Response to Reviewer #1

General comments:

Liu et al. present findings from a set of photochemistry experiments conducted using an environmental chamber where gasoline exhaust from light-duty gasoline vehicles is mixed with SO_2. Liu et al. find that the addition of SO_2 enhances secondary organic aerosol (SOA) production substantially and conclude that the enhancement comes from acid-catalyzed reactions on the aerosol surface.

The experiments are novel (particularly relevant for developing economies with a burgeoning demand for coal-driven electricity and gasoline-powered motor vehicles) and performed with an extensive suite of instrumentation to systematically study SOA formation and perturbations thereof from a very important anthropogenic source, namely light-duty gasoline vehicles. However, the manuscript has two large shortcomings. One, the manuscript is not very clear in motivating the work and do not offer a comprehensive analysis of the data (specific comments below). And two, the written communication can be significantly improved as the current version has lots of problems with sentence construction and grammar (I have flagged a few common mistakes but I recommend that the senior authors on the paper help rewrite the paper). After the authors respond to my technical comments, I would be happy to recommend publication on the scientific merit of the work but do not feel comfortable at the current time.

Reply: For the two aspects raised by the reviewer, we first thank the reviewer for the specific comments on data interpretation below, for which we have responded point-to-point. For the problem in English writing, we have got the manuscript edited by a native speaker.

Major comments:

Role of acidity and the reliance on water: The arguments in the current paper need to be clarified and/or improved significantly if the manuscript is going to convince me that acidity plays an important role in SOA enhancement. Answering the following questions either in the manuscript or in the response could help develop the various arguments for and against the author’s hypothesis.

(a) The authors keep referring to the acid-catalyzed reaction but fail to explain what it means (to the general reader of this literature, offering a brief explanation of the reaction chemistry would help communicate the findings better). When I read ‘acid-catalyzed’, I visualized the SOA formed from isoprene epoxydiols where isoprene epoxydiols are taken up by aerosol water and catalyzed to organosulfates and tetrols; is that what the authors mean? If it is, then the proposed acid-catalyzed reactions (is Figure 8 the only evidence?) would need aerosol water. Does a relative humidity of 50% ensure aerosol water? What does a thermodynamic model (AIM, ISORROPIA) predict? Do the authors measure aerosol water? If the answers to the above questions are no, would the organic compounds depress the deliquescence RH and ensure aerosol water at 50% RH?

Reply: Aromatic hydrocarbons are vital SOA precursors in gasoline vehicle exhaust (Nordin et al., 2013; Gordon et al., 2014; Liu et al., 2015). Aromatics react with OH radicals in the gas-phase and produce multifunctional carbonyls that will be transformed more rapidly to low volatility products through acid-catalyzed heterogeneous reactions, including hydration, polymerization, formation of hemiacetal/trioxane, aldol condensation, and cationic rearrangement (Jang et al., 2002; Cao and Jang, 2007). As shown in Figure 1, aerosol water is needed for the hydration of carbonyls and influences the acid-catalyzed reactions. Liquid water content (LWC) in this study was not measured but predicted by the AIM-II model, with an average value of 5.5±4.5 μg m^{-3} when SOA formation rate peaks. Cao and Jang (2007) observed the presence of acid-catalyzed reactions for oxidation of toluene and 1,3,5-trimethylbenzene even at RH of approximately 22%. As LWC is mainly controlled by RH and temperature (Guo et al., 2015), we conclude that RH of 50% in this study ensured aerosol water for acid-catalyzed reactions.

