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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.

A. P. Grieshop et al.

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AUTHOR COMMENTS

The authors would like to thank the two anonymous reviewers for their positive feedback and helpful comments. All reviewers' comments are addressed below. Reviewer comments are included in italics and author responses are in plain text

Response to Referee #1:

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:

This issue has been discussed in greater detail in the revised manuscript and we have added analysis to constrain the sensitivity of our results to the evolution of the POA spectra.

-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.)

As is noted by the reviewer, the fractional contribution of m/z 60 and m/z 73 decreased over the approximately hour-long period before the lights were turned on in some of the

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Interactive Discussion

Discussion Paper

experiments. This would violate the assumption of a constant POA spectrum. However, the ER estimates were not highly sensitive to which POA spectra from different “pre-lights” periods was used in the MS decomposition method. For example, in Experiment 5 (Fig. 1b) ER values calculated using different MSPOA range from 2.8 to 3.2 after 6 hours of aging, which is within the shaded bands demarcating the range of ER estimates from different techniques. While we cannot explicitly separate the influence of primary species loss from “dilution” due to the condensation of SOA, the consistency of estimates for SOA formation from 3 independent methods (BC as a POA tracer, SMPS wall loss correction and residual decomposition [Grieshop et al., 2009]) gives us confidence that the residual decomposition can be applied even with this complication. We have highlighted this as a source of uncertainty in the revised manuscript.

- 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)?

This is an important point, as it emphasizes the fundamentally dynamic nature of the OA composition. This fact raises some issues in the interpretation of experimental results, though as indicated above these issues do not present serious challenges to our conclusions. However, this fact raises the larger issue of the difficulty of trying to link spectra directly to emission sources. The continuously evolving nature of OA spectra significantly complicates such an effort.

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?)

There was modest (∼15%) decrease in OA-to-BC ratio in some experiments before the lights were turned on. This detail has been added to the revised manuscript. Since this evaporation was due to the dynamics of the aerosol approaching equilibrium, one cannot compare it with the previous dilution results which were all made at equilibrium conditions. The volatilization of primary mass was small relative to wall-loss rates and to the increase in overall mass due to condensation of secondary material during photo-oxidation.

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

There is some indication that the mass fraction of m/z 44 increases before lights were turned on (Figure 5a) across experiments. Other consistent trends in pre-lights composition-change were not 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?

Levoglucosan has an effective equilibrium saturation concentration (C*) of order 0.1 μg m^{-3} at ambient temperatures [Milosavljevic et al., 1996], which means that it should evaporate at temperatures around 60 $^\circ$C - much higher than the observed evaporation temperature of species contributing ions at m/z 60 and 73. Therefore, levoglucosan may not be the dominant contributor to the AMS signal at m/z 60 and 73 in these experiments. It seems likely that compounds other than levoglucosan contribute to these peaks. Laboratory SOA has spectral contributions at m/z 60 as do carboxylic acids [Schneider et al., 2006].

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

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compounds seem to be much less volatile.

A key detail here is that many compounds contribute to the AMS signal at any particular m/z. Therefore, one must be careful not to over-interpret the data. For example, m/z 60 appears to be associated with some of the more volatile components of the POA. Therefore, one might expect, as suggested by the reviewer, that OH attack would enhance evaporation rate by consuming gas phase species. However, it is also well established that SOA species contribute to the AMS signal at m/z 60. These competing effects could potentially explain why there is not an increased fall off of m/z 60 signal with the onset of photo-oxidation.

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?

These other effects may certainly be influencing the evolution of the aerosol. The fact that some of the OA evaporates before the lights are turned on (the 15% change in OA:BC ratio mentioned above) and the fact that ions at m/z 60 and 73 are associated with more volatile material support the evaporation hypothesis. However, these other effects could be occurring as well. The revised manuscript contains text which emphasizes our incomplete understanding of this processing. Again, the key finding is that these spectra are dynamic, which complicates the use of fixed reference spectra in interpreting ambient data.

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

Comparisons were done with a range of wood burning spectra from Schneider et al. [2006]. We have added comparisons with the spectra of Weimer et al. [2008] to the revised manuscript, which indicate that our spectra are more similar to their spectra

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Discussion Paper

from smoldering fires. We also now specifically point out in the discussion that these experiments are not representative of all types of biomass burning emissions.

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).

We agree with this statement. For example, some field studies have shown that BBOA becomes progressively more oxidized in a plume without adding new mass [Capes et al., 2008; Hoffer et al., 2006]. We have added text to this effect in the manuscript. We have also added a qualification that wood-burning emissions from a wood stove are not representative of all biomass-burning emissions.

