

Interactive comment on “Analysis of secondary organic aerosol formation and aging using positive matrix factorization of high-resolution aerosol mass spectra: application to the dodecane low-NO_x system” by J. S. Craven et al.

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Comment 1

The results are very interesting but lack molecular level detail which is disappointing since the authors used a chemical ionization mass spectrometer with high resolution.

Response 1

A more complete analysis of the MOVI-CIMS data is in progress, and will be the focus of a separate manuscript. Its use in this paper was to corroborate the attribution of ion C8659

signals by the AMS with molecular ions measured by an independent instrument.

Comment 2

The composition of the factors 1-3 are not described. Thus it's very difficult to conservatively interpret the meaning of the factors.

Response 2

The fully resolved molecular composition of all three factors is part of an analysis of MOVI-CIMS data that is in progress. While the complete molecular composition was not available for the present work, the authors did hypothesize key molecular-level fragments that were dominant for each factor. The molecular-level fragment with the highest correlation of each factor is labeled with the boxed tag in Figure 7 and listed in Table 3. While these molecular-level fragments do not fully describe all compounds in the aerosol for this factor, these provide insight to the type of compounds existing in the aerosol at that time (for example, first generation photooxidation product versus third generation photooxidation product). The comparison to gas-phase CIMS and aerosol-phase MOVI-CIMS affirms the interpretation that each factor describes the condensation of a group of molecules at a distinct oxidation level.

Comment 3

What is meant by elemental analysis, do the authors refer to elemental ratios O/C and H/C or rather the fragment ion elemental compositions?

Response 3

Elemental Analysis refers to the elemental ratios. The section heading in the paper has been changed to elemental ratios.

Comment 4 Interestingly, the AMS community has adapted the van Krevelen diagram for bulk characterization of the mass spectra by plotting O/C and H/C which are determined from just a few characteristic fragment ions. However the van Krevelen dia-

gram (van Krevelen, 1963) was designed to elucidate the elemental compositions of many individual molecular formula. Since the authors write, "Elemental analysis of the PMF factor mass spectral profiles elucidates the combinations of functionality that contribute to the slope on the Van Krevelen diagram" it would be helpful to show the detected fragment ions representing each factor in a van Krevelen diagram at a few specific points over the experiment.

Response 4

To clarify, the O/C and H/C are based on all organic ions in the AMS spectra from m/z 12- 300, and not just a few characteristic ions. The C12 ion fragments (those retain the most molecular level detail) that are closest in correlation to the time trend of the factors, are plotted with the same color as the factor markers on the Van Krevelen diagram. Additional text and figure caption have been added to the paper.

Comment 5

The motivation for the current work – a study of alkane oxidation – is based on a description of UCM from GC/MS methods from more than 10 years ago. What is the evidence of alkane components; does this contradict the observations from several recent papers which have referred to an aliphatic or terpenylic character in ambient aerosol? Is the oxidation of alkanes suspected to be more significant than terpenes as the source of aliphatic or terpenylic character.

Response 5

With the advent of a recently developed soft ionization gas chromatography technique, the formerly "unresolved complex mixture" has been characterized at the molecular level to contain n-alkanes, cycloalkanes, bicycloalkanes, tricycloalkanes, and steranes (Isaacman et al., 2012). Pye and Pouliot, 2012 predict from the Community Multiscale Air Quality (QMAC) model the SOA yield from alkanes and PAHs to be 20 to 30 % of SOA from anthropogenic hydrocarbons, and a smaller percent (~ 10%) of SOA when

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biogenic precursors are included. This discussion has been added to the Introduction. The oxidation of alkanes versus terpenes is beyond the scope of this paper.

Comment 6

Please provide at least a short summary of the CIMS instrument and its general operation (St. Clair et al., 2010; Paulot et al., 2009; Crounse et al., 2006)

Response 6

A short summary of the gas-phase CIMS measurement has been included in the section 2.2.

Comment 7

Please detail the resolving power with respect to a specific mass and provide the mass range of the observed ions with chemical ionization. Examples of the well resolved molecular ions would nicely complement this work.

Response 7

The authors interpret this comment to be regarding the MOVI-CIMS and not the gas-phase CIMS. The resolution information for the MOVI-CIMS can be found in Yatavelli et al. (2012), which is referenced in the paper. The resolution is around 4500 for mass range > 100 Th. The mass range was 17 – 550 Th. This information has been added to the MOVI-CIMS section of the paper. Resolved molecular ion examples will be included in a separate MOVI-CIMS manuscript.

Comment 8

PHA is an unnecessary acronym, potentially leading to confusion. Please write out peroxyhemiacetal formation.

Response 8

We have replaced "PHA" with "peroxyhemiacetal" in the manuscript.

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Comment 9

The caption for Figure 4 appears to be incorrect, "...early C18 SOA formation."

Response 9

The caption for Table 4 is correct. We ran a C18 experiment to develop a standard to help identify hydroperoxides in the AMS. This is explained in the text.

Comment 10

Seed particles were dried or wet? What were the desired gas-phase concentrations?

Response 10

Seed particles were dry. The initial hydrocarbon loadings are in Table 1.

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