**Atmospheric
Chemistry
and Physics
Discussions**

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

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Received and published: 13 July 2011

Response to Referee 1

The authors would like to thank the reviewer for the careful review and helpful comments to our manuscript. We have prepared responses to each of the concerns and questions, which are listed below. The referee's comments are in italics, followed by the authors' responses. Changes to the manuscript are shown in bold type.

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 ni-

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trates 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.

R1.1. 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.

The reviewer makes a good suggestion. We have added an additional section that discusses the contribution of organonitrate groups and acid groups to the total oxygen content of SOA as determined by AMS, FTIR and speciation techniques. We have also added a second table to the manuscript tabulating these contributions, shown here as Table R1. Additionally we have added points to Figures 2 and 5 representing the average O/C and H/C of data presented in Jaoui and Kamens (2001) and Kautzman et al. (2009), respectively. We have revised the manuscript as follows:

P. 10313, line 27: "The species identified by Yu et al. (1999) are represented in Panel B by gray squares **and closely agree with** AMS data.

P.10314, line 4: New paragraph at "Many of the same products. . ."

P.10314, line 7: ". . .particle-phase products accounted for approximately 20% of the reacted carbon. **Using their particle-phase carbon yields, we calculate an average H/C and O/C ratio of 1.56 and 0.36, closely agreeing with AMS measurements but slightly higher than those measured from FTIR analysis.**"

Since the publication of Yu et al. (1999) and Jaoui and Kamens (2001), several studies have identified oligoesters of α-pinene photooxidation and ozonolysis products in the particle phase (Gao et al., 2004; Muller et al., 2008; Hall et al., 2011). Gao et al. (2004) and Hall et al. (2011) have estimated oligomers to account for 50% of α-pinene SOA mass. It is possible that sample work up in speciation studies hydrates oligomers, separating them into the identified monomers and moving them up the Van Krevelen diagram along a line of slope 2. The original oligomers would reside further to the bottom left of the Van Krevelen diagram. As speciation of oligomers improves, the effect of oligomerization on SOA elemental composition can be better constrained."

P. 10316 line 17: "AMS measurements indicate SOA that is less oxidized than the structures would suggest. **However many of the small acids and carbonyls towards the top of the figure are quite volatile and could represent monomers that have hydrated due to sample analysis. Similarly compounds towards the bottom left of the figure are anhydrides that may have formed from sample work up. This could explain the divergence from AMS data in the Van Krevelen diagram manifested as movement up or down along a line of slope 2.**"

P. 10317, Section 3.5 Second and third paragraphs have been revised as follows: "**Proposed structures of detected SOA products from guaiacol photooxidation are indicated in the Van Krevelen diagram (Fig. 6, Panel B). AMS measured elemental compositions of SOA generated under high and low-NOx regimes generally agree with the proposed compounds formed under low-NOx conditions but have higher H/C ratios than those of compounds formed under high-NOx conditions. It is possible that the UPLC-MS techniques generally used in conjunction with filter sampling is biased to detect the high-NOx compounds shown, compounds with lower H/C ratios. It is also possible that much of the SOA mass remains unmeasured by the UPLC-MS techniques as much of the SOA could be in the form of small ring opened products (and their oligomers) such as those**

measured in monoaromatic SOA. This is supported by the large contribution of oxygen in CO2+ (and other associated ions) in high-resolution AMS spectra as will be discussed in Section 3.8.

The FTIR elemental analysis underestimates the O/C as compared to AMS elemental analysis. This maybe the result of the O/C constraint (as described in the Supplemental Material) that is used to parameterize guaiacol SOA changing with oxidation. It is likely that parameterization of methoxyphenol SOA lies somewhere between the ambient case and the precursor specific case."

P.10319, line 1: "The elemental composition of the limit of a linear oligomer is represented by a circle and approaches the AMS measurement suggesting that the AMS measurement is that of a highly esterified compound rather than individual monomers. **As in the isoprene case, the lower O/C ratios measured by the AMS is likely due to the inability of the AMS to efficiently detect oxygen in an organic nitrate group (Farmer et al. 2010; Rollins et al. 2010) as is discussed in Section 3.9.**

P. 10321 Line 19: Table 2 shows that while nitrate and acid groups contain much of the oxygen in oxidized SOA, a similar fraction remains in other ions such as C2H3O+ at m/z 43. More work needs to be done to quantify these non-acid, non-nitrate oxygenated functionalities and determine how they fragment to form AMS spectra.

