

Interactive comment on “Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer” by P. S. Chhabra et al.

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Response to Referee 2:

The authors would like to thank the reviewer for the insightful comments and suggestions to our manuscript. The referee's comments are in italics, followed by the authors' responses.

1) The elemental analysis figures would benefit from putting a single representative error bar on the elemental ratios so the reader can understand the magnitude of the error.

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We acknowledge the suggestion by the reviewer and have included uncertainty estimates in Table 2. These estimates reflect the measurement uncertainty as determined by Aiken et al. (2008). We have also expanded Section 4.3 considerably.

2) Lines 8-9 of the abstract and page 27510. Looking at the supplementary material I come to a different conclusion from that stated by the authors. In particular, in the abstract they state that m/z 44 is a good measure of SOA oxygenation except for glyoxal. O/C 44 and O/C HR are clearly different for the glyoxal system. However, they also appear to differ significantly and outside of error (assuming 30%) for the low NO_x isoprene experiments (S3), the xylene and toluene experiments (S5), and at least one of the naphthalene experiments. The authors should revise their statement. In many cases, the O/C 44 is half the O/C HR. Error bars on the measurements would help this discussion.

The reviewer makes an excellent comment. We have changed the abstract as follows: “The fraction of organic signal at m/z 44 is generally a good measure of SOA oxygenation for α -pinene/O₃, isoprene/high-NO_x, and naphthalene SOA systems. The agreement between measured and estimated O/C ratios tends to get closer as the fraction of organic signal at m/z 44 increases. This is in contrast to the glyoxal uptake system in which m/z 44 substantially underpredicts O/C.”

3) P 27496, line 5: The 31% uncertainty is probably accurate only when the aerosol is chemically diverse. In particular, the calibration factor and hence the error from using the Aiken calibration factor are may deviate significantly for single species aerosol. Given the glyoxal spectrum is so distinct from other species, it is highly possible the Aiken calibration may not represent glyoxal SOA. Have the authors attempted to calibrate with pure glyoxal or a similar system? Glyoxal was not included in the original calibration samples in Aiken.

The uncertainty stated in Aiken et al. (2008) represents the average absolute value of the relative error of the individual data points with respect to the regression between

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measured elemental ratios and true elemental ratios. Since the uncertainty is an average for pure standards, Aiken et al. (2008) suggest it represents an upper bound to the uncertainty of measurements of complex mixtures of organic aerosol. The reviewer is right in suggesting that the calibration factors for an individual species like glyoxal may be very different than those determined by Aiken et al. (2008). We did not attempt to calibrate with pure glyoxal; due to its very high vapor pressure it would likely evaporate after atomization of a glyoxal solution. Despite these challenges, the O/C calibration factor for glyoxal is likely within a factor of two of the Aiken factor since the upperbound O/C is likely 2 (O/C of hydrated glyoxal monomer), and the average measurement was 1.13.

4) *Is the N content of the aerosol in the glyoxal experiments above the LOD? Given the difficulty of separating CHNO and CHN fragments from CH and CHO fragments, is the 22% uncertainty presented in the supplementary material representative of the true error? It would be good to provide a raw HR spectrum in the supplementary material showing what ions are responsible for the N.*

The nitrogen signal is above the LOD and the spectra of the mass-to-charge ratios with the largest contributions to nitrogen signal have been provided in the supplemental material. As it was stated in the manuscript, the likely sources of these nitrogen-containing fragments are imidazoles that are formed from the reaction of glyoxal with ammonium from the ammonium sulfate seed. The reviewer is correct in noting that the CHNO and CHN fragments lie between CH and CHO fragments which tend to be dominant in high-resolution AMS spectra. However, as one can see from the provided spectra, many of the N-containing ions are the dominant ions in their respective m/z ranges. While these compounds are definitely detectable, it is unclear if the 22% uncertainty for the N/C is representative of the true error since the amount of nitrogen containing compounds in the organic aerosol could not be determined.

The elemental figures are presented with only a time axis. In these experiments, both loading and exposure to oxidants are changing in time. Given that the particle chemical

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composition changes both with loading and with chemical processing, the figures can be difficult to interpret. Adding loading and/or exposure as a second horizontal axis would make interpreting the figures much easier. In addition, in some figures organic mass (4,7) is plotted while in others organic volume (13) is plotted. I suggest plotting all figures as a function of organic mass loading for consistency.

AMS organic mass as a function of experiment time has been added as an additional panel to Figures 1, 3, 4, 6, 8, 11, and 12. Figure 13 has been changed to reflect organic mass calculated from DMA volume multiplied by a density.

P27489, line 6: The statement about the O/C ratio of LV-OOA is somewhat confusing. Earlier in the paper you state the O/C can be as high as 0.9. I suggest revising the sentence to 0.6 and above for clarity, assuming that is your meaning.

The authors meant to state that across data sets, LV-OOA tends to have an O/C ratio of at least 0.6. Regional measurements of organic aerosol in Aiken et al. (2008) had O/C ratios as high as 0.76. P27489, line 5-6 have been changed to "LV-OOA has been characterized as aged OOA, having O/C ratios of at least 0.6 across most ambient data sets and spectra dominated by mass fragment CO₂⁺ at m/z 44." The value stated at P27487, line 22 has been changed to 0.76.

P27490, line 7. Typo in the units.

Fixed.

P27490 Second paragraph: Please state the physical state of the AS aerosol. At 60% it could exist as a metastable solution or as a crystalline solid.

Lines 16-19 are changed as follows: "Once the gas-phase glyoxal concentration reached a steady state, ammonium sulfate seed aerosol, existing as a metastable solution, was introduced and the resulting organic growth was monitored by both the DMA and HR-ToF-AMS."

P27500, line 14/Figure 6. The green points have a significantly higher degree of scat-

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ter. Is this due to the loading? In general, the green points make it difficult to interpret the values on the figure. It may be helpful to exclude this experiment from the paper.

The high degree of scatter is due to the low organic signal in this experiment. We have decided to include this experiment.

P27500, line 10. Can you provide the observed signal split between the ions?

The high-resolution spectrum of m/z 91 has been provided in the supplemental material.

P27501, line 4: The authors rule out one possible source of discrepancy between their filter samples and the on-line measurements. Do they have a positive hypothesis for the difference?

As is discussed in sections 4.2 and 4.3, there are several possible reasons for the discrepancy between the measured O/C ratios and the O/C ratios of identified SOA species from the photooxidation of isoprene under high-NO_x conditions. While we show that just linear oligomerization of 2-methylglyceric acid by esterification isn't enough to explain the difference, oligomerization, dehydration and uncertainties in calibration factors could each contribute to the low measured O/C ratio.

P27503, line 2. Incomplete sentence.

Fixed.

P27509, line 2: Incomplete sentence.

Fixed

P27509, line 5: The data can be corrected for particle wall loss. If the data are wall-loss corrected, do the authors come to the same conclusion?

After a wall loss correction is applied, the total SOA volume plateaus and remains unchanged towards the end of both experiments. Since the O/C ratio is increasing at

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the end of both experiments, this would still suggest that fragmentation reactions are occurring, increasing the oxygen content of the aerosol.

Figures 2, 5,9,10, 14. It is very difficult to distinguish the N from C in the spectra. I suggest using a different color for one or the other.

The color of carbon has been changed from black to green.

Figure 8: Combine the legends into one.

We acknowledge the suggestion but we have decided to separate the legends to indicate that the data sets come from two different sources.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 27485, 2009.

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