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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding evolution of product composition and volatility distribution through in situ GC×GC analysis: a case study of longifolene ozonolysis" *by* G. Isaacman et al.

Anonymous Referee #1

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The manuscript by Isaacman et al. presents a general framework for mapping two-dimensional (2D) chromatography data to 2D organic aerosol model frameworks, using the 2D volatility basis set (VBS) as an example. In addition, the manuscript reports on the evolution of oxidation product volatility/polarity during a typical chamber study of secondary organic aerosol formation. The manuscript represents an important step forward in using chromatographic data to inform organic aerosol models, and likely will be a highly cited paper, appropriate for publication in Atmospheric Chemistry and Physics (ACP). The manuscript is in need of some revisions, largely editorial in nature, though some additional detail regarding development and application of the retention time correlation (RTC) method is recommended before the manuscript is published in

ACP.

Technical Comments: On p.62, lines 11-12 it is stated that the 35 compounds used to derive the vapor pressure and O/C planar-fits are listed in the supplementary information. A list of those compounds did not seem to be available, which made the results presented in Figure 2 difficult to completely understand. For example, looking at Fig. 2b, the acids appear to have the same O/C ratios as the ketones, and the esters generally have the highest O/C ratios. This is not intuitive. One can start to imagine compounds for which that would be possible, but then questions start to arise as to the apparent volatility/polarity distribution of those compounds. Because of the importance of functionality in determining chromatography retention times and model parameters, it is highly recommended that the list of compounds be included in the main body of the manuscript. Furthermore, it is recommended that their O/C and C* (or vapor pressure) values are included in the table and that the symbols in Fig. 2 are color-coded to match the contour lines, giving some indication of the goodness of fit. Given that the RTC method is a significant (and probably the most novel) component of this manuscript, some analysis of how well it works for the known compounds is warranted. It is not sufficient to show the agreement of the vapor pressure planar-fit with estimation model output.

In section 4.2.2, evolution of longifolene oxidation products is described in terms of volatility distribution, particle-phase O/C ratio, and complexity. The chromatograms and VBS distributions in Fig. 7a,b clearly show an increase in lower-volatility compounds between TAG #2 and TAG #3, and an increase in product number. Less clear are the reported shift in O/C ratio (Fig. 3) and the agreement between the O/C mapping in Fig. 3 and the AMS results in Fig. 6. Assuming it is real, the reported shift in O/C may be more clearly illustrated by separately mapping the TAG #2 and #3 samples in 2D-VBS space and/or including an insert (or figure in the supplementary information) isolating the O/C range measured by the AMS. While there are no AMS data to compare with, it would be interesting to see the 2D-VBS mapping of the TAG #4 sample. With regard

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to evolution of the O/C ratio from TAG #1 to TAG #4, it seems an opportunity is being missed to discuss the ability of the 2D data to inform 2D-VBS model representation of aging (oxidation products + OH), assuming that no OH scrubber has been used in the experiments (it is not specified in section 2.1).

Editorial Comments: The quality of writing in this manuscript could be improved, and it is recommended that the manuscript be carefully reviewed for typos, grammar (e.g., verb tense agreement), and unclear and/or awkward sentences. Some examples follow.

Throughout the manuscript "multi-dimensional" is used. Typically, multi refers to more than two. It is suggested that unless a third dimension is being included, multi-dimensional be changed to two-dimensional.

The abbreviations "TAG" and "2D" are introduced in more than one place and are not used consistently throughout the manuscript.

Abstract: In the three listed conclusions, the verb tenses are not in agreement.

Page 56, line 2: "...rely on filter collection in the using chamber,..." ", line 6: The sentence "...biogenic SOA particle speciated organic composition over time from a single BVOC precursor." is awkward. As a start, "biogenic" and "BVOC" are not both necessary.

Page 57 and 58, paragraph starting with line 14: It is my understanding that the model framework proposed in Pankow and Barsanti (2009) has a flexible number of products (see line 20), similarly to the flexible number of bins in the VBS (Donahue et al. 2006). It is not clear what the "as well" on line 21 refers to. It is also not clear what is meant by "more general" in regard to the VBS model. At the end of the paragraph it is stated that both of the model frameworks have been recently modified to include a functionality parameter, which I believe only applies to the VBS.

Page 58, line 11: AMS provides total organic aerosol mass...for some particle size

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range?

Page 60, line 15: The paragraph starting on line 15 is somewhat difficult to follow. It is recommended that the time after ozone addition at which the samples were taken be described first, and the sampling duration second.

Page 63, line 11: It is recommended that “firmly” be omitted.

Page 65, line 1 (starting on page 64): It is recommended that “a variety of the recently” be replaced by “any” to better describe the general applicability of the RTC approach. “, line 8: It is recommended that “. . .meant that. . .” be replaced; possibly. . .high ozone concentration allowed for. . . , line 17: “. . .evolution of particle composition and particle phase evolution. . .”

Page 66, line 10: “. . .from primarily from. . .” “, line 19: On line 19 it is stated that the increase in f44 is due to particle-phase oxidation, while in the following paragraph it is stated that particle-phase oxidation is only one possibility.

Page 67, lines 1-5: This description and figure reference may fit better in the experimental set up section.

Page 68, lines 4-5: The statement “. . .single or double oxygen addition, which creates ketones or aldehydes. . .” is confusing, given that both of those functionalities have only one oxygen atom.

Figure 1 does not add anything to the paper; it is suggested that it be omitted.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 53, 2011.