Response to Reviewer #3

General comments:

Liu et al present a series of smog chamber experiments where secondary organic aerosol (SOA) was generated from the photo-oxidation of gasoline vehicle exhaust. Data are presented from three vehicles. For each vehicle, an experiment was conducted both with and without the addition of SO_2 to the smog chamber. In all cases, adding SO_2 increased SOA production.

Overall the manuscript is topically relevant to Atmospheric Chemistry and Physics and should eventually be published. However, in my opinion the manuscript requires major revisions before it is ready for final publication.

I agree with Reviewer #2 that a thorough copy edit of the manuscript is required. There are many instances where the wording is awkward. My concerns about the manuscript run deeper than simple copy editing. Even after multiple readings, I am still left scratching my head regarding the major conclusions of this work. In many ways the manuscript reads as a long list of observations with very little in the way of interpretation. The authors need to make a stronger case for the new knowledge gained from these experiments and the atmospheric relevance or insight that these results provide.

Reply: The language of the revised manuscript has been edited by a native speaker. The major conclusion of this work is the synergy effect of SO_2 and gasoline vehicle exhaust in forming secondary aerosols. This has been emphasized in the section “Conclusions”. According to the referee’s comments, some paragraphs were rewritten and the interpretations were expanded in the revised manuscript. These revisions were explained when we responded to the specific comments.

Specific comments:

Q1- Section 2.4 - Toluene is used to determine the average [OH] in each experiment. While this is a common method for estimating [OH], it seems inappropriate to assume a constant [OH] for the entire experiment. [OH] is likely to change over the course of photo-oxidation, and therefore it would be more appropriate for the authors to calculate [OH] over shorter time scales (e.g., 1-hr or 30-min averages). Additionally, the authors do not specify if [OH] estimates only account for the portion of the experiment when the UV lamps are on. While [OH] likely drops rapidly to zero once the UV lamps are turned off, if sufficient O_3 is formed during photo-oxidation, it would be possible for [OH] to remain non-zero during the dark period at the end of the experiment.

Reply: We agree with the referee that the concentration of OH was not constant during the entire experiment. The average OH concentrations were reported in order that they can be easily compared with those observed in ambient air. As shown in Figure 1, three constant concentrations could well represent the variation of OH concentration during the irradiation. Segmented OH concentrations would introduce lower uncertainties when determining the steady state concentrations of stabilized CIs. Thus we calculated the segmented OH concentrations for experiments with SO_2 and listed in Table 1 (Table S1 in the Supplement).

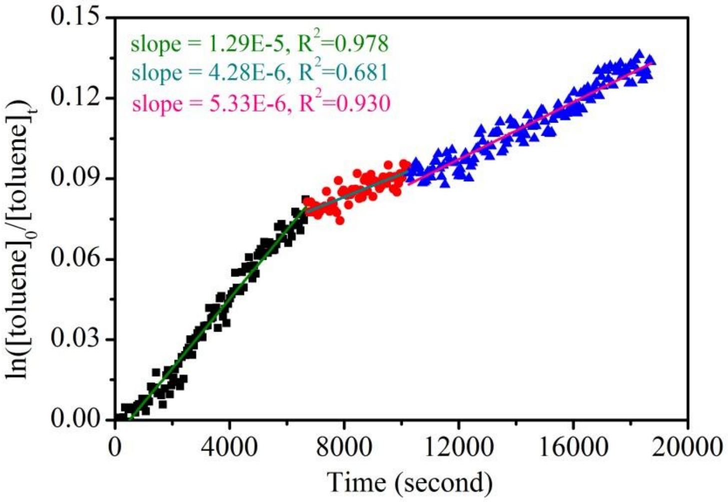
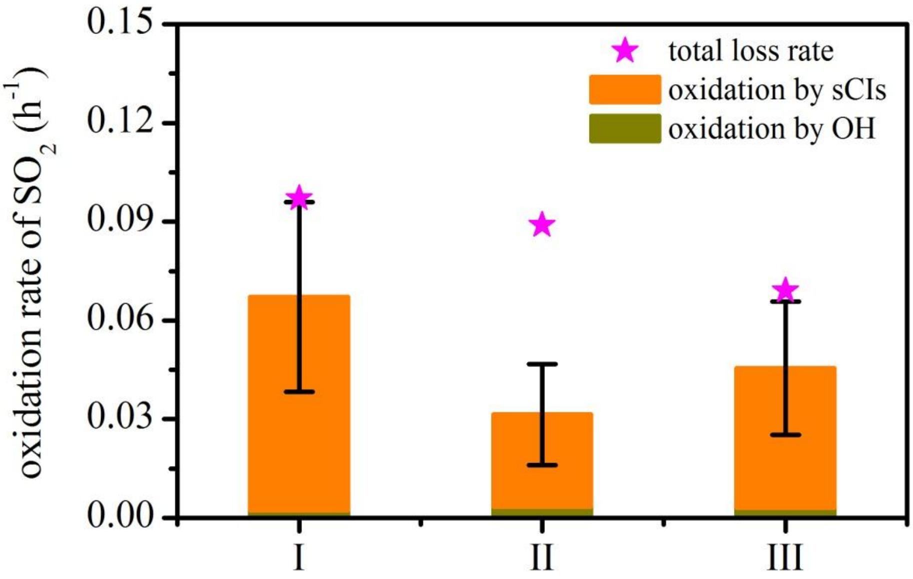