P.10319 "Section 3.8 Oxygen Contribution in Organonitrate and Acid Functional Groups

Having measurements of the chemical composition of oxidized SOA from different analytical techniques allows for a rich comparison of the oxygen contribution from different functional groups. Table 2 summarizes the fraction of oxygen originating from organonitrate and organic acid functionality in SOA formed at the end of oxidation experiments as determined by AMS, FTIR and speciation techniques. The oxygen contribution to organic acids groups in high-resolution AMS

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data was calculated by determining the total oxygen mass measured at CO2+ as well as those ions dependent on the CO2+ signal through the fragmentation table, O+, HO+, H2O+, and CO+ (Aiken et al., 2009). The oxygen contribution to organic nitrate groups in AMS data was determined from the total oxygen contribution at NOx family ions, NO+ and NO2+. Oxygen contribution in acid and nitrate groups are calculated from FTIR measurements by multiplying the measured functional group mass by the mass fraction of oxygen in the group. Contributions of oxygen in speciation studies are calculated similarly but on a species basis.

Table 2 shows that the FTIR, AMS and speciation techniques find that naphthalene and methoxyphenol systems have the greatest fraction of total SOA oxygen in organic acid groups. High-resolution AMS data find that 65-72% of oxygen signal can be found at acid associated ions in naphthalene SOA formed under high and low-NOx conditions, respectively. This is in fair agreement with Kautzman et al. (2009) who found 73-81% of speciated oxygen is contained in acid groups. Further investigation of the AMS data of naphthalene high-NOx SOA shows that at the peak of SOA growth, the acid-oxygen contribution is only 41% while the nitrate-oxygen contribution is 22%. As oxidation continues, the contribution of nitrate-oxygen decreases significantly to 6% while the acid fraction increases to 65%, as listed in Table 2. These observations are supported by the data and structures in Figure 5. SOA formed under both conditions exhibit a steady increase in f44 in Panel A and structures in Panel B are overwhelmingly acid while the nitronaphthalene compounds appear at lower O/C ratios corresponding to lower irradiation times. It is possible that under high-NOx conditions, nitronaphthalene compounds are formed initially but react further to remove nitrogen functionality and add acid functionality. FTIR and AMS data also find significant contributions of oxygen in acid functional groups in guaiacol SOA and relatively small fraction of oxygen in nitrate groups. As was mentioned in Section 3.5, much of the SOA could be in the form of small ring-opening products that are

typically difficult to separate and identify using UPLC-MS techniques.

In contrast, FTIR and AMS high-resolution data measures significantly less oxygen in acid groups than what was determined from the characterization performed by Yu et al. (1999) and Jaoui and Kamens (2001) for the α-pinene SOA systems. The greatest discrepancy occurs for photooxidation SOA where 31 to 40% of the AMS measured oxygen occurs at acid associated ions while Jaoui and Kamens (2001) find the fraction of oxygen in acid groups to be 70%. However, Jaoui and Kamens (2001) do not identify any organonitrates compounds. If the contribution of nitrate-oxygen is removed in FTIR and AMS data, the comparison improves; the FTIR and AMS acid-oxygen contributions become 50% and 36%. It is possible that organonitrates may have gone undetected in the characterization performed by Jaoui and Kamens (2001) either through loss in sample work up or poor sensitivity in the GC-EIMS technique used.

The AMS measures a greater contribution of oxygen in acid associated ions for isoprene SOA formed under low-NOx conditions than under high-NOx conditions. This can be explained by the abundance of methyl glyceric acids and oligoesters detected in high-NOx SOA as opposed to the tetrols and polyols in low-NOx SOA. In high-NOx SOA spectra, nitrate ions contribute 8% of the total oxygen signal while nitrate groups in the structures depicted in Figure 3, Panel B exhibit a much larger nitrate contribution. This is possibly explained by the inability of the AMS to fully detect oxygen in organonitrates compounds, as is discussed in Section 3.9. This would also explain the low contribution of oxygen in nitrate ions for the spectra of unsaturated aldehyde SOA. High-resolution AMS spectra exhibit an acid-oxygen contribution of 37-50% and a nitrate-oxygen contribution of 10-14% for monoaromatic SOA. While the oxygen fraction in nitrate ions decreases slightly over time, it still represents a significant contribution to the measured AMS O/C. It is possible that organic nitrogen is present in particle phase ring opening products that are not easily separated or identified through

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offline methods more work needs to be done to characterize aromatic SOA and determine what effect sample preparation and analysis can have on the measurement.