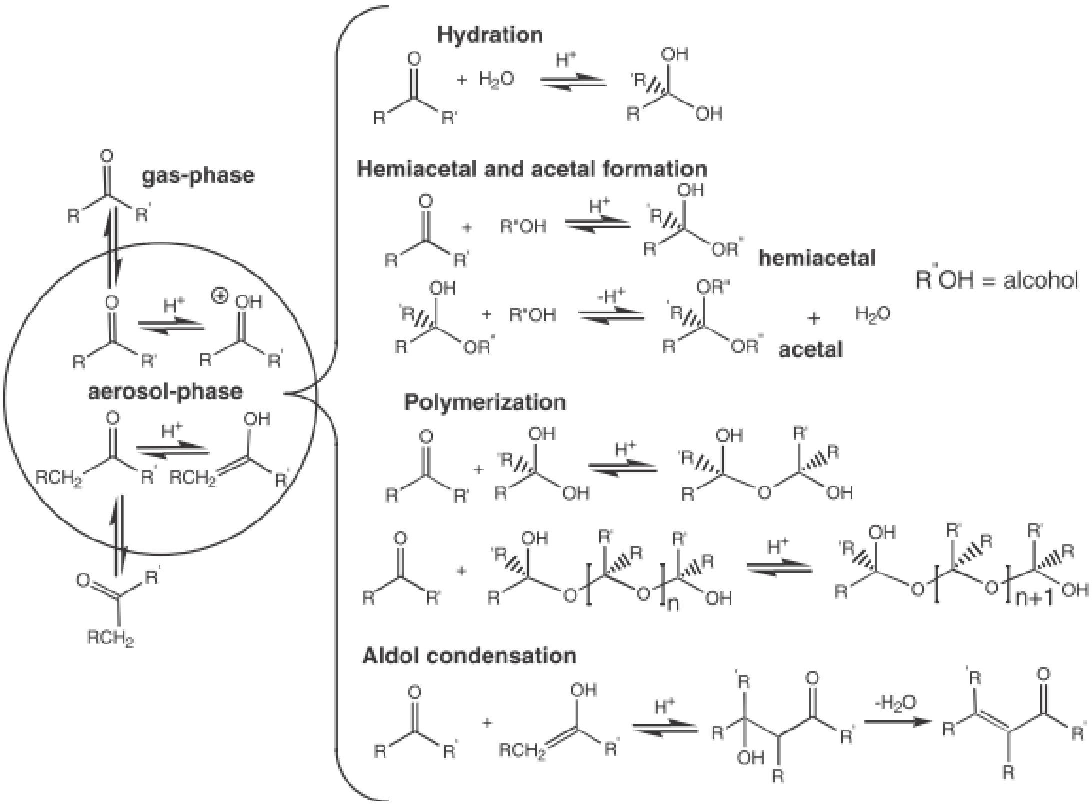


Figure 1. Acid-catalyzed heterogeneous reaction mechanisms of atmospheric carbonyls (derived from Jang et al. (2002)).

The sentence "*Gas-phase oxidation products of aromatic hydrocarbons in the exhausts, like multifunctional carbonyl glyoxal, would be transformed more quickly to low volatility products through acid-catalyzed heterogeneous reactions (Jang et al., 2002; Cao and Jang, 2007) and thus caused increasing SOA production.*" has been revised and now reads:

"Gas-phase oxidation products of aromatic hydrocarbons in the exhaust, like multifunctional carbonyl glyoxal, would be transformed more rapidly to low volatility products through acid-catalyzed heterogeneous reactions (e.g. hydration, hemiacetal and trioxane formation, polymerization, aldol condensation, and cationic rearrangement) (Jang et al., 2002; Cao and Jang, 2007) and thus caused increasing SOA production. Aerosol water is needed for the hydration of carbonyls and therefore it influences the acid-catalyzed reactions. Liquid water content (LWC) in this study was not measured but predicted by the AIM-II model, with an average value of 5.5 ± 4.5 μg m^{-3} when SOA formation rate peaks, ensuring the occurrence of acid-catalyzed reactions.”.

(b) In the simplest terms, the data suggests that the production of SOA is correlated with the additional production of sulfate. Given that the OH exposure is the same, the enhancement in SOA is surprising and novel. However, the correlation with acidity (estimated using a model that will predict a higher acidity with increased sulfate) follows from the production of sulfate and does not necessarily imply an SOA pathway dependent on acidity. While there is prior evidence for acid-catalyzed reactions, how can the authors be sure that the reaction chemistry is in the particle-phase and not in the gas-phase? Could it be possible that the gas-phase chemistry for SO_2 oxidation applies to SOA precursors? Is there prior evidence for such?

Reply: SO_2 is readily oxidized by OH radical and sCIs in the gas-phase or by H_2O_2 and O_3 through in-cloud processes in aqueous-phase (Lelieveld and Heintzenberg, 1992) to form sulfuric acid. To our knowledge, there are still no reports on gas-phase chemistry for SO_2 oxidation applying to SOA formation. Recent studies indicate that sCIs derived from monoterpenes can form organic acid and hydroperoxides, contributing to SOA formation (Heaton et al., 2009; Ma et al., 2009). However, CH_2OO and CH_3CHOO were the main sCIs in this study and formed formic acid and acetic acid in the gas-phase. Thus the contribution of sCIs to SOA formation may be negligible in this study. The fragment m/z 88 can arise only from a glyoxal oligomer that formed through acid-catalyzed reactions (Liggio et al., 2015). As shown in Fig. 9 in the revised manuscript, the relatively higher intensity of m/z 88 under higher acidity condition indicated the important role of acid-catalyzed heterogeneous reactions in the aerosol-phase in SOA formation from gasoline vehicle exhaust.

(c) Since the findings suggest a strong correlation of sulfate and SOA, conceivably, a simpler and more revealing experiment would be to inject dry and wet ammonium sulfate seed. This would test if the SOA production was indeed dependent on the acidity and eliminate doubt regarding the role of unknown gas-phase oxidation pathways (e.g., SCI + SOA precursor).

Reply: A photo-oxidation experiment of exhaust from vehicle I in the presence of ammonium sulfate seeds (53.3 μg m^{-3}) with RH of 59% was conducted to explore the effect of sulfate on SOA formation as particle acidity is typically driven by sulfate. The SOA production factor was 22.2 mg kg^{-1} fuel, comparable with 26.2 mg kg^{-1} fuel for experiment I-1 (without SO_2), indicating that sulfate may not directly influence SOA production. Thus, the SOA production was indeed dependent on the particle acidity. The experimental condition was added to Table 2 in the revised manuscript.