Figure 1. *ln*($[toluene]_0/[toluene]_t$) versus time t.

Table 1. Segmented concentrations of OH radical for experiments with SO_2.

Exp #	Time period (h)	OH (×10^6 molecules cm^{-3})
I-2	0-1.85	2.3
	1.85-2.83	0.76
	2.83-5.0	0.95
II-2	0-0.5	0.7
	0.5-2.7	1.68
	2.7-5.0	0.43
III-2	0-1.57	1.56
	1.57-3.67	0.28
	3.67-5.0	1.31

Using the segmented OH concentrations, we re-run the MCM model and obtained the loss rate of SO_2 reacted with sCIs to be 0.065 h^{-1}, 0.028 h^{-1} and 0.042 h^{-1}, similar to the values of 0.071 h^{-1}, 0.030 h^{-1} and 0.045 h^{-1} when the average OH concentrations were used. This will not change our conclusion that the oxidation of SO_2 by sCIs dominates the conversion of SO_2. The relevant changes of these data and Fig. 6 (now Fig. 7) (listed as follows) have been revised in the manuscript.



[OH] estimates only account for the portion of the experiment when the UV lamps are on. This has been specified in the revised manuscript.

The following text has been added to the revised manuscript.

“Average OH concentrations were determined when the black lamps were on. Segmented OH concentrations were also estimated and listed in Table S1 in the Supplement for experiments with the addition of SO_2. Similar concentrations of sCIs were determined in subsequent section 2.5 when average and segmented OH concentrations were respectively used for the same experiment.”

Q2- Section 2.4 describes how the average [OH] was calculated, but the values are not reported. Average [OH] needs to be reported, especially since the authors argue that OH oxidation alone is insufficient to explain the observed SO_2 loss in these experiments.

Reply: The following text has been added to the revised manuscript.

“The average OH concentrations during photo-oxidation ranged from 0.73 to 1.29×10^6 molecules cm^{-3}, approximately 5 times lower than that during summer daytime (Seinfeld and Pandis, 1998).”

Q3- The factor phi in the numerator of equation 5 is not defined.

Reply: The reaction 1 was revised as follows:

$$\text{alkene} + O_3 \longrightarrow \phi \text{sCIs} + \text{products} \qquad \text{(R1)}$$

where ϕ represents the yield of sCIs from ozonolysis of alkenes. This has been clarified in the revised manuscript.

Q4- Section 2.5-It is not clear how the concentrations of stabilized CI were calculated with the master chemical mechanism. Lines 19-21 of page 23621 suggest that the full chemical mechanism was used to determine concentrations of sCI. However, lines 1-7 of page 23622 suggest that all sCI were treated as CH_2OO, CH_3CHOO, or $(CH_3)_2CHOO$. However, the lumping scheme used to reduce the possible set of CIs to these three is not described. Additionally, the yields of the three possible CIs used in the model sum to a number greater than unity.