R1.2. 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?

The reviewer is correct in noting that in ambient data sets, nitrate is generally considered inorganic and therefore NOx family ions (NO+ and NO2+) are not included as part of the organic elemental analysis, possibly leading to underestimation of ambient SOA O/C values. The manuscript has been revised as follows.

Section 3.9 AMS analysis uncertainty

Much of the uncertainty in AMS analysis data can be attributed to the treatment of organonitrate compounds. In ambient data sets, nitrate is generally considered inorganic and therefore NOx family ions (NO+ and NO2+) are not included as part of the organic elemental analysis, possibly leading to underestimation of ambient SOA O/C values. Farmer et al. (2010) estimated that for the Study of Organic Aerosols in Riverside (SOAR-1) ambient campaign, organonitrates contribute 5-10% of the total nitrate mass, though do not dominate AMS nitrate spectra. In the analysis of high-NOx chamber experiments in which the humidity

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is too low for nitrate acid to appreciably partition to the particle phase, categorizing NOx family ions as organic is an appropriate assumption to make. However, even when NOx family ions are included as part of the total organic mass spectra, their oxygen contribution tends to be underestimated due to the inability of the AMS to detect the nitrogen-bonded oxygen in the –ONO2 group (Farmer et al., 2010; Rollins et al., 2010). This may also occur for peroxides formed under low NOx conditions; upon fragmentation the RO-OH bond can sever leaving the OH fragment effectively undetected. This maybe a reason why SOA formed under different NOx regimes have similar elemental compositions. On average, inclusion of NOx family ions to the organic spectra increases the O/C ratio of the systems studied by 0.05, with m-xylene SOA having the largest difference of 0.10 and crotonaldehyde having the smallest difference of 0.02. These contributions also tend to decrease as a function of experiment time. Thus, the relative formation of organonitrates is precursor and time dependent and, therefore, so is the contribution of NOx family ions to the O/C. However, these differences still fall within the uncertainty reported by Aiken et al. (2008). Organonitrate oxygen is included fully in the calculation of O/C for speciated measurements. However, the detection and quantification of organonitrate compounds is again system dependent. Despite these limitations, we still see that for systems in which SOA can be chemically characterized well, the AMS and average speciated O/C agree. As detection and quantification techniques of organonitrates improve, more robust comparisons between measurement techniques can be achieved, and the contribution of organic nitrogen to ambient SOA can be better constrained.

Another source of uncertainty is the calibration factors and fragmentation table ratios used to correct for ionization biases in AMS spectra and air contamination. The applied correction factors are based on a limited set of standards and have an inherent uncertainty (Aiken et al. 2008). As was discussed by Chhabra et al. (2010), these standards are large alkanols, alkanoic acids, and aromatic species that are similar to those detected in α-pinene and naphthalene SOA. By

contrast, few of the standards have structures similar to species found in isoprene and aromatic SOA like polyols and small acids. Kessler et al. (2010) has shown that for polyhydroxylated species, the default correction factor for O/C underestimates O/C.

There is also uncertainty in the AMS fragmentation table particularly when determining the relative contribution of CO+, H2O+, and CO2+ ions in high-resolution spectra. As shown in the supplemental section, the ratio of organic CO+ to CO2+ was found to be close to unity, the default fragmentation wave value based on Aiken et al. (2009), so this value was used. In a study by Chen et al. (2011), researchers determined fragmentation ratios much different than those measured by Aiken et al. (2008) for the isoprene low-NOx photooxidation system. Using those ratios to calculate O/C ratios for the low-NOx isoprene SOA system presented here increases the O/C by 57%. More work is needed to constrain these ratios in both ambient and chamber environments.

P.10321-10322 End paragraph at: "Conversely, in systems for which mass closure has been difficult, such as monoaromatics, AMS and filter data do not agree."

R1.3. 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., EST 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. . ."