The following text has been added to the revised manuscript.

"A photo-oxidation experiment of exhaust from vehicle I in the presence of ammonium sulfate seeds (53.3 μg m^{-3}) with RH of 59% (Table 2) was conducted to explore the effect of sulfate on SOA formation as particle acidity is typically driven by sulfate. The SOA production factor was 22.2 mg kg^{-1} fuel, comparable with 26.2 mg kg^{-1} fuel for experiment I-1, indicating that sulfate may not directly influence SOA production. Thus, the SOA production was indeed dependent on the particle acidity."

Crigee Intermediates (CI): The conclusions about CIs are based on model predictions of CIs from the MCM. Are the methods described in Section 2.5 or the predictions of CIs validated in the past? (I did not see any relevant references). How confident are the authors in those methods and predictions? In addition, a lot of people outside the atmospheric chemistry realm would be interested in this work since it deals with vehicular exhaust. A short introduction to CIs and citations to the most relevant literature surrounding CIs would help the reader. Also, could stabilized CIs (SCIs) directly oxidize SOA precursors to form SOA? Could one use a well-informed reaction rate for SOA precursor and SCIs to test this hypothesis?

Reply: The equation (5) was widely used to predict the steady state concentration of sCIs (Welz et al., 2012; Newland et al., 2015). New published rate constants and yields of sCIs were adopted in this study to accurately estimate the steady state concentrations of sCIs. Our study provides a method to estimate sCIs by MCM in chamber experiments. Recent studies indicate that sCIs derived from monoterpenes can form organic acid and hydroperoxides, contributing to SOA formation (Heaton et al., 2009; Ma et al., 2009). However, CH_2OO and CH_3CHOO were the main sCIs in this study and formed formic acid and acetic acid in the gas-phase. Thus the contribution of sCIs to SOA formation may be negligible in this study.

The following sentence has been added to the revised manuscript.

"This equation was widely used to predict the steady state concentration of sCIs in the atmosphere (Welz et al., 2012; Newland et al., 2015)."

A brief introduction to the formation of sCIs was added to Section 2.5.

"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)."

Vapor Wall-loss Rates: While the authors mention vapor wall-losses, they do not pay it enough attention. Clearly, there is the issue of determining the right emission factors for SOA. Presumably these would scale linearly for all the experiments and not have a large impact on the findings from this work. However, vapor wall-loss is chemistry dependent (volatility as shown by Zhang et al. and structure as shown by Matsunaga and Ziemann). Can the authors speculate or look at the data in more detail to identify biases that might result in varying wall-loss rates with the addition of SO_2? More importantly, the authors speculate that the increased SOA production could come from differences in the condensable sink (very low to begin with due to very low POA concentrations) associated with sulfate production; the fact that the SOA/sulfate production does not show up for the first 30 minutes and there large increases in particle number concentration are additional pieces of evidence. This can be easily tested by applying the work of Zhang et al to the calculated particle surface areas observed in this work; see Figure 2C in Zhang et al. If this reasoning is true, the authors would have demonstrated that the SOA enhancement is not linked to SO_2/sulfate and changes the major findings from this work. In the revised manuscript, I would like vapor wall-losses to be considered in more detail to better elucidate the role of SO_2. Based on this analysis, the authors should also consider the simpler seeded experiment I mention above.

Reply: The wall accommodation coefficient ($\alpha_{w,i}$), governing the extent of wall deposition of a compound i, was observed to be inversely dependent on its effective saturation concentration C_i^* (Zhang et al., 2015). Partitioning coefficients for different C_i^* ranging from 0.01 to 10^6 μg m^{-3} were calculated using gas-particle partitioning theory (Donahue et al., 2006) and listed in Table 1 (Table 6 in the revised manuscript). Partitioning coefficients for experiments with and without the addition of SO_2 mainly exhibited big differences for C_i^* bins of 10 and 100 μg m^{-3} with $\alpha_{w,i}$ calculated to be 3.1×10^{-7} and 2.0×10^{-7}, respectively. The wall loss rate for C_i^* bin of 10 μg m^{-3} would then be approximately 50% higher than that for C_i^* bin of 100 μg m^{-3} assuming a linear relation between wall loss rate and $\alpha_{w,i}$ (Zhang et al., 2015). An increase of 50% in wall loss rate would lead to 11.5% higher vapor loss to walls when assuming the wall loss rate to be 2.0×10^{-5} s^{-1}, similar to a product of the photo-oxidation of toluene. Thus, biases of vapor wall loss rates due to the addition of SO_2 may have negligible influence on estimation of SOA production.

