

**Referee's Comment in Italic Font; Author's response in Blue without Italic Font.**

*1-page 31153, In title and in many places throughout article it would be more accurate to say "monocyclic aromatic hydrocarbons" instead of the more general "aromatic hydrocarbons" to make clear that the focus of this study was benzene and substituted benzene compounds.*

Agree. We will change all "aromatic hydrocarbons" to "monocyclic aromatic hydrocarbons".

*2-page 31154, line 2, The wording "determines the SOA formation" is unclear. Does it refer to SOA yield? composition? Both?*

The "SOA formation" means both the SOA yield and SOA chemical composition. We will insert "(SOA yield and chemical composition)" after "determines the SOA formation".

*3-page 31154, line 16, Unclear what is meant by "less oxidized per mass/carbon."*

"less oxidized per mass/carbon" corresponds to two parameters which are used to compare the SOA formation difference in different aromatic hydrocarbons in this paper. "oxidized per mass" refers to SOA yield which determines SOA formation potential on a mass basis. "oxidized per carbon" refers to SOA chemical composition (e.g. OSc, O/C and H/C) which determines SOA formation potential on a mole or carbon number basis. To clarify the meaning of "less oxidized per mass/carbon", we will add "on a basis of SOA yield or chemical composition" after "less oxidized per mass/carbon".

*4-page 31155, line 13, Define what is meant by "methyl group branching"*

Good point. We will replace "methyl group branching ratio" with "the increase of branched structure".

*5-page 31158, line 14, How are the yield values found in this study different from those in previous studies? Higher or lower?*

The differences in absolute values of SOA yield in previous studies and this studies depend on the photooxidation conditions. For example, earlier work (Odum et al., 1997b; Kleindienst et al., 1999; Cocker et al., 2001b; Sato et al., 2012) observed much lower SOA yield than this study due to the higher NO<sub>x</sub> conditions in these earlier work. Ng et al. (2007) observed similar SOA yields to this study under low NO<sub>x</sub> conditions with seed added before photooxidation. Nevertheless, this study focuses on the SOA yield difference among aromatic hydrocarbons with difference number of methyl substitutes on aromatic ring. We found the SOA yield trend in this work agrees with previous studies.

*6-page 31158, line 17, How much higher are the current benzene SOA yields compared to the cited studies?*

Current benzene SOA yield are more than two times higher than the cited studies under similar mass loadings. Borrás and Tortajada-Genaro(2012) and Martín-Reviejo and Wirtz (2005) use natural light which might cause some fluctuation in light intensity, temperature and other conditions and therefore affect SOA yield. Sato et al (2012) provided only one data point under low NO<sub>x</sub> condition at a comparatively low mass loadings (18 ug/m<sup>3</sup>) under different light source (19 Xe

arc lamp) compared with this study.

*7-page 31159, line 11, Change “suppresses SOA formation” to “suppresses formation of lower volatility products”*

Agree. We will fix it.

*8-page 31159, lines 12-14, The claim in this sentence has not yet been supported.*

*Perhaps change “indicates” to “suggests”*

Agree. We will fix it.

*9-page 31159, lines 25-26, Possibility (3) seems to be just an observation of behavior, not an explanation for the methyl group effect.*

Agree. We will change “three” possibilities to “two”. We will replace “;” before “(3)” with “.” Replace possibility (3) with the following sentence “Therefore, the methyl group increases hydrocarbon mass consumption more than particle mass formation”.

*10-page 31159, line 29, SOA yields at what point in the experiment? Yield varies with time/ $M_o/\Delta HC$  so it is important to specify what yield values are being used for the correlation.*

Agree. We will replace “average radical parameter” at page 31159, line 29 with “average radical concentrations throughout photooxidation”. The SOA yield we used is the final SOA yield at the end of the photooxidation. This work uses “average radical concentrations throughout photooxidation” and “average radical concentrations are calculated by dividing time integrated radical parameters with photooxidation time” as mentioned in Table S3. Therefore, the time and  $\Delta HC$  are considered in the “average radical concentrations”. Most SOA yield are under comparable mass loading ( $M_o < 60 \text{ ug/m}^3$ ) and the few large mass loading points should not dramatically the overall relationships we found.

*11-page 31160, line 2, OH is the only parameter with a statistically significant correlation ( $p < 0.05$ ). The strength of correlation values for all the other parameters are meaningless since the relationships aren’t statistically significant.*

Agree. Replace “the best correlated parameter” with “the only parameter investigated with a statistically significant correlation ( $p < 0.05$ )”.

