already very familiar with AMS data analysis, so it may be that some parts may be confusing to someone not as familiar with this instrument or its application. This is an important paper and suitable for publication in Atmospheric Chemistry and Physics, but I would ask the authors consider the following points first:

Specific comments

The authors do not go into any detail concerning the types of oxidation reactions they

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think are occurring other than that they are UV initiated. While these are not constrained, the reader should be told of what sort of reactions that could be expected in this system, be they through OH, O3 or NOx chemistry.

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.

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

While this wouldn't 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.

Further comments by page number

10070: The method by which the gas-phase N2 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

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subtracted from the data matrix, or was the air referenced to a different peak in the mass spectrum?

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.

10076: The CO2 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.

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

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.

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.

Technical comments

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".

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

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legend.

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