Zhang et al. (2014) assumed a wall loss rate of 2.5×10^{-4} s^{-1}, almost 10 to 100 times higher than those of products of toluene photo-oxidation, observed in their recent study (Zhang et al., 2015). Thus, the method of Zhang et al. (2014) may be not appropriate to explore the influence of surface area. As discussed above, the seeded experiment indicated that the formation of sulfate might not influence the SOA production, consistent with the observation that the presence of ammonium sulfate seed aerosols has no impact on SOA formation from the photo-oxidation of m-xylene and 1,3,5-trimethylbenzene (Cocker III et al., 2001).

Table 1. Partitioning coefficients for different C_i^* calculated using gas-particle partitioning theory.

$\log_{10}^{C_i*}$ (μg m^{-3})	I-1	I-2	II-1	II-2	III-1	III-2
-2	1.000	1.000	1.000	1.000	0.999	1.000
-1	0.999	0.999	0.997	0.997	0.994	0.999
0	0.987	0.989	0.968	0.974	0.946	0.987
1	0.886	0.901	0.754	0.789	0.638	0.885
2	0.437	0.477	0.235	0.272	0.150	0.435
3	0.072	0.084	0.030	0.036	0.017	0.071
4	0.008	0.009	0.003	0.004	0.002	0.008
5	0.001	0.001	0.000	0.000	0.000	0.001
6	0.000	0.000	0.000	0.000	0.000	0.000

The sentences "*Recent studies indicated that the presence of high concentrations of seed aerosols might decrease the loss of organic vapors to the walls and thus increase the SOA formation (Kroll et al., 2007; X. Zhang et al., 2014, 2015). Therefore, the increase of condensation sinks due to the formation of sulfate with adding SO_2 might be another reason that caused the enhancement of SOA production.*" has been revised as a new paragraph and now reads:

"The addition of SO_2 may vary the vapor wall loss rate and influence the estimation of SOA production. The wall accommodation coefficient ($\alpha_{w,i}$), governing the extent of wall deposition of a compound i, was observed to be inversely dependent on its effective saturation concentration C_i^* (X. Zhang et al., 2015). Partitioning coefficients for different C_i^* ranging from 0.01 to 10^6 μg m^{-3} were calculated using gas-particle partitioning theory (Donahue et al., 2006) (Table 6). Partitioning coefficients for experiments with and without the addition of SO_2 mainly exhibited big differences for C_i^* bins of 10 and 100 μg m^{-3} with $\alpha_{w,i}$ calculated to be 3.1×10^{-7} and 2.0×10^{-7}, respectively. The wall loss rate for C_i^* bin of 10 μg m^{-3} would then be approximately 50% higher than that for C_i^* bin of 100 μg m^{-3} assuming a linear relation between wall loss rate and $\alpha_{w,i}$ (X. Zhang et al., 2015). An increase of 50% in wall loss rate would lead to 11.5% higher vapor loss to walls when assuming the wall loss rate to be 2.0×10^{-5} s^{-1}, similar to a product of the photo-oxidation of toluene. Thus, biases of vapor wall loss rates due to the addition of SO_2 may have negligible influence on estimation of SOA production. Recent studies indicated that the presence of high concentrations of seed aerosols might decrease the loss of organic vapors to the walls and thus increase the SOA formation (Kroll et al., 2007; X. Zhang et al., 2014, 2015). However, comparable SOA PFs for experiments with and without seed aerosols observed in this study indicated the negligible impact of seed aerosols on SOA production. Cocker III et al. (2001) also observed that the presence of ammonium sulfate seed aerosols had no impact on SOA formation from the photo-oxidation of m-xylene and 1,3,5-trimethylbenzene .”

Conclusions: The conclusions and subsequent regulatory/policy implications are stated too strongly regarding the role of SCIs and particle acidity. Either the authors need to perform more experiments or develop their arguments better to justify their level of certainty.

Reply: The issues of the role of sCIs and particle acidity have been addressed in above responses. The following sentence “*Consequently, high concentration of* SO_2 *and high levels of aerosol acidity together with rapid increase of LDGVs in heavy polluted cities such as Beijing (Pathak et al., 2009; He et al., 2014) would make the air quality worse if there were no stricter control strategies on emissions of* SO_2 *and vehicle exhausts.*” has been revised and now reads:

“High concentration of SO_2 and high levels of aerosol acidity combined with rapid increase of LDGVs in heavily polluted cities such as Beijing (Pathak et al., 2009; He et al., 2014) might consequently worsen the air quality in the absence of stricter control strategies on emissions of SO_2 and vehicle exhaust.”

“*Thus, limiting the content of alkenes in China's gasoline would benefit the control of both ozone and secondary aerosols.*” was changed to “Thus, limiting the content of alkenes in China’s gasoline might benefit the control of both ozone and secondary aerosols.”