The reviewer is correct in noting that the applied correction factor is based on a limited set of standards and has an inherent uncertainty. We discuss the uncertainty of these calibration factors in Chhabra et al., (2010) as this manuscript is continuation of that work (P. 10314, line 3). We have changed the manuscript as shown above and as follows to briefly discuss the errors associated with AMS analysis:

P. 10306, line 20: "α-pinene ozonolysis and naphthalene photooxidation SOA systems have had the highest degree of mass closure in previous chemical characterization studies and also show the best agreement between AMS elemental composition measurements and elemental composition of identified species **within the uncertainty of the AMS elemental analysis.**"

P. 10313, line 3 has been removed and the following has been added to Experimental Section 2.2: **"Raw measurement of elemental ratios requires calibration factors derived from the elemental analysis of laboratory standards. The calibration factors determined by Aiken et al. (2008) of 0.91 for H/C and 0.75 for O/C. were used The uncertainty estimates of the calibration factors reported by for O/C and H/C are 31% and 10% respectively. Uncertainty in AMS elemental analysis and offline speciation is discussed in detail in Chhabra et al. (2010)."**

P. 10321, line 20: "The Van Krevelen diagrams of the elemental composition of individual SOA systems reveal that elemental ratios measured by the AMS agree most closely with SOA systems for which the greatest degree of mass closure has been achieved, **within the uncertainty of the AMS analysis.**"

- 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 OO bond is substantially weaker than most O-N bonds, so hydroperoxides will dissociate to RO and OH radicals on the heater. The OH is not tabulated directly by the AMS "fraglist"; 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.

R1.4. 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.

We have changed the manuscript as follows to address the aforementioned points in R1.2.

R1.5. 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.

The reviewer makes an important observation regarding the differences between the areas occupied by chamber SOA reported in Ng et al. (2010) and those reported here.

The SOA systems that are investigated in both studies, and therefore can be legitimately compared, are α-pinene ozonolysis (Figure R1), α-pinene photooxidation (Figure R2), isoprene photooxidation (Figure R3), m-xylene photooxidation (Figure R4), and toluene photooxidation (Figure R4). Figures R1 and R2 compare the "triangle plot" data for α-pinene systems. We find fairly good agreement between f43 and f44 data presented by Ng et al. (2010) and those presented here given the absolute 2% uncertainty in f43 and f44 observed for UMR Q-AMS laboratory spectra (Ng et al. 2010). In particular there is excellent agreement between ozonolysis data from the highest loading experiment in Shilling et al. (2009) and those of this study. Isoprene SOA presented by Ng et al. (2010) exhibits a wide range of f43 and f44 values and occupies area both inside and outside the triangle plot. Values of f43 and f44 of high-NOx isoprene SOA spectra are in good agreement given the 2% uncertainty. The largest discrepancy is for low-NOx spectra. Loading differences between the high-NOx isoprene experiments spectra in Ng et al. (2010) and those presented here may be the reason for the different f43 and f44 values. It is the toluene and m-xylene SOA experiments that show the greatest disparity in f43 while in agreement for f44. A possible cause for the difference in spectra could be loading dependence. Figure R5 shows that f43 tends to increase with organic loading (Shilling et al., 2009) and the experiments presented in this manuscript had high loadings. Closer investigation into the spectra of toluene and m-xylene SOA show that the enhanced f43 is offset by lower signals of masses smaller than m/z 43, particularly f29, f15, and f12 (Figure R6). It is also possible that differences in heater temperature could have affected the fragmentation pattern and that certain systems like aromatic SOA could be more susceptible to this difference than α-pinene systems due to higher f43 values. In general, the authors still believe that there is significant agreement between the f43 and f44 values presented in Ng et al (2010) and those presented here. P. 10320, lines 20-21 are modified as follows.

We find general agreement between the f43 and f44 values presented in Ng et al. (2010) and those presented here for the traditional set of SOA systems:

monoaromatics, α-pinene, and isoprene SOA. Possible descrepancies in cases where f43 and f44 differ by more than 2% are possibly due to differences in organic loading, which have the tendency to increase f43 (Shilling et al. 2009), or differences in heater temperature leading to small differences in spectral signals at low m/z.

R1.6. 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 "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.