Reply: Table 2 (Table 4 in the revised manuscript) shows the concentrations of alkenes included in the model and the category of sCIs. N-alkenes and branched alkenes respectively contributed 89.9%-93.0% and 7.0%-10.1% of the alkenes, of which ethene and propene were two main components, accounting for as high as

66.8%-81.3%. Due to the unavailability of reaction rate coefficients for C_2H_5CHOO, C_3H_7CHOO, $C_2H_5(CH_3)COO$ and $(CH_3)_2CHCHOO$ with SO_2, NO_2 and H_2O, we assumed these parameters were same as CH_2OO. This assumption seems reasonable as the precursors of C_2H_5CHOO, C_3H_7CHOO, $C_2H_5(CH_3)COO$ and $(CH_3)_2CHCHOO$ contribute only a small portion of alkenes.

Table 2. Concentrations of alkenes included in the model and the category of sCIs.

Sepecies	Concentration (ppb)			sCIs
	I-2	II-2	III-2	
ethene	333.1	113.8	202.0	CH_2OO
propene	95.8	50.3	52.6	CH_2OO, CH_3CHOO
1-butene	30.9	49.1	13.1	CH_2OO, C_2H_5CHOO
cis-2-butene	7.6	4.8	7.1	CH_3CHOO
trans-2-butene	9.9	6.4	9.6	CH_3CHOO
1-pentene	3.8	0.3	3.1	CH_2OO, C_3H_7CHOO
cis-2-pentene	5.2	1.2	5.2	CH_3CHOO, C_2H_5CHOO
trans-2-pentene	8.5	2.6	9.4	CH_3CHOO, C_2H_5CHOO
2-methyl-1-butene	11.9	5.4	12.4	CH_2OO, $C_2H_5(CH_3)COO$
3-methyl-1-butene	2.4	0.8	2.4	CH_2OO, $(CH_3)_2CHCHOO$
2-methyl-2-butene	17.8	10.9	22.7	CH_3CHOO, $(CH_3)_2COO$
cis-2-hexene	0.8	0	1.5	CH_3CHOO, C_3H_7CHOO

The ozonolysis of alkene will form a primary ozonide that rapidly decomposes to two carbonyl compounds in conjunction with so called excited CIs. The excited CIs can decompose or be stabilized by collision to form sCIs. Thus it is reasonable that the sum of the yields of CH_2OO, CH_3CHOO, and $(CH_3)_2CHOO$ is larger than unit because they might be formed from different primary ozonides.

This section has been revised and now reads:

"Ozonolysis of alkenes will form a primary ozonide through a 1,3-cycloaddition of ozone across the olefinic bond. The primary ozonide then rapidly decomposes to two carbonyl compounds, called excited CIs, which can be stabilized by collision to form sCIs (Heard et al., 2004; Johnson and Marston, 2008).

$$\text{alkene} + O_3 \longrightarrow \phi\text{sCIs} + \text{products} \qquad \text{(R1)}$$

where ϕ represents the yield of sCIs from ozonolysis of alkenes. The four main losses of sCIs are reactions with H_2O, SO_2 and NO_2 and unimolecular decomposition.

$$sCIs + H_2O \longrightarrow products \qquad (R2)$$

$$sCIs + SO_2 \longrightarrow SO_3 + products \qquad (R3)$$

$$sCIs + NO_2 \longrightarrow products \qquad (R4)$$

$$sCIs \longrightarrow products \qquad (R5)$$

The steady state concentration of sCIs will be

$$sCIs_{steady-state} = \frac{\phi K_{R1}[O_3][alkene]}{K_{R2}[H_2O] + K_{R3}[SO_2] + K_{R4}[NO_2] + K_{R5}} \qquad (5)$$

where K_{R1} is the rate coefficient for the ozonolysis of alkene; K_{R2}, K_{R3}, K_{R4} and K_{R5} represent the rate constant for reactions of sCIs with H_2O, SO_2, NO_2 and decomposition, respectively.