Minor comments:

Q1- The sentence structure, grammar and the usage of words in the manuscript can be improved and I would recommend the use of a professional service to offer recommendations. Let’s consider the example of the text in the ‘Introduction’. The sentence “A detailed understanding of the magnitude and formation pathways of sulfate and OA is therefore critical to formulate control strategies and accurately estimate their impact on air quality and climate, yet this attempt is often complicated due to the missing or underestimated oxidation pathways of sulfur dioxide (SO_2) (Berglen et al., 2004), which is the precursor of sulfate, and the unclear formation mechanisms of secondary organic aerosols (SOA) (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006), which account for a large fraction of OA (Zhang et al., 2007).” Is too long and can be split into several sentences to improve readability. “A plenty of NO_x and aromatics” is grammatically incorrect and the word “pipe exhausts” is unclear. Exhaust’ already encompasses a mixture compound and there is not need to pluralize to ‘Exhausts’.

Reply: The language of the revised manuscript has been edited by a native speaker as suggested. The sentence “*A detailed understanding of the magnitude and formation pathways of sulfate and OA is therefore critical to formulate control strategies and accurately estimate their impact on air quality and climate, yet this attempt is often complicated due to the missing or underestimated oxidation pathways of sulfur dioxide (SO_2) (Berglen et al., 2004), which is the precursor of sulfate, and the unclear formation mechanisms of secondary organic aerosols (SOA) (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006), which account for a large fraction of OA (Zhang et al., 2007).*” has been changed to “Thus, a detailed understanding of the magnitude and formation pathways of sulfate and OA is critical to formulate control strategies and to accurately estimate their impact on air quality and climate. Complications often arise due to missing or underestimated oxidation pathways of sulfur dioxide (SO_2) (Berglen et al., 2004), the precursor of sulfate, and the unclear formation mechanisms of secondary organic aerosols (SOA) (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006), accounting for a large fraction of OA (Zhang et al., 2007).”. “A plenty of ” was deleted and “exhausts” was changed to “exhaust” throughout the entire manuscript.

Q2- The introduction is too short, in my opinion. It doesn't cover the vast body of work published on SOA from vehicle exhaust; for example work of Platt et al and Nordin et al. While I am sure the authors are appropriately motivated to conduct the work and are well aware of the gaps in the literature, the introduction did not convince me of that. I would recommend a much more detailed literature review.

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

"Recent smog chamber studies have demonstrated that the amount of SOA formed from dilute gasoline vehicle exhaust often exceeds primary OA (POA) (Nordin et al., 2013; Platt et al., 2013; Gordon et al., 2014; Liu et al., 2015). Aromatic hydrocarbons were found to be vital SOA precursors in gasoline vehicle exhaust. Up to 90% of SOA from idling Euro 1–4 vehicle exhaust could be attributed to aromatics (Nordin et al., 2013; Liu et al., 2015). Gordon et al. (2014) concluded that traditional precursors could fully explain the SOA production from old vehicles with model years prior to 1995."

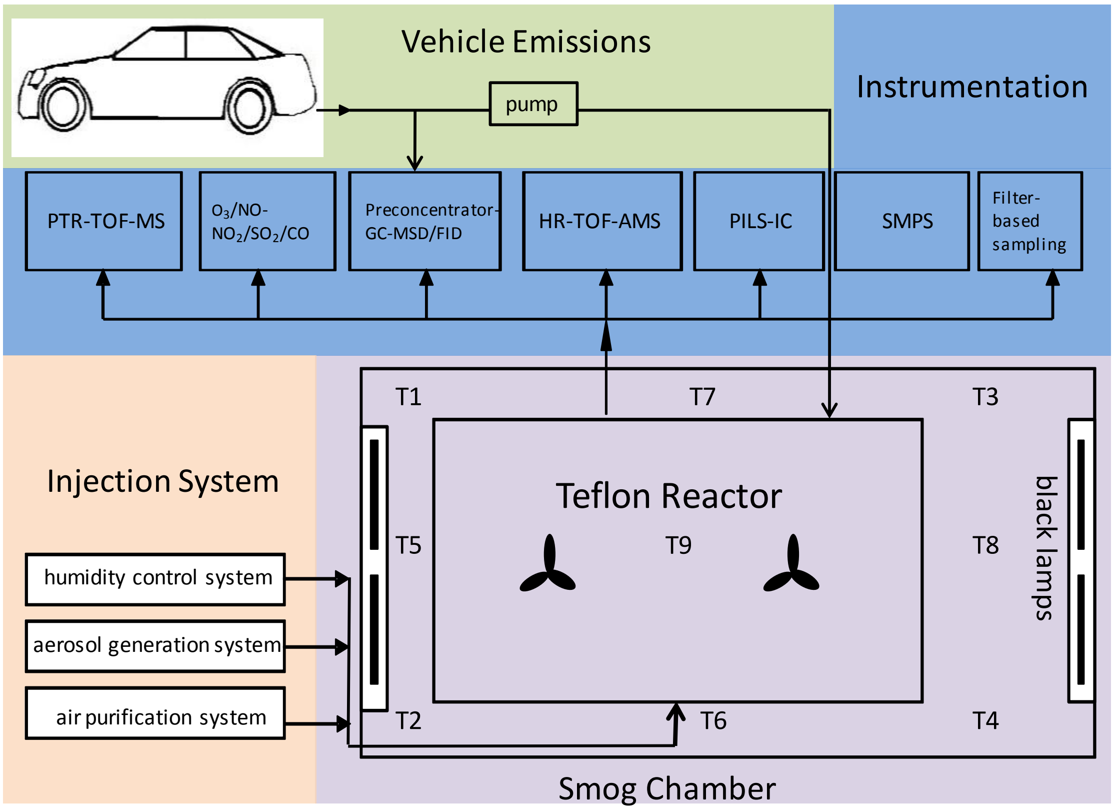
Q3- What do the Euro standards mean? A one sentence explanation of the Euro standard and its implication for vehicle emission standards and vehicle fleet globally would help put the choice of vehicles in context.