The authors are in agreement with this comment and it may have been unclear what we meant by "extremes". We do not claim our data represent the spectral extremes of chamber or ambient SOA as the complete set of SOA precursors is far from being known. Instead it was in reference to the extremes of the "triangle plot" as presented by Ng et al. (2010) as a visual depiction of changing SOA spectra with age. The reviewer is absolutely correct that SV-OOA and LV-OOA are formed from known (and likely many more unknown) SOA precursors that individually could fall outside the triangle or within it, but when taken as whole form the shape in Ng et al. (2010). Recently work by Lee et al. (2011) show that oxidized solutions of pinonic acid, glyoxal, and SOA from laboratory and ambient sources map out a larger triangular area than what

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was depicted by Ng et al. (2010) and that mixing aerosol sources also mixed their spectral signals. Additionally, Lambe et al. (2011) showed that the "triangle plot" could be expanded with Potential Aerosol Mass (PAM) measurements and that systems that individually lie on the edges of the triangle could be mixed to form SOA that falls in the center of the triangle. The manuscript has been revised to include this discussion as follows:

P.10322, line 28. "The SOA spectra lying on the boundaries of the triangle do not mean that they are not representative of ambient spectral components **nor do they represent the spectral extremes of chamber or ambient SOA** as the complete set of SOA precursors is far from being known. Rather this SOA lies along the outlines of the triangle depicted by Ng et al. (2010). Ambient spectra and components falling within the triangle represent the ensemble average of many different SOA precursors and oxidative processes that mix spatially and temporally. And as SOA becomes more oxidized, it loses its source history. **Recently, work by Lee et al. (2011) show that oxidized solutions of pinonic acid, glyoxal, and SOA from laboratory and ambient sources map out a larger triangular area than what was depicted by Ng et al. (2010) and that mixing aerosol sources also mixed their spectral signals. Additionally, Lambe et al. (2011) showed that the "triangle plot" could be expanded with Potential Aerosol Mass (PAM) measurements and those systems that individually lie on the edges of the triangle could be mixed to form SOA that falls in the center of the triangle."**

R1.7. 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.

The manuscript is revised as follows:

P. 10312, Line 10: "FTIR O/C and H/C ratios were determined from measured organic bond absorbances by calculating the estimated moles of oxygen, carbon,

and hydrogen associated with each measured bond and its associated functional group, as described in the Supplemental Material (Russell et al., 2009; Russell, 2003). Since alkene groups were below detection, an upper bound was considered to be their detection limit and a lower bound was considered zero. The degree of saturation for other functional groups was weighted by the saturation in the reactants (α-pinene and guaiacol). Hydrogen associated with amine groups was omitted since it is assumed that any ammonium is part of the inorganic seed rather than SOA."

R1.8. 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.

The Reviewer is correct in noting that this is the first time that H/C has been explicitly calculated, however, as the H was included in the organic functional group mass in previous calculations, there actually is no new assumption required per se here. As the organic functional group mass (and hence the H/C calculation) has never been applied to smog chamber products, there are a few issues worth discussing explicitly. Consequently we have added to the supplemental material the calculations and assumptions used in determining elemental ratios from FTIR-measurements, explicitly expressing the uncertainty as a function of a parameter ϕ. A table containing the C, O, and H atom apportionment to each FTIR-measured functional group is included for added clarity.

R1.9. 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?

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The co-variation is the result of both H/C and O/C depending on the number of functional groups per carbon used in the calculation of the associated number of carbon atoms (which appears in both denominators but affects the numerators differently). This arises because FTIR absorbance is proportional to bonds, rather than mass, and the number of (non-carbon) bonds per molecule varies with the structure. For ambient aerosols the simplistic assumption that on average there are 2 organic functional groups per carbon atom (ϕ=0.5) provides a conservative lower estimate of OM and a reasonably accurate estimate of longer organic chains that has been shown to contribute to ambient aerosol (Russell, 2003). This value is consistent with a <5% error for C10 and longer alkane chains, which are expected to result from ambient alkane emissions as well as products from unbranched aromatics after unsaturated bonds have been removed by oxidation. In the Discussions version of the manuscript we included calculations using a ϕ consistent with the precursor. In H/C vs. O/C space, using these two values of ϕ results in a diagonal line. This range overestimates the uncertainty of H/C and O/C because the ambient/alkane ϕ values are clearly not appropriate (this would be akin to using the wrong AMS fragmentation table). Thus in the revised version of the manuscript we have only included elemental ratios calculated using the precursor specific ϕ, however in the supplemental section elemental ratios using both ϕ values are provided for comparison.

R1.10. 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.

We have changed the term "degree of saturation" to "number of organic functional

groups (or non-carbon bonds) per carbon atom."

R1.11. 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.)