The steady state concentration of sCIs throughout the entire experiment was estimated in this study. The production rate of sCIs was dependent on both the concentrations and composition of alkenes in the exhausts. Detailed gas-phase mechanisms of alkenes from the MCM v3.3 were run to determine the time-resolved concentrations of sCIs in the experiments. The concentrations of alkenes included in the model and the category of sCIs are presented in Table 4. N-alkenes and branched alkenes respectively contributed 89.9%-93.0% and 7.0%-10.1% of the alkenes, with ethene and propene as two main components accounting for 66.8%-81.3%. Only the gas-phase mechanisms of alkenes were included in the model, with the concentrations of OH radicals, SO_2, O_3 and NO_2 constrained to measured concentrations. Thus, the neglect of alkanes and aromatics would not influence the steady state concentrations of sCIs, as was confirmed by running the models including alkanes and aromatics. K_{R2}, K_{R3}, K_{R4} and K_{R5} for CH_2OO, CH_3CHOO, and $(CH_3)_2COO$ used in the model were listed in Table 5. The rate coefficients for other sCIs including C_2H_5CHOO, C_3H_7CHOO, $C_2H_5(CH_3)COO$ and $(CH_3)_2CHCHOO$ reacted with H_2O, SO_2, NO_2 and their unimolecular decomposition were assumed to be same as CH_2OO. This assumption seems reasonable as the precursors of C_2H_5CHOO, C_3H_7CHOO, $C_2H_5(CH_3)COO$ and $(CH_3)_2CHCHOO$ contributed only a small portion of alkenes in this study. The yields of CH_2OO, CH_3CHOO, and $(CH_3)_2COO$ used in the model were 0.37, 0.38 and 0.28, respectively, while yields of other sCIs were assumed to be same as CH_2OO."

Q5- Page 23623, Line 4: "NO was fast oxidized" needs to be edited.

Reply: "fast oxidized" was changed to "rapidly consumed" in the revised manuscript.

Q6- Vehicle 1 and 2 (Fig 2 and 3) both generate particulate nitrate in the no-SO_2 experiment, and in each case the nitrate mass falls after an initial peak (I am assuming that Figs 1-3 show wall loss corrected masses of PM components). Nitrate formation is suppressed in the with-SO_2 experiments for both vehicles. The nitrate is not discussed at all in the text. This needs to be remedied. Is the nitrate dominated by inorganic or organic nitrates? If the nitrate is organic, and adding SO_2 causes a large loss of organic nitrates in the SOA, this would be an extremely interesting finding.

Reply: The nitrate portion of inorganic and organic nitrates primarily fragments to NO^+ and NO_2^+. The NO^+/NO_2^+ ratio is usually substantially higher for organic nitrates compared with ammonium nitrate (Farmer et al., 2010; Sato et al., 2010). The NO^+/NO_2^+ ratios for the no-SO_2 experiments were 1.99-2.60, within the range 1.08-2.81 for ammonium nitrate (Farmer et al., 2010; Sato et al., 2010), suggesting that nitrates detected in these experiments could be attributed to ammonium nitrate. Ammonium nitrate was likely formed by reactions of nitric acid formed from NO_x and ammonia, which is substantially higher in China's LDGV exhaust (Liu et al., 2014). The NO^+/NO_2^+ ratios for experiments with SO_2 were 3.9-5.0, significantly higher than ratios measured for ammonium nitrate and also similar to ratios for organic nitrates (3.82-5.84) from the photo-oxidation of aromatic hydrocarbons (Sato et al., 2010), indicating organic nitrates dominated nitrate formation in these experiments. High concentration of SO_2 suppressed the formation of ammonium nitrate in experiments with SO_2 as NH_3 was liable to react with sulfuric acid rather than nitric acid (Pathak et al., 2009).

The following text has been added to the revised manuscript:

"Substantial nitrates were formed for vehicles I and II (Figs. 3a and 4a) and could be attributed to ammonium or organic nitrates. The identification of ammonium and organic nitrates may be obtained from the NO^+/NO_2^+ ratio, which is typically substantially higher for organic nitrates compared with ammonium nitrate (Farmer et al., 2010; Sato et al., 2010). The NO^+/NO_2^+ ratios for experiments I-2 and II-2 were 1.99-2.60, within the range 1.08-2.81 for ammonium nitrate (Farmer et al., 2010; Sato et al., 2010), suggesting that nitrates detected in the two experiments could be attributed to ammonium nitrate. Ammonium nitrate was likely formed by reactions of nitric acid formed from NO_x oxidation and ammonia, which is substantially higher in China's LDGV exhaust (Liu et al., 2014). The NO^+/NO_2^+ ratios for experiments with SO_2 were 3.9-5.0, significantly higher than ratios measured for ammonium nitrate and also similar to ratios for organic nitrates (3.82-5.84) from the photo-oxidation of aromatic hydrocarbons (Sato et al., 2010), indicating organic nitrates dominated nitrate formation in these experiments. High concentration of SO_2 suppressed the formation of ammonium nitrate in experiments with SO_2 as NH_3 was liable to react with sulfuric acid rather than nitric acid (Pathak et al., 2009)."