Reply: In Europe, vehicle emissions are classified by "Euro Standards", currently ranging from Euro 1 to Euro 6. China implemented the Euro 1, Euro 2, Euro 3 and Euro 4 emission standards in 2000, 2004, 2007 and 2012 for LDGVs and the Euro 5 standard will be implemented in 2018. The following text has been added to section 2.1 in the revised manuscript.

"In Europe, vehicle emissions are classified by "Euro Standards", currently ranging from Euro 1 to Euro 6. China implemented the Euro 1, Euro 2, Euro 3 and Euro 4 emission standards in 2000, 2004, 2007 and 2012 for LDGVs and the Euro 5 standard will be implemented in 2018."

Q4- Can the authors offer a schematic of the experimental setup that detail the instrumentation and hardware used?

Reply: A schematic of the experimental setup was presented in Fig. 1 in the revised manuscript.



The following text has been added to the revised manuscript.

"A schematic of the experiment setup is presented in Fig. 1. Eight thermocouples are placed between the enclosure and the reactor walls to control the temperature. The temperature inside the reactor (T9) was measured by Siemens QFM2160 (Siemens AG, Germany)."

Q5- How was the exhaust transferred to the chamber? Through a vacuum on the chamber or was it passed through the pump?

Reply: As discussed in the manuscript, vehicle exhaust was introduced directly by two oil-free pumps (Gast Manufacturing, Inc, USA) into the reactor at a flow rate of 40 L min^{-1}.

Q6- Do the authors use the measured SO_2 loss rate and apportion it to CIs and other pathways using the MCM? This detail is important since it means that the approach is unconstrained and could also indicate other loss processes that the authors have ignored.

Reply: Yes, the measured SO_2 loss rate was apportioned to CIs and other pathways using the MCM model.

Q7- How did the authors determine particle acidity using AIM-II? What were the inputs to the model and what measurements were used to do so? Are the authors aware of the recent work of Hennigan et al. (2015) that demonstrates problems associated with using thermodynamic models to calculate particle acidity?

Reply: Inputs to the model include temperature, RH, [SO_4^{2-}], [NO_3^-], [NH_4^+] and [H^+]$_{total}$, calculated based on ion balance. Hennigan et al. (2015) demonstrates that thermodynamic models constrained by gas + aerosol measurements provide the best available predictions of aerosol pH. However, gas-phase aerosol precursors, HNO_3 and NH_3, were not measured in this study. Thermodynamic models using measured aerosol compositions as inputs are also frequently applied to analyze ambient and experimental data. The uncertainty in [H^+]$_{in\text{-}situ}$ is expected to be negligible compared to the big difference in aerosol composition for experiments with and without the addition of SO_2.

The sentences "*Accordingly when adding SO_2, the in-situ particle acidities at the time when SOA formation rate peaks, calculated as H^+ concentrations based on AIM-II model H^+–NH_4^+–SO_4^{2-}–NO_3^-–H_2O with gas-aerosol partitioning disabled (http://www.aim.env.uea.ac.uk/aim/model2/model2a.php) (Clegg et al., 1998; Wexler and Clegg, 2002), were 1.6–3.7 times as high as those without adding SO_2 (Table 3).*" has been revised and now reads:

"The in-situ particle acidities at the time when SOA formation rate peaks were calculated as H^+ concentrations based on AIM-II model H^+–NH_4^+–SO_4^{2-}–NO_3^-–H_2O with gas-aerosol partitioning disabled (http://www.aim.env.uea.ac.uk/aim/model2/model2a.php) (Clegg et al., 1998; Wexler and Clegg, 2002). Inputs to the model include temperature, RH, [SO_4^{2-}], [NO_3^-], [NH_4^+] and [H^+]$_{total}$, calculated based on ion balance. SO_4^{2-}, NH_4^+ and NO_3^- contributed virtually all of the aerosol phase ions mass in this study, thus determining the aerosol acidity. Though other ions (i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+) had negligible influence on the aerosol acidity, it is worth noting that the reported values of H^+ may be the upper bound. The in-situ particle acidities with the addition of SO_2 were 1.6–3.7 times as high as those without the addition of SO_2 (Table 3)."

Q8- Although not related directly to the paper, can the large differences in ammonium nitrate and ammonium sulfate be explained simply by gas/particle partitioning predicted by AIM-II?

