Response to the comments of Anonymous Referee #1

Referee General Comment:

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.

Response:

We thank Anonymous Referee #1 for the review and the positive evaluation of our manuscript. Based on your constructive suggestions for improvement, we will expand discussions in the revised manuscript as detailed below.

Referee Comment 1:

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.

Response:

As pointed out, heterogeneous reactions may mainly occur at the particle surface or near-surface bulk. Multiphase reactions, particularly cloud processing, may proceed in the particle bulk. We will clarify this point in the revised manuscript.

Referee Comment 2:

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.

Response:

Thanks for pointing this out. We will remove the sentence on soft ionization from the abstract. We will clarify that molecular information of the biogenic SOA were mostly obtained by GC/EI-

MS but also with help of soft ionization mass spectrometry such as ESI-MS and MALDI-MS (Surratt et al., 2006). Even though traditional hard ionization mass spectrometry is capable of identifying molecular structure of oxidation products, the recent advent of soft ionization mass spectrometry (e.g., ESI, MALDI, APCI, DART-MS) and combination with several different instruments have certainly broaden a way to identify chemical composition and molecular structure (e.g., Surratt et al., 2006; Kalberer et al., 2006; Vogel et al., 2013; Chan et al., 2013). To further clarify this point, we will add the below paragraph in the revised manuscript.

"Common techniques applied for the analysis of SOA are gas chromatography/electron impact ionization mass spectrometry (GC/EI-MS) and liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS) (e.g., Surratt et al., 2006). Hard ionization, such as electron impact ionization, generally causes significant fragmentation of organic molecules, which makes molecular identification challenging, but can provide molecular structural information. The recent advent of soft ionization methods such as electrospray ionization (ESI), matrix-assisted laser desorption ionization (MALDI), atmospheric pressure chemical ionization (APCI), and direct analysis in real time (DART) ionization has facilitated the identification of the dominant fraction of the compounds constituting SOA by preserving analytes as intact or nearly intact during ionization (Kalberer et al., 2006; Williams et al., 2010; Laskin et al., 2012a; Laskin et al., 2012b; Chan et al., 2013; Nguyen et al., 2013; Vogel et al., 2013; Schilling-Fahnestock et al., 2014)."

Referee Comment 3:

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.

Response:

In Figure 1 we will include identified oxidation products in the suggested references (Lin et al., 2012, 2013; Kristensen et al., 2014). We combined low and high NO conditions for biogenic SOA, because the number of identified products in previous literatures is not many (<50) and separating into low and high NO conditions make data points small in the each panel. As specified in Table 1, the number of identified compounds of C12 alkanes by DART-MS in this study is very high (>~100) for both low and high NO conditions. Thus, we prefer to keep figures for low and high NO condition separately for C12 alkanes.
In the new Table A1 we summarize the experimental conditions (oxidants, NO level, seed) of previous studies that identified biogenic SOA products. Thanks for pointing out that chemical composition of SOA may depend under different NO conditions and oxidants. The molecular corridor for isoprene (Fig. 1a) is relatively tight, even though oxidation products under various conditions are included. Moreover, there are not big differences in the resulting molecular corridors of alkanes under low and high NO conditions. How NOx level affects the molecular corridor should be subject to future studies. We will add the below paragraph in the revised manuscript.

"The composition of SOA may vary depending not only on the organic precursor but also on the oxidant and other reaction conditions of formation and aging (Presto et al., 2005; Surratt et al.,

2006; Lin et al., 2012; Lin et al., 2013; Kristensen et al., 2014; Loza et al., 2014; Xu et al., 2014). The atomic O:C ratio tends to be higher at high NO concentrations, partly due to the formation of organonitrates (Nguyen et al., 2011; Schilling-Fahnestock et al., 2014). Even though Fig. 1(g), (h), (i) contain biogenic SOA oxidation products measured under different conditions as specified in Table A1, the molecular corridors are relatively tight with $R^2 > 0.85$. The molecular corridors of alkane SOA formed under low and high NO conditions are also quite similar (Figs 1a-f). Thus, the molecular corridors of SOA formation appear to be determined primarily by the organic precursor, and the extent to which they are influenced by reaction conditions warrants further studies."