*12-page 31160, line 15, Add a sentence explaining what  $f_{44}$  and  $f_{43}$  represent relative to degree of oxidation.*

We will add “A higher  $f_{44}$  and a lower  $f_{43}$  indicates a higher degree of oxidation (Ng et al., 2010, 2011).” before “The  $f_{44}$  and  $f_{43}$  evolution” at page 31160, line 15.

*13-page 31160, line 25, Explain what is meant by “evolution trend”. Also, tetramethylbenzene seems to shift too.*

Good point. We will add “and tetramethylbenzene” after “*m*-xylene” and will delete “and” before “*m*-xylene”. We will also add “Evolution of SOA composition (Heald, et al., 2009; Jimenez, et al., 2009) refers to SOA chemical composition changes with time and  $f_{44}$  and  $f_{43}$  evolution refers to the

change of  $f_{44}$  and  $f_{43}$  with time” before the “Significant  $f_{44}$  and  $f_{43}$  evolution” and delete “trend” after “evolution” at line 25 page 31160.

14-page 31161, line 1, Here and throughout the article it refers to general trends of parameters increasing or decreasing with the number of methyl groups. It would be helpful to make clear that it is not a uniform or consistent trend. For example, in Figure 2 the number of methyl groups is in the order 0,1,2,3,5,4,6, while in Figure 3a it is 0,1,3,2,4,6,5.

Agree. The slight difference in the order is due to the isomer impact on the chemical composition and yield, which is addressed in Li, et al (2016) (another paper submitted to ACP). We will add “It should also be noticed that the higher O/C and lower H/C observed in SOA formed from 1,2,4-trimethylbenzene (three methyl substitute aromatic hydrocarbon) than that from *m*-xylene (two methyl substitute aromatic hydrocarbon) is due to the isomer impact on SOA chemical composition, which is discussed in details by Li, et al (2016).” at line 25 on page 31162 after “SOA yield is dependent on SOA chemical composition”

15-page 31162, line 11, What is the “elemental ratio evolution trend” and how does it agree with the  $f_{44}$  vs  $f_{43}$  trend?

The elemental ratio evolution is defined similarly to  $f_{44}$  vs.  $f_{43}$  evolution. We will add “The change of elemental ratio (H/C and O/C) with time is referred as elemental ratio evolution.” before “The elemental ratio evolution trend agrees with the  $f_{44}$  vs.  $f_{43}$  trend.” and replace “evolution trend” and “trend” with “evolution” in this sentence. We will add “(significant evolution in benzene and slightly for toluene, *m*-xylene and 1,2,4,5-tetramethylbenzene)” in the end of the sentence “The elemental ratio evolution agrees with the  $f_{44}$  vs.  $f_{43}$ ” in order to clarify the point that the similarity of the two chemical evolution is about how significant the chemical evolution is during the SOA formation from each aromatic precursor.

16-page 31164, line 16, Only *m*-xylene results are reported. Would there be differences for the other xylenes (*o*-xylene, *p*-xylene)? Similarly for the tri- and tetra- methylbenzenes.

Good point. We have a detailed analysis on isomer structure impact (three different xylenes and three different trimethylbenzenes) on SOA chemical composition which can be found in Li et al.(2016).

17-page 31164, line 23, Pentamethylbenzene also shows a significant overestimation and should be mentioned.

Agree. We will insert in the end of line 4 page 31165 “It is also noticed that O/C and  $OS_c$  is slightly overestimated in SOA formed from pentamethylbenzene. This indicates that the methyl group hindrance impact on aromatic hydrocarbon oxidation should be explained by multiple pathways which have different impact on SOA formation.”

18-page 31166, line 14, Density underestimation doesn’t seem to “enlarges with increasing methyl group”, but appears about the same for 2,3,4,5 methyl groups. And should also mention, and possibly discuss, the overprediction for benzene and toluene.

Agree. The underestimation is not monotonically increasing with the number of methyl group since

similar products are expected to form even with the increase of methyl group as mentioned in Discussion 4.1. We will focus more on the general trend of the difference between density prediction and measurement while more methyl groups are attached to aromatic ring.

page 31166, line 14: We will replace "SOA density underestimation enlarges with increasing methyl group number" with "SOA density difference between prediction and measurement change from positive (0&1 methyl group) to negative (2,3,4 or 5 methyl groups) with increasing methyl group number."