Reply: This issue has been addressed in the response to Q6 of Reviewer 3. 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).

Q9- The authors claim that the differences in the O:C of the OA could be a result of gas/particle partitioning. Based on known differences in the O:C of aromatic SOA, the authors could potentially test this hypothesis (~0.1 delta_O:C for ~50 µg/m3 delta_OA) based on historical data.

Reply: The O:C ratios were observed to decrease 0.1 with an increase of approximately 50 µg m^{-3} of OA concentrations for m-xylene and p-xylene (Kang et al., 2011). However, in this study the slope was 0.1 ΔO:C for approximately 26 µg m^{-3} ΔOA. The differences may be due to that some other precursors other than aromatics contributed to SOA formation from gasoline vehicle exhaust (Liu et al., 2015).

The following text has been added to the revised manuscript.

"The O:C ratios were observed to decrease 0.1 with an increase of approximately 50 µg m^{-3} of OA concentrations for m-xylene and p-xylene (Kang et al., 2011). However, in this study the slope was 0.1 ΔO:C for approximately 26 µg m^{-3} ΔOA. The differences may be due to that some other precursors other than aromatics contributed to SOA formation from gasoline vehicle exhaust (Liu et al., 2015)."

Q10- It might be helpful to provide the relevant O:C values in the abstract in addition to the oxidation state.

Reply: The average values of H:C and O:C have been added to the abstract and section 3.3.

Q11- What are the units of VOC/NOx? In my experience, this is usually expressed as ppbC/ppb.

Reply: It is ppb/ppb here. "(ppb/ppb)" has been added to the revised manuscript to clarify.

Q12- Was only one experiment considered for each vehicle? Do the authors have a sense of the experiment-to-experiment variability and is this smaller than the observed effect?

Reply: Yes, one experiment was considered for each vehicle. However, the comparable SOA PFs for vehicle I with and without seed aerosols indicate that the experiment-to-experiment variability is negligible compared with the observed differences with and without the addition of SO_2.

Q13- What is the intent of Figure 8? In the manuscript, Figure 8 gets a one-sentence mention.

Reply: The ion fragment m/z 88 can only arise from a glyoxal oligomer, typically formed from acid-catalyzed heterogeneous reactions. Figure 8 (now Fig. 9 in the revised manuscript) shows 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."

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Response to Reviewer #2

General comments:

Liu et al. describe photochemical oxidation experiments of gasoline vehicle exhaust with and without SO_2 gas. This manuscript is technically sound, provides detailed methodology, and addressed a highly relevant topic in the field of atmospheric chemistry. I recommend its acceptance for publication in Atmospheric Chemistry and Physics pending an adequate response to the comments listed below.

In this reviewer's opinion, this paper could use some copy-editing for language. While the text is comprehendible at present, it is, in some cases, awkwardly worded.

Reply: The language of the revised manuscript has been edited by a native speaker.

Specific comments:

Q1- Page 23620, line 8: What molecular weight was assumed for hydrocarbons? Was this a weighted-average based on the gas-phase analyses?

Reply: The hydrocarbons measured in this study include methane and C_2-C_{12} hydrocarbons. The carbon content of different hydrocarbon was respectively calculated. Thus, $[\Delta HC]/MW_{HC}$ in the equation represents the sum of different hydrocarbons.

To clarify this, we add the following text to the revised manuscript.

"The carbon content of each hydrocarbon was respectively calculated and then summed in Eq. (1)."

Q2- Page 23620, line 17: It may be worth stating the reference from which the authors are obtaining the rate constant for the toluene + OH radical reaction, since this appears to be known a priori (or at least the assumed value).

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

"The value of k is obtained from the Master Chemical Mechanism version 3.3 or MCM v3.3 (http://www.chem.leeds.ac.uk/MCM) (Jenkin et al., 2003)."

Q3- Page 23621, line 16-page 23622, line 7: It may be useful to provide examples of which compounds may be participating in this chemistry (e.g., ethene, 1,2-butadiene, 2-methyl-propene, cyclohexene). Given that the authors have input these species to the MCM, this should be relatively straightforward, and it could be as simple as saying XX% straight alkenes, YY% branched alkenes, and ZZ% cycloalkenes.

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, with ethene and propene as two main components accounting for as high as 66.8%-81.3%.

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 following text has been added to the revised manuscript.

"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 as high as 66.8%-81.3%."

Q4- Another comment related to the MCM work: Given that alkenes are only ~10-20% of the total VOCs, how might these reactions be biased due to neglecting the presence of alkanes, aromatics, etc.? This answer may that there is no bias, due to the constraints placed on OH, SO_2, O_3, and NO_2, but perhaps the authors should explicitly state this. Maybe this could be validated by re-running the MCM simulations including aromatics in addition to alkenes to assess any differences in model outputs.