Referee Comment 4:

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

Response:

Following your suggestion, we will move a part of this sentence to the figure caption.

Referee Comment 5:

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 a-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.

Response:

Thanks for this helpful comment. Based on your comment, we will expand the discussion substantially by including the new panel b in figure 4, which depicts characteristic reaction pathways on the molecular corridor. The main text will be revised substantially to discuss the chemical pathways and location of oxidation products, including exceptions. We will include the below paragraphs in the revised manuscript.

"Characteristic reaction pathways and relevant kinetic regimes are outlined in Fig. 4(b). SOA precursor VOCs with high volatility and low molar mass are located in the lower right corner of the molecular corridor ensemble. As illustrated in the insert in Fig. 4(b), single-step functionalization usually leads to a small increase in molar mass, corresponding to one order of decrease in volatility (Donahue et al., 2006), while dimerization and oligomerization tend to multiply molar mass, and thus decrease volatility by multiple orders of magnitude (Trump and Donahue, 2014) (e.g., three to four orders of magnitude for alkane and terpene SOA, see Fig. 1). Fragmentation, on the other hand, can lead to a substantial decrease of molar mass and increase in volatility (Bertram et al., 2001; Yee et al., 2012; Schilling-Fahnestock et al., 2014). As a result, simple gas-phase oxidation products are confined to the lower right area in the 2D space. Such oxidation products (C_0 > 10 μg m^{-3}) tend to fall into the gas-phase reaction limiting case G_{rx} (quasi-equilibrium growth), as their gas-particle equilibration timescale is on the order of seconds to minutes (Shiraiwa and Seinfeld, 2012) (see Appendix C&D). "

"Aqueous-phase processing of glyoxal and methylglyoxal is an efficient pathway for formation of low volatility and semi-volatile HOC compounds (Liggio et al., 2005; Carlton et al., 2007; Lim et al., 2010; Ervens et al., 2011; Zhao et al., 2012). Uptake of glyoxal into the particle phase leads to hydration and acid catalysis to form hemiacetals, aldols, imines, anhydrides, esters and organosulfates (Lim et al., 2010). Reactive uptake of isoprene epoxydiols (IEPOX) and subsequent formation of oligomers (Surratt et al., 2010; Lin et al., 2012; Lin et al., 2013) also progresses over the HOC corridor. Whether multiphase chemistry of glyoxal and IEPOX is limited by mass transfer or chemical reactions may depend on various factors including reaction rate coefficients, relative humidity, particle pH, and Henry's law constant (Ervens and Volkamer, 2010; McNeill et al., 2012; Kampf et al., 2013). Recently, highly oxidized extremely low volatility organic compounds (ELVOC) have been detected in field and chamber experiments (Ehn et al., 2012; Schobesberger et al., 2013; Ehn et al., 2014). Such compounds may populate the upper left corner of the HOC corridor."

