**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Elemental composition and oxidation of chamber organic aerosol" by P. S. Chhabra et al.

Anonymous Referee #1

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This paper examines the chemistry of secondary organic aerosol (SOA) in terms of elemental ratios (H/C and O/C) and degree of oxidation of the constituent organics. A large dataset of chamber-generated SOA is compiled and described using two visualization techniques, the "triangle plot" and the Van Krevelen diagram. Data from a high-resolution aerosol mass spectrometer (AMS) are compared to both FTIR data and molecular data. The different approaches broadly agree, though agreement between the bulk and speciated approaches are generally best when mass closure in the speciated studies is high. Other results include the findings that high- and low-NOx SOA do not vary greatly in terms of the key parameters examined (f43, f44, O/C, H/C), and that already-oxidized precursors can lead to the formation of SOA that is of the same level of oxidation as the most-oxidized fraction of ambient OA. These important results will be of great interest to the organic aerosol community; the scope and detail of the

work is impressive; and the paper is well-written. Thus this paper certainly should be published in ACP. However, in a number of places in the paper the analysis/discussion of the results could use some improvement; these are discussed below. Once these are addressed I recommend publication.

(1) Right now the paper focuses only on a few simple parameters covered by the triangle plot (f43 and f44) and Van Krevelen diagram (O/C and H/C). I think it would be greatly improved if the analysis of the data went beyond that to include some consideration of key functional groups. The importance of some functional groups (acids and nitrates in particular) are discussed throughout the paper, but the relationship of these to AMS spectra are never discussed in anything but the broadest qualitative terms, which leaves open many questions about the comparison of "bulk" and "speciated" measurements.

For example, on p. 10319 the underestimate of nitrate-associated oxygen by the AMS is mentioned as a possible explanation for the low measured O/C values. This hypothesis is easy enough to test – what is the contribution of nitrate oxygen to the total measured oxygen, and how does this compare to that of the individual molecules? A similar treatment can also be done for all acid/ester groups (from m/z 44). The present manuscript lumps all organic oxygen together, thereby ignoring this potentially useful chemical data. Instead, I recommend that the authors calculate "nitrate oxygen", "acid oxygen", and "other organic oxygen", for AMS and FTIR data, and compare those to similar values for key molecular species when possible.

Additionally, the confounding roles of functional groups such as nitrates, peroxides, and organosulfates in the determination of elemental ratios of OA (and in the Van Krevelen plot) need to be discussed. In the analysis of ambient AMS data, most oxygen in organic nitrates (or sulfates, etc.) is not tabulated as "organic", so the O/C of ~1 for LV-OOA does not include contributions from these moieties. Yet nitrate oxygen is (partially) included in the O/C ratio measurement of the present chamber data; this risks an "apples and oranges" problem when comparing elemental ratios from chamber

and ambient data (e.g., Figure 9). Complicating matters even more, nitrate oxygen is fully included in the calculation of O/C for the molecular species and for the FTIR data. To what extent do such differences in the determination of O/C matter when comparing these various datasets?

(2) For the most part, differences between elemental ratios measured by the AMS and those of the marker compounds are attributed to the lack of mass closure in speciated measurements of SOA. This is certainly an important effect, but potential errors in the AMS measurements need to be explored and discussed also. Examples include:

- The O/C and H/C ratios are determined from AMS data by summing up the molar abundances of each element within a mass spectrum, and applying an empirical correction factor (determined by Aiken et al) to the ratios. The dataset used for to determine this factor was limited, and may not be representative of the components of the SOA examined in this study. The "correct" factors might vary for each system, changing the conclusions about differences in elemental ratios among different precursors, NOx conditions, etc. For example, it has been shown that the AMS tends to underestimate O/C ratios for polyhydroxylated species (Kessler et al., ES&T 2010, 44:7005–7010), suggesting that the low-NOx isoprene SOA (which is abundant in tetrols, and oligomers thereof) may have a much higher O/C ratio than determined in this study. Such uncertainties need to be discussed explicitly, and broad conclusions (such as those listed in the abstract) need to caveats such as "within the uncertainty of the AMS determination of elemental ratios...".

- As mentioned above, the authors state (p. 10319, lines 4-6) that the AMS probably undercounts oxygen from nitrate groups. This is brought up only within the context of the aldehydes, but it matters for all the high-NOx photooxidation experiments. (isoprene, pinene, etc.).

- Similarly the AMS probably does not measure both O's of a peroxide moiety – the O-O bond is substantially weaker than most O-N bonds, so hydroperoxides will dissociate

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to RO and OH radicals on the heater. The OH is not tabulated directly by the AMS "frag list"; so this oxygen is left effectively unmeasured. As a result, the O/C ratios measured by the AMS in all low-NOx photooxidation SOA (with high peroxide contents) may be substantial underestimates.

