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Atmospheric
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Discussions

Interactive comment on “Laboratory investigation of photochemical oxidation of organic aerosol from wood fires – Part 2: Analysis of aerosol mass spectrometer data” *by* A. P. Grieshop et al.

Anonymous Referee #1

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This manuscript describes laboratory measurements of the changes to the chemical composition of wood burning aerosol upon photochemical oxidation. Measurements were made with an aerosol mass spectrometer (AMS), and a simple deconvolution scheme is used to separate out the spectrum of the primary organic aerosol (POA) from that of the secondary organic aerosol (SOA). The mass spectra are compared to ambient measurements, showing that the aerosol ultimately looks similar to "oxygenated organic aerosol" (OOA), which appears to be ubiquitous in the atmosphere. This is a similar result to what the authors saw previously with the oxidation of diesel

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exhaust, suggesting that photochemical aging of distinct mixtures of organics ultimately forms products that share many chemical features, and possibly are indistinguishable with the AMS.

This is an excellent paper: it addresses several important topics in atmospheric chemistry (biomass burning emissions, aerosol composition, and photochemical aging), the experiments and data analysis were carried out carefully, and the manuscript is well-written and easy to follow. Thus it definitely warrants publication in ACP. I have one major concern about the analysis/interpretation of data that needs to be addressed prior to publication, described below. Other minor comments are listed after that.

Major concern:

The composition of the aerosol changes rather dramatically prior to the initiation of photochemical oxidation. This is mentioned in the manuscript (p. 17107, lines 17-24) but only briefly. I think this needs to be discussed in much greater depth, as it has potentially serious implications, both for the analytical approach employed in the manuscript and for biomass burning aerosol chemistry overall. [Simply referring the reader to a previous publication (Sage 2008) is not sufficient, as no such effects were reported in that work.]

Specifically, two of the most common AMS "marker peaks" of biomass burning aerosol, m/z 60 and m/z 73, drop dramatically prior to the lights being turned on. This is explained in terms of volatilization chemistry, but this raises a number of questions/issues:

- to what extent is the residual method even valid for these peaks? When the lights are turned on, the loss rate of those two ions does not change at all. Thus one must assume that the observed loss of m/z 60 and m/z 73 when the lights are on is a result of continued volatilization and not by any new photochemistry. It seems photochemical oxidation simply cannot be described in terms of these peaks. This uncertainty should be addressed, and possibly those peaks be removed from the analysis (Fig. 1, etc.)

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- With the mass spectrum changing, how does one pick a true "POA spectrum"? The statement "averaging the AMS data for 15 to 25 min before turning on the chamber lights" is too vague. How do results depend on the timeframe used (1 hour before, or 5 minutes before, the lights turn on)?

- If volatilization from dilution is causing the decrease, the absolute aerosol mass (measured with the AMS or SMPS) should decrease; does it? This was not reported in this work or in the companion paper. (If it does, how does it affect the previous dilution factor results by one of the authors?)

- The mass fraction of one peak decreasing necessarily means the mass fraction of other peaks must increase. Is this observed?

- The AMS community often associates m/z 60 and 73 with levoglucosan, though this may be overly simplistic. Is the decrease in these peaks consistent with the vapor pressure of levoglucosan?

- How exactly can a peak decrease from volatilization but not decrease more rapidly with OH exposure? All organics react with OH; that reaction would be expected to speed up the volatilization (shifting the gas-particle equilibrium), but this is not observed. It's possible some sort of kinetic bottleneck may obscure this effect, but such a bottleneck is not observed for the m/z 137 peak; this is unusual since the m/z 137-containing compounds seem to be much less volatile.

In other words, it's not completely clear that the observed effect is from volatilization, as the authors assert. Could other effects - nonoxidative decay of freshly-emitted organics, heterogeneous oxidation, etc. - be playing a role?

Other points:

- Throughout the paper, very little is made of the fact that this study focuses on only one specific type of biomass-burning emissions (wood burning). The spectra are compared with several AMS spectra, including "BBOA" factors, but not with published wood

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burning spectra (Weimer et al. JGR 2008), which is important.

I think it needs to be noted that results from this study might not be completely applicable to other types of biomass burning; as the authors point out, the chemical composition of biomass burning aerosol can vary hugely based on the type of fuel burnt (and the burning conditions). Such differences could explain the differences in OA production measured in aged biomass burning plumes (discussed on p. 17098).

- P. 17100, lines 25-26: This sentence is hard to understand. If total OA mass decreases, why must other peaks increase?

- P. 17115, line 8: the assertion that chamber SOA from traditional precursors never looks like OOA is incorrect. See, for example, Fig 1A(i) of Shilling et al. 2008 (ACPD 8:15343), showing SOA from a-pinene ozonolysis at low loadings. (Even an SOA spectrum from one of the papers cited (Bahreini et al. 2005) looks rather OOA-like.) While traditional chamber SOA is GENERALLY higher in volatility (and lower in oxygen content) than ambient OOA, this seems to be a result of past chamber studies being run at high loadings and/or little aging. Those that are run at low loadings (Shilling) or that include multigenerational oxidation (Bahreini) seem to be able to make SOA with spectra quite similar to OOA.

- Fig. 2: the distributions of the different ions aren't actually the same. In both plots m/z 44 is pretty clearly shifted to higher "sizes". (This is probably a vaporization effect, but should be mentioned explicitly.)

- in the companion paper, a "high-NOx" experiment was carried out. Did this run make aerosol with an obviously different AMS spectrum?

- I disagree rather strongly with the other reviewer's point that fragment ions cannot be referred to as "tracers" or "markers". Whether one is talking about individual molecules or individual ions, in either case an analytical chemical approach is used to infer information about a complex mixture of a huge number of organics - so both are used as tracers. While individual molecular species are certainly more chemically specific, it is unclear to me in what way the terms "marker" and "tracer" have been "reserved" for molecules only.

- Nonetheless, the authors should be careful not to discuss ions as if they were individual compounds. For example, in discussions of the thermodenuder results (p. 17109, lines 16-26), the "volatilities of fragments" are discussed. Such a wording makes no sense physically, and should be changed to reflect that fragments are derived from (or are associated with) the molecules of varying volatilities.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 17095, 2008.

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