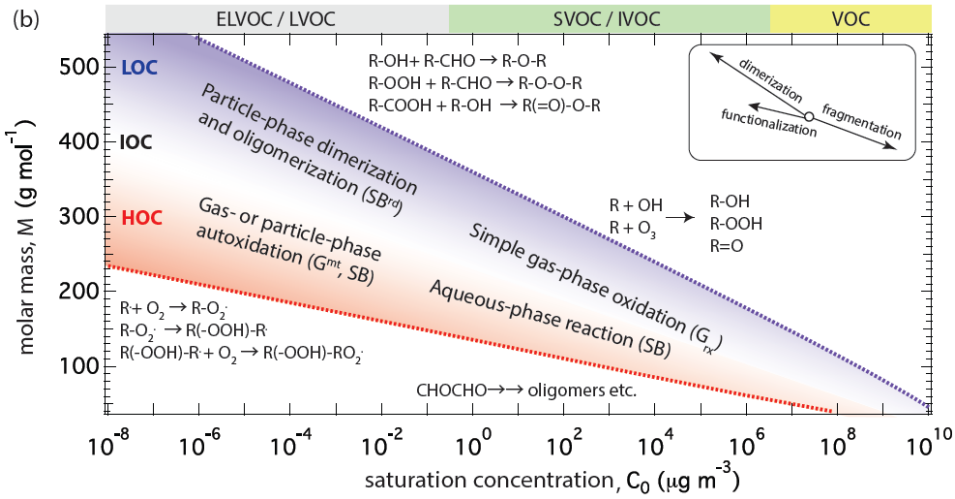

Figure 4. (b) Characteristic reaction pathways with most probable kinetic regimes. The split of molecular corridors between high and low O:C compounds (HOC, red shaded area; LOC, blue shaded area) reflects the median correlation fitted lines from Fig. 1. SOA products evolve over the molecular corridor driven by three key reaction types of functionalization, oligomerization and fragmentation as illustrated in the insert (note different lengths of arrows indicating different intensities of effects on volatility).

Referee Comment 6:

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?).

Response:

Based on your comment, we extend the range of Figure 3 to be consistent with Figure 1. Isoprene SOA follows the HOC corridor; dodecane and cyclododecane follow LOC corridor. We will clarify this point in the revised manuscript as below.

"Many early generation gas-phase oxidation products of alkanes as well as dimers or oligomers with low O:C ratio (LOC) fall into a molecular corridor close to the C_nH_{2n+2} line, which we designate as LOC corridor ($-dM/d\log C_0 \geq \sim 25$ g mol^{-1}, blue shaded area). Aqueous-phase reaction and autoxidation products with high O:C ratio (HOC), on the other hand, tend to fall into a corridor near the $C_nH_{2n+2}O_n$ line, which we designate as HOC corridor ($-dM/d\log C_0$ of $\leq \sim 15$ g mol^{-1}, red shaded area). The area in between is characterized by intermediate O:C ratios and accordingly designated as IOC corridor ($-dM/d\log C_0 \approx \sim 20$ g mol^{-1}). Among the SOA systems investigated in this study, the small precursor VOCs glyoxal, methylglyoxal and isoprene (C_2-C_5) evolve through the HOC corridor, and the terpenes α-pinene and limonene (C_{10}) through the IOC corridor. The alkanes dodecane and cyclododecane (C_{12}) evolve through the LOC corridor, while hexylcyclohexane exhibits a branching between the LOC and HOC corridors, suggesting the involvement of different reaction pathways."

Referee Comment 7:

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 _-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?

Response:

Thanks for pointing it out. Please also see the response for comment 5. We will revise and include the below paragraph in the revised manuscript:

"Figure 4(a) shows that most identified oxidation products with molar masses higher than 300 g mol^{-1} are particle-phase products (solid markers). Thus, the relatively high average molar mass observed for laboratory-generated SOA points to the importance of particle-phase chemistry in these systems. Some SOA compounds with higher molar mass are gas-phase oxidation products including ELVOC and ester dimers observed in α-pinene oxidation (Ehn et al., 2014; Kristensen et al., 2014), and there are also some particle-phase products with relatively low molar mass including furans and dihydrofurans in dodecane and cyclododecane SOA (Yee et al., 2012; Loza et al., 2014) as well as glyoxal and IEPOX products in isoprene SOA (Lim et al., 2010; Surratt et al., 2010). Nevertheless, the clustering of identified reaction products in molecular corridors may facilitate estimation of the relative importance of gas- vs. particle-phase routes to SOA formation (Fig. 1). "

Referee Comment 8:

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.

Response:

Thanks for pointing out. C5 alkene triols (Mw =118), 2-methyltetrols (Mw=136), and 3-methyltetrahydrofuran-3,4-diols (Mw=118), and 2-methylglyceric acid (Mw=120) will be treated as particle-phase products with solid markers. We will add Lin et al., ES&T, 2012; PNAS, 2013 as references. For newly observed ELVOC, we will include dimer ester for a-pinene observed by Kristensen et al., ACPD, 2014. As Ehn et al., 2013 did not provide molecular identity and volatility of ELVOC compounds (only elemental formula were provided), it is not yet possible to include them in Fig. 1. Kinetic regimes of ELVOC compounds are investigated in Appendix C and Fig. A4(d).