The primary amine measured by FTIR is $C-NH_2$ bonds. The "hydrogens associated with amine groups" is referring to the hydrogen in the $C-NH_2$ bonds. Thus, the hydrogen associated with amine groups are omitted in the H/C calculation for comparison with the AMS. However, the C in the $C-NH_2$ groups is retained, as would be the case for the AMS. To clarify this distinction we have included a table in the supplemental material that includes carbons as part of an "amine group" and we specify that it is only the hydrogens (rather than the carbons) that are excluded.

R1.12. 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.

The addition of 3/7 to the O/C is not related to the correction by ϕ, and has been applied to both extremes of the diagonal line, shifting the diagonal line to the right on the O/C axis. This 3/7 correction is an upper bound on the effect on the O/C of OFG that are missed by FTIR, namely ethers. The value 3/7 is now explicitly explained in the appendix.

R1.13. 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).

While ethers are possible from alkoxy radical isomerization, the identification and quan-

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tification of ethers in SOA from α-pinene oxidation has yet to occur (Jaoui and Kamens 2001, Winterhalter et al., 2003, and Szmigielski et al. 2007). Since α-pinene does not contain ether groups nor do any of the products identified in this work, we do not add a correction. Conversely, guaiacol itself contains one ether group, has been found to be relatively unreactive, with minimal atmospheric destruction from photolysis and ozonolysis (Calvert and Pitts, 1966, Atkinson and Carter, 1984). The ether bond in guaiacol is retained within several of the guaiacol oxidation products proposed. Due to the low reactivity of ether bonds under these conditions, we chose to include a correction factor (3/7) for the O/C elemental ratio in the extreme case of the guaiacol experiments to account for missing ether and peroxide bonds (due to interference from Teflon (C-F) absorption).

R1.14. (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?

We have tabulated ΔO/C, ΔH/C, and ΔOSc in the Supplemental Material and have included the following discussion.

P. 10321, New paragraph at line 20: **"Figure 9, Panel B demonstrates that change in elemental composition that occurs from SOA precursor to SOA is a function of the precursor identity and structure. α-pinene ozonolysis SOA exhibits the smallest change in O/C because ozone is only reactive to alkene functionality, and once the double bond in α-pinene has reacted, the potential for aging through ozonolysis is halted. OH radicals will react with saturated aliphatic carbon but to a much lesser extent than alkene functionality so further oxidation is dramatically slowed. Aromatics, however, show much greater potential for in-**

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creases in O/C because aromaticity allows many more oxidative steps starting with OH attack to bicyclic radical formation, to ring cleaving. Both naphthalene and phenol undergo large changes in O/C as the unsaturated rings add oxygen. In the case of naphthalene, H:C remains low because OH cleaves on ring at a time leaving one aromatic ring intact. For phenol, the H:C is higher due to the fact that the monoaromatic ring opens allowing for OH radicals to saturate double bonds."

R1.15. 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.

The reviewer's suggestion is noted. We have removed the legend in Panel B since the legend in Panel A is sufficient to distinguish the NOx regime of the AMS data. In the revised manuscript, figures will be larger and easier to read.

R.1.16. P. 10306, line 7: mention these are from the AMS data.

Fixed.

R1.17. P. 10306, line 8: the triangle plot (like the Van Krevelen diagram) is not a "model" but rather a visualization tool.

Fixed

R1.18. 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

We have added the following references:

Rudich et al. "Aging of Organic Aerosol: Bridging the Gap Between Laboratory and

Field Studies" Annu. Rev. Phys. Chem. 2007. 58:321-52.

Kroll and Seinfeld. "Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere." Atmos. Environ. 2008. 42:3593-3624.

R1.19. 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)?

In high-NOx experiments in which ammonium sulfate seed is added prior to irradiation, the ammonium concentration is typically 1.5 ug/m3 and decreases slowly due to wall loss. In these experiments the amount of NH4 is in stoichiometric proportion to sulfate. In the high-NOx phenol experiment, no ammonium sulfate seed was added and upon SOA formation, about 0.1 ug/m3 of NH4+ is formed; this would result in approximately 0.34 ug/m3 of NO3-.

R1.20 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.

The manuscript has been revised as shown in R1.1 above.

R1.21. Figure 2: This figure is particularly hard to read – the speciated points really obscure the AMS data.

In the revised manuscript, the figure will be enlarged to make it clearer.