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

The original sentence (referring to a decrease in total OA mass due to change in frag_organic[18] for H_2O^+ ions):

For example, it reduces the AMS OA mass by 1 to 7% with corresponding increases in the relative contribution of other peaks.

Was changed to:

Updating the fragmentation scheme for m/z 18 to that proposed by Aiken et al. [2008] only has minor effects on our results; it reduces the signal at m/z 18 attributed to OA so the total OA mass decreases by 1 to 7%, which, in turn, slightly increases the fractional contribution of the other peaks to the OA spectrum.

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.*

We agree with the reviewer’s concerns and have removed comparisons of our secondary aerosol with chamber SOA. We feel that such a discussion would distract from the main finding of this work, that these “primary” emissions take on a much more OOA-like character with fairly minimal aging.

- 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.)

We agree that vaporization delays likely cause a small increase in the measured flight time for components contributing signal at m/z 44 and thus appear at slightly larger dva. We have noted this in the revised manuscript.

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

There was no marked difference between the OA produced in the high-NOňx experiment and that produced in the other experiments. Inter-experiment regressions of residual spectra extracted after 3 hours of aging from all six experiments yield mean and median R^2 values of 0.94. This uniformity (in contrast to fairly variable POA spectra) has been noted in the revised manuscript.

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 infor-

mation 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.

We generally agree with this reviewer. However, we have made efforts to clarify and qualify our use of terms in the revised manuscript. This is discussed in more detail in response to the other reviewer's comments below.

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.

This is an important clarification. We have revised the manuscript at several points to make it clear that it is not fragments that are evaporating, but the compounds that contribute to them. In addition, we also now state in several places that multiple compounds likely contribute to each AMS mass given the extensive fragmentation of compounds which occurs in the instrument. Finally, the revised manuscript now explicitly discusses using individual fragments as tracers for sources.

Response to Referee 2

In particular, the use of the terms "tracer" and "marker" for mass fragment peaks (from page 17101 onwards) can be misleading (these terms are reserved for specific individual compounds in source apportionment studies). However, AMS is clearly not a technique for speciation and quantification of individual organic compounds. Several mass fragments may result from any single compound in the ionization process with highly variable ionization efficiencies. Therefore the conclusions regarding the evolution of single mass peaks must be treated with great care. The AMS data in general imply the evolution of the chemical functionalities rather than that of individual com-

Full Screen / Esc

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Discussion Paper

pounds with assumed volatilities and chemical characters. This is vaguely implied by the authors when they discuss the high degree of similarity between AMS spectra of wood smoke aerosols and aged Diesel emissions, in spite of their obviously distinct chemistry on the molecular level (page 17114 lines 10-15). The approach taken by the authors may also be used within this concept: a functionality can still be regarded as a measure of primary emission or secondary formation, and its evolution can be discussed accordingly. The main conclusions presented by the authors are still important and valid; however, putting them in a different context may help bridge the gap between organic aerosol speciation and AMS studies which would be highly desirable.

The reviewer makes a very good point. The AMS certainly does not provide speciated data. The revised manuscript now clearly states that multiple species likely contribute to each AMS m/z because of the complex fragmentation that occurs within the instrument. Therefore, one must be careful associating AMS mass fragments with specific sources.

We also agree that molecular-level information is very useful for source apportionment. The unit-mass-resolution AMS data clearly provide some information about the source of aerosols, but the fact that aged emissions from different sources have similar AMS spectra presents a major challenge for AMS-based source apportionment studies. To apportion the OOA/SOA will likely require more information on the molecular composition of the OA. However, the molecular fingerprint of the OA evolves with chemistry (it is not the static fingerprint measured in source tests); therefore, apportioning OOA will require understanding how the gas- and condensed-phase emissions evolve through several generations of chemistry. This is a major challenge. These issues are discussed in the revised manuscript.

However, as noted above, we disagree that the terms “marker” and “tracer” have been reserved for specific individual compounds in source apportionment studies. The term “molecular markers” is commonly used to refer to individual species used in source apportionment models. However, many source apportionment studies, even ones primarily based on molecular markers, also include BC, crustal elements, and other “species” as markers for sources. These other “species” are clearly not individual compounds but are used as markers for sources (BC for diesel, Si for crustal materials, etc). Given the fragmentation of compounds that occurs within the AMS, one must proceed with great caution when linking certain mass fragment to specific sources, but the same caveat applies to BC or Si. Our paper illustrates this challenge. We have revised the manuscript to clarify this point and have pointed out examples of problems which arise if one blindly assumes a particular mass fragment is associated with POA. For example, it is clear that m/z 60 or 73 (common AMS wood smoke “markers”) were not very good indicators of wood smoke POA in certain experiments.

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