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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Molecular corridors represent the multiphase chemical evolution of secondary organic aerosol" *by* M. Shiraiwa et al.

Anonymous Referee #1

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General Comments: This manuscript provides a conceptual model: the characteristic "molecular corridors" with a correlation between volatility and molar mass to represent the multiphase chemical evolution of secondary organic aerosol (SOA). Overall, it is a novel proposal to compare the volatility and molar mass of identified SOA constituents in a 2-D map. However, more work needs to be done to demonstrate how the "molecular corridors" could benefit future modeling work and how the detailed chemical mechanisms affect SOA molecule's positions in the 2-D map. This is a short manuscript and the authors should consider expanding their discussion and building up a linkage between components' behaviors in the molecular corridors and the SOA formation mechanisms behind them. The comments below should be addressed before consideration for publication in ACP.

Specific comments: P5931, L5-7: The heterogeneous oxidation reactions are likely triggered by oxidants colliding with particles and the reactions largely occur on particle surface and a limited area at sub-surface. It is not accurate to say "in the particle phase". Need to clarify.

P5931, L11-15: The authors claim in both the abstract and introduction that the recent advance in soft ionization mass spectrometry provides molecular information that can be used in the 2-D map for SOA evolution of molar mass vs. volatility. However, in the further discussion, the molecular information for the biogenic SOA (Figure 1a-c) was not from soft ionization mass spectrometry techniques (mostly from GC/EI-MS); the DART-TOF-MS provides molecular formulae for the chamber alkane oxidation shown in Figure 1d-i, but the molecular structures which are necessary to estimate volatility cannot be resolved if not from oxidation of known VOCs. Under such conditions, the authors' method works only for lab generated SOA, but molecular structure information is essentially needed for a broader use. Thus, I think the linking between soft ionization mass spectrometry and the volatility vs. molar mass map is not fully justified.

P5931 L22-27: In Figure 1, the authors show biogenic and anthropogenic SOA constituents. However, it is not entirely clear why the authors choose to present NOx-dependent data for the anthropogenic, but not for biogenic SOA. Recent studies demonstrate that biogenic SOA have very different constituents under different NOx conditions and oxidant types (Lin et al., 2012 ES&T 46, 250-258; Lin et al., 2013 PNAS 110, 6718-6723; Kristensen et al., 2014 ACPD). If the authors are concerned the number of data points will become too small in each figure, I suggest combining the NOx-dependent figures (i.e., Figure 1 d-e, f-g, and h-i) to be consistent with the biogenic figures.

P5933 L12-15: Some of these descriptions can be moved to figure caption.

P5933 L20-25: In Figure 3, the authors show the molecular corridors of molar mass vs. volatility. However, it is not a surprise that most of the identified SOA compounds locate

within the area shown in Figure 3, because: (1) from linear alkane (O:C =0) to sugar alcohol (O:C) is quite a large volatility and mass range and (2) it is generally known as molecular mass increases, volatility decrease (gas phase moving towards particle phase). It is totally expected that most molecules sit in this wide range. However, what is more interesting and I think the authors should spend a little more time (where the authors already briefly discussed a few examples) discussing is the exceptions and the chemistry explanation behind the observations. The rules generally acknowledged based on the multiphase chemistry and Figure 3 can be summarized as: (1) Gas-phase products are confined to the lower right area (lower mass and higher volatility); (2) Early generation particle-phase products (or fresh SOA) are semi-volatile and tend to locate in the middle part of the corridors; (3) Particle-phase reactions lead to the formation of high mass, low volatility products, which locate in the upper left area;

Here are some examples of exceptions that could be discussed: (1) Some recently observed gas-phase products have low volatility (extreme low volatile organic compounds (ELVOC) from α-pinene + O3 reactions (Kristensen et al., 2014 ACPD; Ehn et al., 2014 Nature)). They locate on the upper left even though they are initially formed in the gas phase. This suggests a new chemical pathway that was not captured by traditional understanding: fast formation of low volatility and highly oxygenated products. (2) Semi-volatile compounds undergo gas-particle partitioning, leading to fresh SOA formation and tend to locate in the middle part of the corridors. But some gas-phase compounds are quite volatile and they can still participate in SOA formation due to reactive uptake (for example, isoprene epoxydiols (IEPOX)). (3) Particle-phase reactions do not necessarily lead to formation of high mass, low volatility products. The authors mentioned dihydrofurans and furans. The reason for their exception is likely they were formed from dehydration which transfered a -OH group to a double C=C bond and the volatility largely increased. Another example is glyoxal oligomers (lower mass due to the low mass of glyoxal). It would be nice if the authors could expand their discussion and point out a number of possibilities and chemical mechanisms that may cause exceptions, because these are the aspects that current chemical models do not

incorporate.

P5935, L6-8: It will be helpful if the authors can specifically point out which precursor system follows which behavior, because the range shown in Figure 1 is different from that in Figure 3. Some explanations would also be helpful (why they follow different behaviors? Biogenic vs. anthropogenic? It takes more oxidation generations for some VOCs to produce semi-volatile products that can partition to the particle phase than the others?).

P5935, L11-13: It is not entirely true that 250-300 g/mol is a threshold between gas- and particle-phase products. In additional to furans and glyoxal products, IEPOX products and α-pinene products are also exceptions. There might be many other exceptions. The interesting question is not where the threshold is, but rather what are the chemical differences that cause different thresholds?

Figure 1: Some data points in Figure 1a might be wrong (not updated enough). There are a number of particle-phase products within the 100-200 g/mol range that should be shown in solid markers. Under the low-NOx pathway, C5 alkene triols (Mw =118), 2-methyltetrols (Mw=136), 3-methyltetrahydrofuran-3,4-diols (Mw=118) are all particle-phase products; under the high-NOx pathway, 2-methylglyceric acid (Mw=120) is also a particle-phase product (Lin et al., 2012 ES&T 46, 250-258; Lin et al., 2013 PNAS 110, 6718-6723). New observed “ELVOC” should be updated in Figure 1b as well.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 5929, 2014.