**Atmospheric
Chemistry
and Physics
Discussions**

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

Anonymous Referee #1

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Donahue et al. have developed a two dimensional volatility-oxidation representation to describe organic-aerosol chemical evolution. This 2-D space, which has been applied to analyze the alpha-pinene + ozone system, wood smoke and diesel-engine emissions, offers promise as a tool to gain insight into organic aerosol evolution. The paper could profit from a clearer description of the use of this model, as suggested below. It should be noted clearly that this is a descriptive model as opposed to a predictive model.

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.

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?

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?

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?

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? 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? Since the minimum resolution for volatility is 10 μg m-3, how can these blue contours be so smooth? Oligomers are formed in the ozonolysis of alpha-pinene; why are oligomers not within the range of the

blue contours?

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). 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?

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?

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