Q7- A major theme of the manuscript is described in Figure 6 - SO_2 losses cannot be explained by OH oxidation alone. The authors attribute additional SO_2 loss to reactions with stabilized CI. I do not find their argument convincing. Part of my skepticism arises from comments 3 and 4 above, and the author's generally cursory description of their use of the MCM in this work.

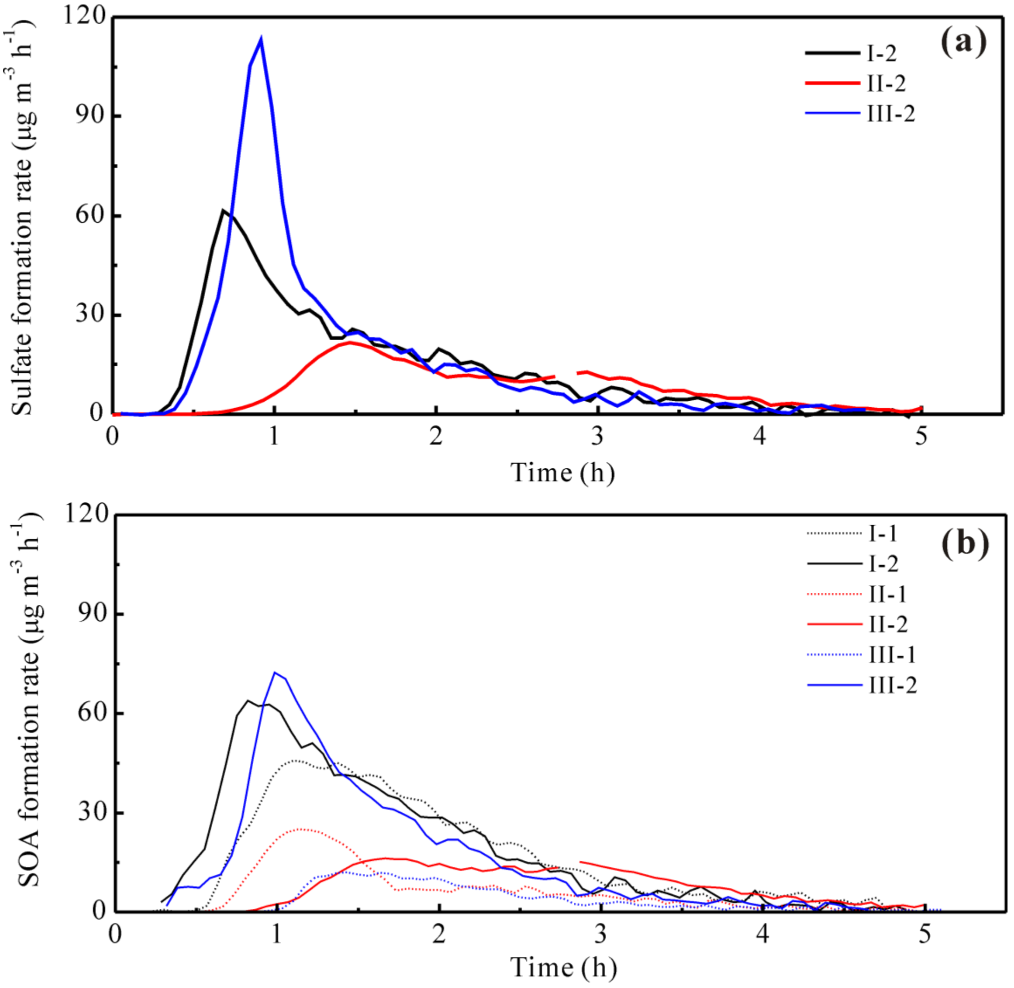
Reply: This issue has been addressed in Q3 and Q4.