R1.22. 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.

They have been added and referenced appropriately.

R.1.23. P. 10315, line 22: "decreased" may be a better word than "suppressed".

Fixed

R1.24. P. 10315, line 23: "Monoaromatic" may be a better term than "single-ring aromatic".

We have changed all instances of "single-ring aromatic" to "monoaromatic"

R1.25. 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).

This has been addressed in R1.1

R1.26. 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.

This has been addressed in R1.14

R1.27. 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?

Yes we are referring to the fact that due to the size of the precursor, only about 2 generations of photooxidation can occur before the carbon skeleton fragments. This has been made clearer in the manuscript.

R1.28 .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?

Yes, the authors are referring to changes in RO2 chemistry as a function of NO concentration. We have changed the lines to read: **"Methacrolein, a gas-phase product and major SOA intermediate of isoprene photooxidation that forms when the isoprene hydroxyperoxy radical reacts with NO, yields SOA with f43 and f44 values just beyond those of isoprene SOA range. It is likely that isoprene SOA formed under high-NOx conditions falls short of methacrolein SOA in the "triangle plot" because the isoprene SOA would also include products that form from RO2-HO2 reactions that occur at lower NOx concentrations."**

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

The reviewer is correct in noting that –OH and –OCH3 are electron donating when in resonance structures. This has been fixed. The authors speculate that the methyl group(s) in toluene and m-xylene form part of the C2H3O+ ions when the SOA is ionized in the AMS. More work is needed to better understand the fragmentation that occurs in the ionizing region of the AMS to form these ions.

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)

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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 HO2 reacts with RO2) – 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.

The authors have decided not to include slope and intercept data for the systems studied because many of the systems do not encompass a large range of H/C or O/C ratios, thus yielding large uncertainty in the fit parameters.

The manuscript has been revised as follows:

P. 10322 Line 7; **"From Fig. 9, Panel B, for the set of SOA systems on the Van Krevelen diagram tend to map a slope shallower than -1.** Aging pathways on the Van Krevelen diagram. . ."

Table S1: The CO+/CO2+ ratios seem to be at odds of those from another recent study (Chen et al., EST 2011, dx.doi.org/10.1021/es104398s). The authors should comment on this difference, and discuss implications of (errors associated with) this uncertain parameter.

The manuscript has been revised as shown in R1.2.

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.

Fixed

Response to Referee 2

The authors would like to thank the reviewer for the suggestions to our manuscript. We have prepared responses to each of the concerns and questions, which are listed below. The referee's comments are in italics, followed by the authors' responses. Changes to the manuscript are shown in bold type.

R2.1. My main concern is that several interesting observations were done for specific VOC systems but such complexity is not adequately acknowledged in the abstract and in the conclusions of the paper where the Authors tend to emphasize only common behaviours. For instance, a highlight was the fact that the fraction of organic acids (f44) tends to increase with ageing (Abstract, line 17 – 18), but this tendency is actually shown to very different extents by the specific SOA types: naphthalene > monoaromatic HCs   isoprene > alpha-pinene > carbonyls. For the latter, the migration of the functional group composition in the f44 vs. f43 space is very modest or absent. Therefore, stating that precursor structure determines the functionality only at the "starting point" on the triangle plot and that spectral uniqueness is lost with ageing (Conclusions, page 10322, lines 20 to 24) is not an appropriate summary of the observations.

The author is correct that the aging presented here is largely precursor specific. In our study we find that individual SOA systems age different amounts in the chamber and the path taken on the triangle plot varies based on the precursor identity. However, our data support the finding of Ng et al. (2010) that the average trend is to migrate towards the pinnacle of the triangle as the oxygen content of SOA increases as opposed to diverging from the "triangle plot." In responses R1.1 and R1.14, we have greatly expanded the discussion of the complexity of AMS spectra and elemental analysis as a function of precursor. We have also revised the discussion as provided in R1.6.

R2.2. Indeed, Figure 9 highlights that the functional group and elemental compositions of SOA are dependent on the identity of the SOA precursors irrespectively of ageing. This is in a quite sharp contrast with the results reported in the paper by Lambe et

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al. (ACPD, 13617-13653, 2011), still in review, which show that under more oxidizing conditions the "migration" of the SOA composition across the f44 vs. f43 space occurs to a much larger extent than presented in this study.

