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Atmospheric
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Discussions

Interactive comment on "A two-dimensional volatility basis set – Part 2: Diagnostics of organic-aerosol evolution" *by* N. M. Donahue et al.

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We thank the reviewer for a very useful and informed discussion. Our replies are in *italics* below, while the reviewer comments are in plain text.

Page 24888, Line 25: Here the authors compare their framework with other 2-D representations: carbon number polarity grid (Pankow and Barsanti, 2009) and carbon number oxidation state space (Kroll et al., 2011). They point out that the other two representations are more focused on tracking molecular structures. However, the carbon number vs. oxidation state space need not rely on the specific molecular structure of organic constituents. The carbon number in that representation can either be related to vapor pressures or determined from speciated measurements.

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The point is well taken that "molecular structure" is much more than carbon number. However, we still maintain that the principal strength of the n_c*-*$\overline{OS_c}$ *space is the ability to analyze complicated chemical processes when information about carbon number is known. Our intention is to contrast frameworks where volatility must in some way be calculated or inferred from other intrinsic properties (i.e., molecular structure) vs the VBS where volatility is the known quantity and those other properties must be inferred.*

Page 24891, Line 8: The authors combined direct (volatility-based chromatography) and indirect methods (isothermal dilution) to determine C*. But these equations developed by Donahue et al., 2006 consider neither the effects of variable MW nor activity corrections (Pankow, 2011). It would be better to test if the results from the indirect method are consistent with those from the direct method. Specifically, suppose there is a set of data points with increasing volatilities within the range of direct measurement. Can the results derived from the indirect method match the measured data points with low volatilities?

The reviewer appears to be commenting on some combination of the Donahue et al 2006 ES&T (1D-VBS) paper and the Donahue et al ACP 2011 paper that preceded this one in the 2D-VBS sequence. However, this section deals with determination of volatility in ambient samples. In that context a set of data points is not really useful – the issue is to infer volatility from an amorphous ambient sample.

We shall add "from an ambient sample" following "C^**".*

Page 24891, Line 25: It is probably acceptable to assume that the overall aerosol composition remains constant during the ozonolysis of alpha-pinene. But in most OH-initiated oxidation systems, the aerosol composition varies with the organic mass loading. Then the indirect method for the estimation of volatility should be used carefully. Could the authors discuss the application of this 2-D representation to photooxidation experiments that are more likely to exhibit aging?

That is precisely the point we are making. Section 4.2 of this paper is devoted to this

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task, but note that we do NOT attempt to derive a volatility distribution for the products of these SVOC/IVOC aging reactions because to do so requires a forward model of aging that is beyond the scope of this paper (that comes next).

Page 24901, Line 26: The authors plot four observed products from the ozonolysis of alpha-pinene on the 2-D space. What is the fraction of these four products in the total aerosol mass?

Point well taken. We have added some ranges for each.

Page 24901, Line 4: What does the sentence "The OSc values are manually adjusted to obtain reasonable values" mean? Does one arbitrarily choose a value for each volatility bin? Or does one choose typical products for each volatility bin?

This paragraph will be reworked to describe our procedure in more detail.

In the upper panel of Fig. 3, the blue contours represent the product mass distribution. What are the values and units for each of the blue contours?

We shall provided the 2D carbon yield array as supplemental information. The contours are a mass yield (equivalent to the 1D mass yields in Fig 3b when the columns are added) and so must be converted from carbon mass to organic mass by application of the C, H, O arrays described in Donahue et al. 2011a.

Since the minimum resolution for volatility is 10 μ g m^{-3}, how can these blue contours be so smooth?

Contouring algorithms involve smoothing.

Oligomers are formed in the ozonolysis of alpha-pinene; why are oligomers not within the range of the blue contours?

We shall add some discussion of this. There is clear evidence for oligomer formation (and so oligomers are indicated in Fig. 3a), but quantitative estimates of oligomer yields are hard to come by. Consequently, the mass yield distribution shown here is the same

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mass yield distribution one obtains by application of the Odum analysis to chamber data. As noted above, this analysis is only valid if the product distribution remains constant during an experiment. If this is indeed true for α-pinene, there is very little room in the SOA mass yield data for substantial oligomer production. Conversely, if there is substantial oligomer formation and the yields vary with the amount of SOA formed, this complicates the traditional Odum analysis. Overall, our presentation shows that the mass yields are broadly consistent with monomer products, and that the SOA mass yield variation with loading is consistent with the Odum/Pankow interpretation. Consequently, these data are consistent with oligomer mass yields being relatively small.

Page 24907: Biomass burning emits a complex mixture of organics that span a wide range of volatility. Some of these organics have very low vapor pressures (SVOC/IVOC) and thus partition directly into the particle phase, creating primary organic aerosol (BBPOA). Some of these are volatile organic compounds (VOC), which can be further oxidized, producing secondary organic aerosol (BBSOA). Recent studies demonstrate that the oxidation of biomass burning vapors can only account for less than 20% of BBSOA (Grieshop et al., 2009).

That is not at all what Grieshop et al. concluded; they contended that vapors were the dominant driver for BBSOA formation but most of those vapors were not the relatively light VOC observed during the experiment. The plot in the inset of our Fig. 5 is derived from that very study. Measured VOC emissions from biomass burning accounted for less than 20% of the observed SOA, which strongly suggests that the SVOC/IVOC vapors used in this example were the source of the SOA.

However, it is still difficult to elucidate the BBSOA formation mechanism from such a complex mixture that consists of both volatile and semivolatile vapors. Are there caveats in using the biomass burning case to illustrate the general behavior of SVOC and IVOC?

As the reviewer indicated, this paper focuses on the diagnostic use of the 2D-VBS. The *discussion of biomass burning is designed precisely to show that we can make strong conclusions about the key processes involved in BBSOA formation even though we can not directly write a mechanism. However, the broad trajectory of semi-volatile product formation involving a high degree of fragmentation in the product molecules is clear in the diagnostic analysis presented. Thus the data do inform a general mechanism. Furthermore, the similarity of the results from wood smoke and diesel vapors also supports the conclusion that these experiments reveal general behaviors of SVOC and IVOC compounds.*

Page 24912, Line 9: The 2-D space is a clear and simple representation to infer broad patterns in OA behavior. However, to what extent will full development of a 2-D-VBS model require some knowledge of the detailed chemistry in both gas and particle phases?

This is really a topic for the next paper in this series. The Murphy et al. paper describes the essential features of our initial 2D-VBS modeling implementation, but ultimately many model-measurement comparisons will be required to determine just how much detailed knowledge of specific chemical mechanisms will be required. The ansatz of the 2D-VBS is that there is a reasonably well defined average behavior for the large ensemble of different compounds found at any given location in the 2D-VBS, and that this average behavior will be well represented by a product distribution that we can distill into fairly simple rules constituting oxidation "kernels" within the 2D VBS. Furthermore, our hypothesis is that the rules will vary smoothly and systematically as one moves around the 2D-VBS space. This is one reason we included both Figs 5 and 6, with wood smoke and diesel vapor oxidation, as these fairly different systems do indeed exhibit similar behavior.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 24883, 2011.

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