Q8- I fundamentally disagree with the author's assertions (summarized in the Conclusions) that gasoline exhaust has sufficient alkenes to be a major source of sCI in the atmosphere and that these sCI could play a major role in SOA formation. I simply don't see the evidence presented in this manuscript to properly justify this claim. Gasoline exhaust is dominated by alkanes and aromatics (e.g., May et al 2014; Schauer et al 2002), not alkenes, and there are many other, larger sources of atmospheric alkenes (e.g., isoprene and monoterpenes).

Reply: We agree with the referee that gasoline vehicle exhaust is not the major source of sCIs, but its contribution to alkenes will influence the formation of sCIs and thus facilitate the formation of secondary aerosols, especially in urban areas with high density of gasoline vehicles. For instance, Zhang et al. (2015) estimated that vehicle exhaust contributed 32-49% of ethene and 35-41% of propene in the Pearl River Delta region. Considering the higher limit of alkene content in China's gasoline fuel standard, we point out that limiting the content of alkenes in China's gasoline might benefit the control of both ozone and secondary aerosols.

Q9- I cannot tell what I am supposed to learn from Figure 5. The figure is very hard to read and interpret. It either needs to be edited for clarity or removed.

Reply: This figure mainly shows the burst increases at the initial stage of sulfate and SOA formation, which may be related to fast increase of $PM_{2.5}$ and occurrence of haze (He et al., 2014). The same y-axis scale, suggested by Reviewer 2, was used to facilitate direct comparisons between the time series of sulfate and SOA production rates.



Q10- Is it possible that some of the SO_2 loss, and some of the resultant PM mass during photo-oxidation, is in the form of organosulfates? Organosulfates have been observed in the ambient atmosphere using AMS, so marker ions should be available to investigate this possibility.

Reply: The S-bearing organic fragments $C_xH_yO_zS$ can be used as marker ions to quantify organosulfates (Huang et al., 2015). In this study the fragments $C_xH_yO_zS$ were almost not appreciable. Using the methods of Huang et al. (2015), we estimated the mass ratio of organosulfates to sulfate was less than 0.5%. Thus the formation of organosulfates could be negligible in this study.

The following text has been added to the revised manuscript.

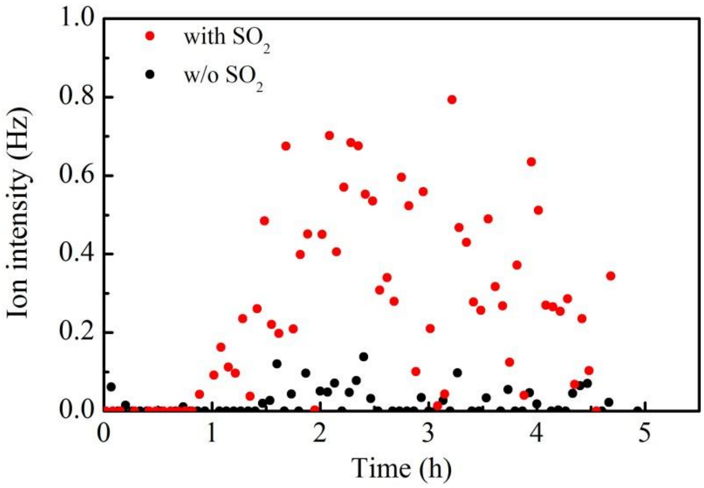
"The S-bearing organic fragments $C_xH_yO_zS$ determined by HR-TOF-AMS can be used as marker ions to quantify organosulfates (Huang et al., 2015). In this study the fragments $C_xH_yO_zS$ were almost not appreciable. Using the methods of Huang et al. (2015), we estimated the mass ratio of organosulfates to sulfate was less than 0.5%. Thus the formation of organosulfates could be negligible in this study."

Q11- Figure 8 is nearly uninterpretable. What does the intensity on the vertical axis indicate? It seems to first order that m/z 88 is more abundant in the SO_2 experiment, but there is a lot of scatter in the data.