- Since both nitrates and hydroperoxides are probably measured as RO radicals in the AMS, one would expect the AMS to treat them similarly. Thus the agreement between results at high and low NOx may be largely because the AMS cannot detect these key functional groups well; this possibility should be mentioned.

(3) There needs to be more in the way of comparison between these results and ambient data (from Ng et al 2010), as well as between these results and previous chamber results. Most importantly the statement that there is "close agreement between the f43 and f44 values presented in Ng et al (2010) and those presented here" (P. 10320, lines 20-21) doesn't seem to be borne out by the data – most of the chamber data lie outside of the triangle defined by the ambient resulted compiled in Ng et al. (In fact, in Figure 9, the triangle is mostly empty, with the vast majority of the data lying outside of it!) While I understand the authors' point that ambient OA is a mix of many types of SOA, the assertion that the agreement is "close" is a bit of a stretch. Further, in Ng et al., most of the previous chamber data (which included several datasets from the same chamber used in this work) fell cleanly within the triangle. Why, for many of the same precursors, are the new data outside it (mostly with higher f43 than in the previous work)? Such differences need to be discussed.

Related to this, the final paragraph discusses the idea of ambient OOA as a mixture of SOA formed under different reaction conditions from many precursors; this is an important point, but I think this paragraph needs to be expanded substantially. How do the authors know they've found the "extremes"? Given how little we know about which precursors contribute to ambient OA, might there be other reactive systems that lead to SOA with (for example) even higher f43 than what was seen in this study? And, based on Figure 9, it would seem one would need something like a 50-50 mix of the

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"high-f43" and "low-f43" SOA to make anything that resembles ambient SV-OOA. Is it reasonable to think SV-OOA is made up of equal parts biogenic/monoaromatic SOA and naphthalene/glyoxal SOA? I think it's much more likely that a lot of SV-OOA is formed from precursors that are different from those covered in this study (whose SOA might fall cleanly within the triangle). The possibility of unknown precursors needs to be at least mentioned.

(4) The FTIR analysis and interpretation need to be discussed in much more detail. As written the paper is very unclear as to just how the elemental ratios were determined.

-To my knowledge the determination of hydrogen atom content (and therefore H/C) from FTIR data has not been discussed in the literature. Presumably each functional group is assigned a certain number of H atoms – but what are these numbers? (For example: does an "alkane group" have 1, 2, or 3 H atoms?) A table listing the numbers of each atom assumed per functional group (for H, C, and O) is needed.

- What do the "upper bound" and "lower bound" numbers for the elemental ratios mean? These ranges are shown as diagonal lines (rather than squares) in Figure 2 and 6, suggesting that the FTIR data indicate a narrow range of possible (co-varying) elemental ratios. How does this co-variation come about? Are the uncertainties from the functional group assignment/peak fitting, or from the number of each element per functional group?

- P. 10312, lines 14-16: This needs to be explained in more detail. What does "degree of saturation of other functional groups" mean? Alcohols and carbonyls lead to different degrees of saturation, but since these are distinguished in FTIR, I don't see why this weighting is necessary. Moreover, such a weighing probably isn't valid, since the degree of saturation is not conserved with oxidation. For example isoprene (which is doubly unsaturated) is known to form tetrols (which are fully saturated); similarly, terpenes and aromatics are well-known to lose C-C double bonds as well as undergo ring-opening upon oxidation.

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- P. 10312, lines 16-17: Does "hydrogen associated with amine groups" simply mean "N-H bonds"? (If so, calling these "amine groups" is confusing, since "amines" are by definition organic.)

- P. 10312, lines 18-22: Is this "incrementing" simply an increase of O/C by 3/7? Why does this affect H/C, as implied by the diagonal line in Figure 6? In any case this value seems to be based on a major assumption about the product distribution, so it is hard to see how this is in any way an "upper limit" to the data.

- P. 10312, line 22: What is the relevance of this statement? How would the presence/absence of ether groups affect the analysis, and why is this only mentioned for a-pinene? Ethers are in fact possible: they form from alkoxy radical isomerization, which could be an important process in the reaction of OH + first generation pinene oxidation products (Lim and Ziemann, Environ. Sci. Technol. 2005, 39:9229-9236).

(5) In the abstract, and again in the conclusions, it is mentioned that methoxyphenols form the "most oxidized aerosol", with O/C ratios similar to LV-OOA. As noted, this is largely a result of the fact that methoxyphenols are also the most oxidized precursors (the unsaturated aldehydes, which are also quite oxidized, form highly oxidized SOA as well). Given this, it might be useful to tabulate and discuss how the CHANGE in degree of oxidation (O/C, H/C, OSc) depends on precursor type. How do these changes vary with carbon skeleton, carbon number, etc?