31167 line 1: We will replace "where a larger negative error is seen as the number of methyl groups increases" with "where a change of error from positive to negative is seen as the number of methyl groups change from less than two to two or more than two "

Hence, the overprediction for benzene and toluene is also mentioned discussed.

*19-page 31172, line 6, Change "A decreasing trend" to "A generally decreasing trend"*

Agree. We will fix it.

*20-page 31172, line 10, Clarify what is meant by "aromatic aging". Aging can refer to many different changes. The statement would be correct if it defines aging as transformation to less volatile compounds.*

Agree. We will replace "aromatic aging" with "the oxidation of aromatic hydrocarbon to less volatile compounds".

*21-page 31172, lines 15-16, Are benzene and toluene always the most important precursors of those studied here? Or is it just under low NO<sub>x</sub> conditions?*

This study confirms the importance of benzene and toluene to the SOA formation among all aromatic hydrocarbon under low NO<sub>x</sub> conditions. Earlier work on SOA formation from aromatic hydrocarbons suggest that benzene and toluene are dominating SOA precursors under high NO<sub>x</sub> and NO<sub>x</sub> free conditions (Odum, et al., 1997; Takekawa, et al., 2003; Ng, et al., 2007; Borrás and Tortajada-Genaro, 2012). The key point that low NO<sub>x</sub> conditions are much more atmospherically relevant than high NO<sub>x</sub> conditions and therefore benzene and toluene are critical aromatic precursors for SOA formation especially in urban areas.

*22-page 31172, lines 17-19, Hexamethylbenzene is not the only compound with a discrepancy between predicted and measured oxidation, calling into question the claim of uniqueness. Both m-xylene and pentamethylbenzene are much less oxidized than predicted.*

We agree that we also observed discrepancy between prediction and measurement in the oxidation of *m*-xylene and pentamethylbenzene. However, only hexamethylbenzene is more oxidized than the prediction and *m*-xylene and pentamethylbenzene are less oxidized than the prediction. The lower oxidation of *m*-xylene than the prediction is associated with the xylene isomer impact on SOA formation and chemical composition which is further discussed in Li, et al (2016) ACPD paper. The lower oxidation of pentamethylbenzene than the prediction is explained by the methyl group hindrance on oxidation. What is unique in hexamethylbenzene is that the oxidation is higher than the prediction even with maximum methyl group hindrance possibility. The slight H/C decrease in Fig 3b and the underestimation in OSc and O/C all support the uniqueness

of hexamethylbenzene.

*Technical Corrections:*

23-page 31158, line 7, Should "(Table 2)" read "(Table S2)"?

Good point. Corrected.

24-page 31164, lines 14-15, add "\_SOA" to subscripts for "O/C<sub>pre,i</sub>" and "H/C<sub>pre,i</sub>" to make clear it is the elemental ratio of SOA, not of the precursor.

Agree. We will change "O/C<sub>pre,i</sub>" and "H/C<sub>pre,i</sub>" to "O/C<sub>pre,i\_SOA</sub>" and "H/C<sub>pre,i\_SOA</sub>".

25-page 31165, line 7, The R<sup>2</sup> correlation values listed in the text seem too high for the data shown in Figure S3.

Good point. We will replace "R<sup>2</sup>" with "Pearson correlation".

26-page 31167, line 8, Define VFR the first time the acronym is used.

Agree. We should be consistent with the terminology we use. In page 31175, line 12, we will replace "Volume remaining fraction (VRF)" with "Volume fraction remaining (VFR)".

27-page 31168, lines 4-5, Correlation coefficients and p-values listed in the text are not the same as those in Table S5.

Fixed. Replace "O/C (0.932, p = 0.02) and OSc (0.931, p = 0.002)" with "O/C (0.937, p = 0.002) and OSc (0.932, p = 0.02)".

28-pages 31190-31191, The coloring in Figures 2 and 3 that corresponds to the number of methyl groups would be much more useful if it was consistent. In Figure 2 and Figure 3a the colors for 0/1/2/3/4/5/6 methyl groups appears to be red/yellow/green/light blue/dark blue/orange/gray (but with purple dots for 5 and 6). In Figure 3b, however, the colors are red/orange/green/green/light blue/dark blue/purple.

Thanks for suggestion. We will change Figure 3b color to match the colors in Figure 2 and Figure 3a. See below for the update in Figure 3b color. We keep the dashed line between toluene precursor and SOA as orange since yellow is too bright to show clearly in a white background.

