Interactive comment on "Mapping gas-phase organic reactivity and concomitant secondary organic aerosol formation: chemometric dimension reduction techniques for the deconvolution of complex atmospheric datasets" by K. P. Wyche et al.

Anonymous Referee #2

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Overview:

Wyche et al. describe development of a chemometric mapping of gas-phase and particle-phase matrices from oxidation of several relevant compounds: isoprene, terpenes (i.e. linalool, myrcene, limonene, a-pinene, B-caryophyllene), toluene, as well as the oxidation products of fig and birch trees. This is done via principal component analysis (PCA), hierarchical cluster analysis (HCA), and positive least squares-discriminant

analysis (PLS-DA) on the mass spectra of the oxidation products from several systems. PCA is performed on gas-phase observations of chamber data using chemical ionization reaction time-of-flight mass spectrometry for the gas-phase to separate distinct regions associated with oxidation of isoprene, cyclic monoterpenes, B-caryophyllene, single chain monoterpenes, and toluene. Addition of mesocosm data (plant emission oxidation experiments) shows expected mapping of oxidation products from fig and birch trees as related to the expected emissions being isoprene-dominated and cyclic monoterpene-dominated, respectively. HCA analysis is performed, supporting the relation of the mesocosm oxidation products with associated precursor oxidation schemes represented in chamber data. Similar PCA and HCA analysis applied to the particle-phase data (liquid chromatography-ion trap mass spectrometry and compact time-of-flight aerosol mass spectrometry) also shows separation by precursor type. Using a zero-dimensional box model simulation based on the Master Chemical Mechanism for alpha-pinene photooxidation, it is argued that the employed statistical deconvolution techniques could be applicable for determining precursor type and potential mechanisms from ambient data on the basis that "model mass spectra" simulated under increasingly complex (closer to ambient conditions) are generally well-captured by "model mass spectra" under conditions more like a typical chamber experiment.

Reviewer's recommendation:

The article overall is well-written and is novel in that it seems to provide great potential for use as identifying chemistry from a particular precursor type given complex sets of mass spectra from oxidation products in the gas and particle phases. The weakest argument is that made for use of this technique to elucidate chemical mechanisms in addition to identifying precursor type, as the specificity for separating mechanistic pathways is not fully demonstrated in the current analyses. Still, the content is appropriate for ACP readers and I would recommend publication after the following comments are addressed.

General Comments:

1) Abstract: The reader would benefit from more specific result statements included here, similar to the lines included in the Introduction section p. 1657, lines 7-15.

2) P. 1656, lines 20-25: Discussion of currently used statistical techniques is rather cursory. There is not even mention of the commonly used positive matrix factorization technique widely used for AMS data analysis. Additional details of why the presented technique is novel/necessary should be discussed.

3) The authors mention p. 1657, lines 16-25, the potential for this technique to be used on ambient data sets, but the paper would be stronger references were provided for which similar statistical analyses are being done to map out oxidation chemistry related to certain precursors as is done here, or utilize available and published field data in the described analyses of the paper to prove the point. For example, why would this technique be useful over positive matrix factorization techniques, which now includes a way of identifying SOA formation contributions from isoprene?

4) P. 1659, lines 9-12: While the precursors were reacted to near completion in the chamber experiments, how can one verify that the oxidation scheme went to completion to match, for example, major oxidation products in the MCM schemes presented in Figure 9. That is, should not theoretically the PCA analysis for the chamber experiments ideally match the MCM PCA if the chamber experiments are covering the same range as the simulated chemistry?

5) P. 1659, Section 2.2: What impacts on the comparison of the chemical oxidation would be expected for the systems, considering that these systems were run across several environmental chambers?

6) P. 1667, lines 2-4: Aromatic compounds are also observed to be emitted from the biosphere, (e.g. aromatics like toluene as well as aromatic monoterpenes; see Guenther et al., 2012 and references within; doi:10.5194/gmd-5-1471-2012). Would the authors expect addition of these compounds to map onto the same region as toluene/monoterpenes, and would this not change the interpretation that the analy-

sis can separate anthropogenic and biogenic precursor sources vs. just precursor structure? Do the authors have potential ideas for why there is overlap with toluene and the single chain monoterpenes? Would single chain sesquiterpenes (e.g. far-nasene) also map out separately from B-caryophyllene as the cyclic and straight chain monoterpenes do?