Reply: This figure (now Fig. 9 in the revised manuscript) has been revised as follows. The y-axis is the ion intensity of m/z 88 measured by AMS. The scatter of the data might be due to the low intensity of m/z 88. But it is obvious that m/z 88 is more abundant in the SO_2 experiment, indicating the important role of acid-catalyzed heterogeneous reactions in the SOA formation from gasoline vehicle exhaust.

The sentence "*As shown in Fig. 8, the ion fragment m/z 88 that can only arise from a glyoxal oligomer (Liggio et al., 2005) had a higher intensity under higher acidity condition, indicating the important role of acid-catalyzed heterogeneous reactions in the SOA formation from gasoline vehicle exhaust.*" has been revised and now reads:

"Fig. 9 shows the ion intensity of fragment m/z 88 that can arise only from a glyoxal oligomer (Liggio et al., 2015). The scatter of the data might be due to the low intensity of m/z 88. However, the experiment with the addition of SO_2, with higher particle acidity, exhibited relatively higher m/z 88 intensity. This indicated the important role of acid-catalyzed heterogeneous reactions in SOA formation from gasoline vehicle exhaust."



Q12- What does Figure 9 add to the manuscript that is not present in Fig 7? Its presence in the manuscript seems redundant.

Reply: Fig. 7 (now Fig. 8) mainly shows the correlation between aerosol acidity and the SOA production factor. While Fig. 9 (now Fig. 10) provides information about the burst increase of SOA, which may be related to fast increase of $PM_{2.5}$ and occurrence of haze (He et al., 2014).

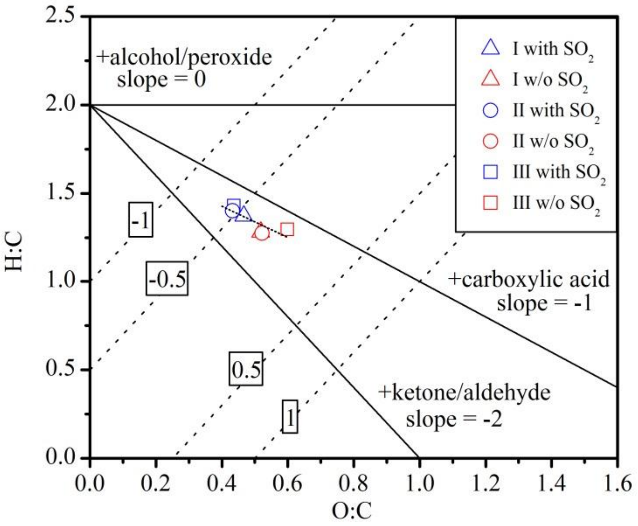
Q13- Fig 10 should include the composition of the POA.

Reply: Concentrations of POA in this study were lower than 0.5 μg m^{-3}, typically regarded as not appreciable (Presto et al., 2014) and insufficient to determine the initial H:C and O:C. The six data points fall along a line with a slope of -0.87. This suggests that SOA formation in these experiments is a combination of carboxylic acid and alcohol/peroxide formation (Heald et al., 2010; Ng et al., 2011). The slope for the mixture of SO_2 and exhausts is slightly higher than those for exhausts alone (Liu et al., 2015). The slope of -0.87 and intercept of around 1.8 are similar to the observation for ambient data with a slope of approximately -1 and intercept approximately 1.8 (Heald et al., 2010), suggesting that SOA chemistry for the mixture of SO_2 and gasoline vehicle exhausts is atmospheric relevant.

The following text has been added to the revised manuscript.

"Concentrations of POA were lower than 0.5 μg m^{-3}, typically regarded as not appreciable (Presto et al., 2014) and insufficient to determine the initial H:C and O:C, thus only SOA data were plotted on the diagram."

"The slope of -0.87 (Fig. 11) for the mixture of SO_2 and exhaust, slightly higher than those for exhaust alone (Liu et al., 2015), indicates that SOA formation in these experiments is a combination of carboxylic acid and alcohol/peroxide formation (Heald et al., 2010; Ng et al., 2011). The slope of -0.87 and intercept of approximately 1.8 are similar to the observation for ambient data with a slope of approximately -1 and intercept approximately 1.8 (Heald et al., 2010), suggesting that SOA chemistry for the mixture of SO_2 and gasoline vehicle exhaust is atmospheric relevant."



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