We state on P.10322, line 20 that "Figure 9, Panel A shows that precursor structure and functionality determine the *'starting point'* on the triangle plot and that the path taken is largely dependent on the identity of the SOA precursor." We agree with the reviewers point here and in R2.3 that the higher OH exposure in the PAM experiments of Lambe et al. (2011) allows for greater exploration of the f44 and f43 space. This is not in conflict with our point which is that at lower OH exposures and at oxygenation levels of SV-OOA, there is greater variation in f43, dependent on the precursor identity and that as the oxygen content of SOA increases, the spectral data tends to converge to the pinnacle.

R2.3 The Authors are encouraged to express their opinion on the actual importance of OH exposure of SOA particles in standard reaction chamber experiments on the observed formation of organic acids. This is an important point, because the Authors acknowledge that the conditions of chemical ageing reached in the chambers cannot fully reproduce the atmospheric processing, but at the same time they tend to convey the message that the organic oxidation states observed in a suite of laboratory experiments can be adequate to account for the variability in the real atmosphere provided that a sufficient number of gaseous precursors are considered.

We have revised the manuscript as follows:

P.10321 line 1 "...OH exposure is the limiting variable in SOA oxidation. The OH exposure for the photooxidative experiments vary from 1 to 2x109 molec cm-3 min which is equivalent to approximately 1-2 days in the ambient atmosphere. In contrast, Lambe et al. (2011) report minimum and maximum OH exposures of 1x1011 and 2x1011 molec cm-3 s, respectively, for Potential Aerosol Mass (PAM) flow tube experiments, corresponding to 1 to 23 days in the ambient atmosphere.

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The much higher OH exposures allow Lambe et al. (2011) to start with SOA at the bottom of the "triangle plot" and move all the way to the top. While f44 has the ability to increase significantly in chamber experiments (naphthalene for example), movement from the bottom of the triangle with a single precursor is not possible with the smaller OH exposures. To account for this, already oxidized precursors can be used as surrogates for creating highly oxidized SOA."

P.10321 line 8 "In the extreme case, methoxyphenols, effectively a continuation of naphthalene SOA, are subject to multiple oxidation steps on an already oxidized compound, leading to O/C ratios that approach unity."

R2.4. The Authors must support their conclusions by providing examples of environments where an appropriate mix of SOA from different precursors (the "extremes" of page 10323 line 2) can be found.

The Authors are not aware of any published ambient data which show two different air masses that reside near opposite edges of the "triangle plot" and that when mixed, the result is spectra in the middle of the triangle. There are laboratory data that clearly show that mixing two SOA precursors, each on different sides of the triangle, produces SOA that resides in the middle of the triangle. Lee et al., (2011) shows this with aqueous mixtures of glyoxal and pinonic acid of various concentration ratios, and Lambe et al. (2011) shows this with a mixture of α-pinene and naphthalene SOA in a PAM flow reactor. We have added discussion of this to the manuscript (R1.6).

R2.5. I have another major comment: FTIR data, in the way they are presented here, are not of any use for the discussion and conclusions. FTIR functional group distributions can be very informative and directly compared to the AMS functionalities in the f44 vs. f43 space, whereas here the Authors have tried to squeeze the FTIR compositions into the Van Krevelen domain in spite of the large uncertainty on the H:C dimension. This is a pity because the functional group data provided by FTIR analyses could be exploited to extract information on the chemical composition of SOA for the systems

characterized by a poor degree of mass closure in chemical speciation measurements. To do that, the discussion of FTIR data must be significantly expanded, otherwise it adds no significant pieces of information to the discussion of the AMS datasets.

The Reviewer's suggestion is well noted and is similar to the suggestion made by Referee 1 (R1.1). In the revised manuscript we have included extensive discussion comparing the oxygen contribution from different functional groups using as indicated by FTIR, AMS, and speciation measurements. Tabulated data is also provided in the Supplemental Material.

R2.6. Fig. 9 is the most informative of the paper, but it is rather crowded and it is difficult to identify the data for specific VOC systems in the f44 vs. f43 space as well as in the Van Krevelen domain. The palette helps but it is not enough: I suggest to include tags with acronyms or numbers to help the identification of the specific types of experiments shown in the previous figures.

Thank you for the helpful suggestion. We will enlarge the figure in the revised manuscript and we will add a color coded legend above the graphs.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C6316/2011/acpd-11-C6316-2011-supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 10305, 2011.