7) P. 1669, lines 17-20: Why are the birch trees sensitivity cited to be low due to only two repeat experiments, but the fig trees experiments also only having two repeat experiments have high sensitivity and specificity?

8) Section 4.5: Why do the authors choose to do separate PCA analyses on the gas-phase data versus the particle-phase data? Considering that there would be overlap for semi-volatiles (e.g. B-caryophyllinc acid as stated p. 1670, line 10), should not a PCA analysis (though mindful of the different analysis technique) be more ideal (as well as for interpreting ambient data) to map regions of any chemistry associated with various precursor types? Should it be inferred that the separation of analysis on gas vs. particle-phase data is the recommended approach to apply this type of analysis to ambient data? I would be curious to see how the analyses would compare between gas-phase only, particle-phase only, and gas and particle-phase together.

9) Figure 7a: The plot is produced using LC-MS particle data, but what biases might be at work here based on this technique's sensitivity to certain organic aerosol products?

10) Figure 8a and accompanying discussion p. 1671, lines 15- p. 1672, line 3: The meaning of M43, M44 should be discussed in context as to whether the relative aging of the oxidation systems were actually comparable. Although the precursors were near complete reaction, did the oxidation develop enough such that B-caryophyllene schemes could take on additional spectral contributions from M43, M44? That is, was their sufficient oxidant such that secondary reactions (producing characteristic oxidation products and associated ions) could occur equally across precursor systems?

11) P. 1677, lines 25-27: Can the authors give a statistic that relates the similarity

of the "model mass spectra" to the experimental data set from the chambers? If this model mass spectra generated from the MCM is similar enough to the experimental MS obtained, why not run the PCA on MCM generated model mass spectra for each system and see if the results are similar to the PCA for the gas and particle-phase data? Or at least, in Discussion section, when trying to relate ions characteristic of particle-phase oxidation products from grouped precursors, can a metric be used for testing similarity of the MCM model mass spectra expected and the weight of ions affecting the various B-caryophyllene and myrcene mappings for example?

12) P. 1678, lines 26-29: This argument would be strengthened if the authors did similar MCM analyses as in Fig. 10 for the other precursor types represented in Fig. 9 and provided metrics for the similarity of the model mass spectra with that observed in the chamber experiments.

13) P. 1679, line 12: Authors claim that the gas-phase oxidation products of each structural type can be grouped "according to the controlling chemistry and the products formed." While it is evident that the products formed (as interpreted by the accompanying MS) informs this grouping, what chemical controls are derived from the PCA analysis? I think of e.g. varying NOx and O3 levels as different chemical regimes/controls on the chemistry, but this point is not emphasized in the PCA mapping of the various experiments grouped by precursor. Where is this shown/taken from the figures? Or, please clarify what is meant here.

14) P. 1679, lines 13-15: In line with comment above, this sentence is rather vague. No description thus far has really emphasized "decoding of mechanisms" by starting with an ensemble of summed mass spectra. I agree you can get to the precursor compounds based on tracer ions indicative of chemistry from a particular precursor, but what in the PCA analysis maps to particular mechanistic pathways? Do the authors envision additional mappings in the PCA plots within the precursor groups to show oxidation from one oxidant versus another, for example, which would be evident in unique tracer compounds from associated pathways?

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Technical Comments:

1) P. 1659, Experiment design: It is not clear in Table 1 which experiments were conducted in which chamber.

2) P. 1661, lines 14-16: Since it is not clear which experiments were conducted in which chamber, as in the proceeding comment, please also make clear here which experiments actually had particle-phase data. Later inspection of Figures 7-8 warrants the reader questioning of why the mesocosm experiments and isoprene experiments are not included in the analysis of the particle-phase data.

3) Figure 2 would benefit from caption description of the mass spectral ions populating the figure.

4) P. 1669, line 13: Change "been" to "be"

5) For aid in interpretation of the ions mapped onto figures 2 and 7a, it may be helpful to include a table that lists all ions (LC-MS/MS, CIR-Tof-MS, and AMS), their chemical assignment, and precursor type, so the information is more readily available than filtering through the text for these ion assignments.

6) Figures 7b and 8b: It would be more helpful if the color scheme used for the cyclic monoterpenes was consistent with that used in Figure 5.

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