Other points:

Figures 2-9: In general these figures are a bit hard to read, with sparse data in panel (A) and many more data points, as well as chemical structures, in panel (B). Readability would be helped if, instead of legends, panel (A) included the structure and name of the precursor molecules, drawn in the same color as the corresponding data points.

P. 10306, line 7: mention these are from the AMS data.

P. 10306, line 8: the triangle plot (like the Van Krevelen diagram) is not a "model" but

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rather a visualization tool.

P. 10310, line 1: this sentence is written as if this disconnect in the degree of oxidation between chamber and ambient studies is a new result from 2010; but it was known well before that. I would recommend bringing in older references as well.

P. 10311, line 21: Nitric acid is certainly too volatile to condense, but ammonium nitrate (formed by the reaction of HNO3 with background ammonia) still might be a concern. To bracket this effect, what is the ammonium mass concentration (as determined from high-resolution analysis of the m/z 15-18 ions)?

P. 10313, line 27 (and p. 10321, line 23): since the discovery of oligomers, etc. in SOA (which are believed to degrade during derivatization/GC analysis), this ">90%" figure probably isn't accurate.

Moreover, if one applies the same logic used in the isoprene case – that oligomerization will tend to move the molecules down and to the left in Van Krevelen space - then the agreement between AMS and speciated data actually becomes worse. Many of the molecules shown are believed to oligomerize, via the same mechanisms important in isoprene, so the "center of gravity" of these molecules would also move down and to the left, away from the AMS data. This needs to be discussed.

Figure 2: This figure is particularly hard to read – the speciated points really obscure the AMS data.

Figures 2 and 4: The oxidized species measured by Edney et al. (Atmospheric Environment 2003, 37 :3947–3965) and Kleindienst et al. (Journal of Atmospheric Chemistry 2004, 47:79–100) should also be included here.

P. 10315, line 22: "decreased" may be a better word than "suppressed".

P. 10315, line 23: "Monoaromatic" may be a better term than "single-ring aromatic".

P. 10316, first full paragraph (and Figure 4B): I think it's worth noting here that most of

the identified molecular products are quite volatile, and so probably arise from degradation of condensed-phase molecules upon aerosol collection/workup/analysis. As in the isoprene case (Fig 3) the molecules above the AMS data in Van Krevelen space are probably monomers that make up larger oligomeric species, which would be located lower down (closer to the AMS data). Similarly, the molecules below are largely acid anhydrides, and may be dehydrated versions of polyfunctional acids, which would be located higher up (again, closer to the AMS data).

p. 10316, section 3.4: it should be mentioned here that the precursor (naphthalene) starts out already very low in H/C, which likely explains its unique position in the two plots.

P. 10320, lines 14-15: I don't understand the assertion that "aldehydes are not large enough to support continued oxidation". Small molecules can react with OH almost as fast as big ones (and in fact product formation can involve larger changes in O/C as a result of the small carbon numbers). Do the authors instead mean that any more oxidation and the molecules will start falling apart?

P. 10321, lines 7-8: This needs to be explained/worded better. In this paper I've assumed "High-NOx" and "low-NOx" are operationally defined to mean the HONO and H2O2 experiments, respectively. In that context this sentence is a bit tautological. Are the authors referring to shifts in the RO2 chemistry?

P. 10321, lines 16-18: -OH and –OCH3 are actually electron donating groups (more strongly activating than –CH3 groups). What's the explanation for the difference in f43?

P. 10322, line 9: what does "a y-intercept within the range of SOA precursors" mean? More importantly, why would one even consider a precursor (which is in the gas phase) when discussing the Van Krevelen slope of organic particulate matter? The authors need to discuss slopes without taking into account the precursor.

At the same time, some discussion of the relationship between the position of the initial

precursor and the position of the SOA would be helpful. Going from precursor to the aerosol, O/C obviously always goes up, but the change to H/C varies from precursor to precursor. H/C will generally go down with oxidation, but it will increase when OH is added to double bonds (and when HO_2 reacts with RO_2) – is this consistent with the data?

On this note, given the general interest in the interpretation of these slopes, a table with slopes (and other fit parameters) for each precursor would be a valuable addition to this paper.

Table S1: The CO^+/CO_2^+ ratios seem to be at odds of those from another recent study (Chen et al., ES&T 2011, dx.doi.org/10.1021/es104398s). The authors should comment on this difference, and discuss implications of (errors associated with) this uncertain parameter.

Captions, Supplementary Figures 1-7: These aren't really high-resolution spectra; there unit-mass-resolution spectra, broken down by elemental composition (by mass) according to high-resolution analysis.