Reply: According to the Eq. (5), the steady state concentrations of sCIs depend on the concentrations of O_3, alkenes, OH, SO_2, O_3 and NO_2. Due to the constraints of OH, SO_2, O_3 and NO_2, the neglect of alkanes and aromatics would not influence the concentrations of sCIs. Re-running the MCM simulations including aromatics and alkanes did not change the steady state concentrations of sCIs. The following text has been added to the revised manuscript:

“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.”

Q5- Page 23623, lines 3-8: Is this how the authors are accounting for collection efficiency? Presumably, this approach biases the concentrations of OA, sulfate, ammonium, and nitrate high because LDGVs also emit black carbon (Forestieri et al., 2013; Kamboures et al., 2013; May et al., 2014). In the cited Gordon et al. (2014) reference, those authors do account for black carbon. An approach such as the Middlebrook et al. (2012) composition-dependent CE may be necessary.

Reply: Theoretically, the difference of PM mass measured by AMS and SMPS should be attributed to black carbon (BC). As shown in Figure 1, the initial mass of PM measured by SMPS was comparable with that measured by HR-TOF-AMS, thus we assumed that the mass of BC in the reactor was negligible. It is then reasonable to use AMS data combined with SMPS data to derive the time-resolved concentrations of OA, sulfate, ammonium and nitrate.

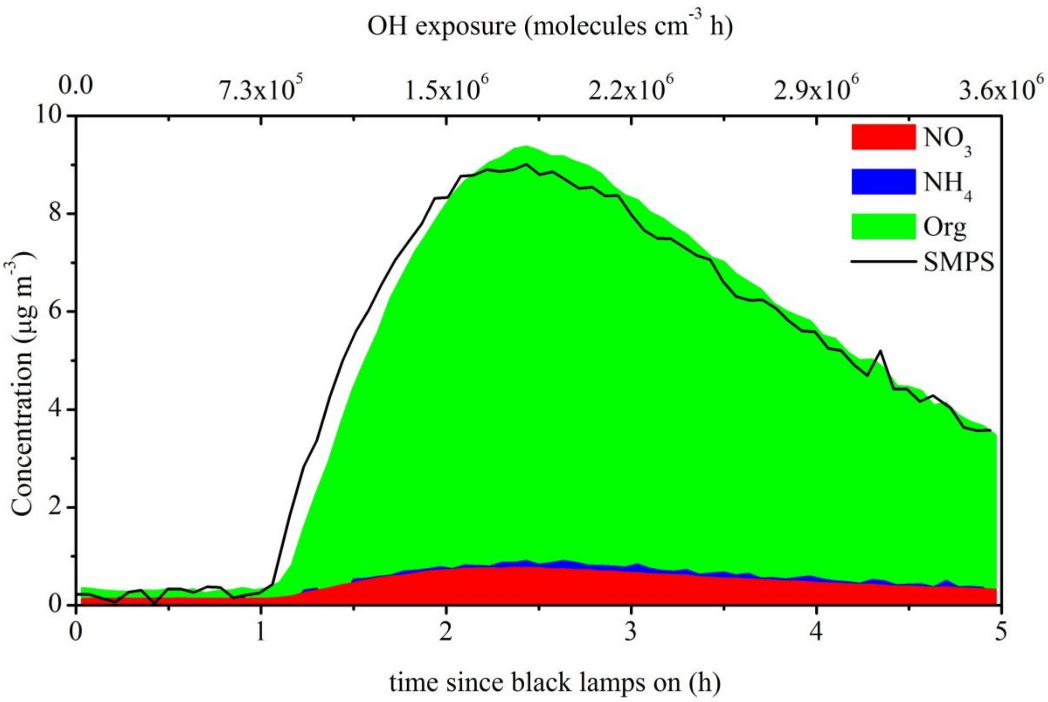


Figure 1. Comparison of the sum of organics, nitrate and ammonium (measured by AMS) against the total particle mass measured by the SMPS for experiment III-1.

The following text has been added to the revised manuscript:

"The emission of black carbon (BC) from LDGVs was negligible according to a previous study (Liu et al., 2015), thus…"

Q6- Page 23623, line 23-page 23624, line 6: Previously, the authors state that NMHCs, NOx, and average OH are different than typical urban conditions. How similar is the injected SO_2 concentration (~150 ppb) to urban or urban-downwind conditions? Could these discrepancies resolve the large differences between chamber observations and field observations? Due to potential differences in these conditions, it may be useful to normalize the sulfate production rate (e.g., µg-m^{-3}-sulfate hr^{-1} ppt-OH^{-1} or similar) to explore any biases. If the differences still exist, this may enhance the argument related to the role of Creigee intermediates.

Reply: The formation rate of sulfate was related to the concentrations of SO_2 and OH, which were respectively approximately 7 times higher and 2-16 times lower than those in the study of Xiao et al. (2009). Significant differences of sulfate formation rates between chamber and ambient observations could, however, indicate that there might be other processes dominating the oxidation of SO_2 rather than gas-phase oxidation by OH in this study. We still reported the sulfate production rates in μg m^{-3} h^{-1} in order that they can be easily compared with those in previous studies, like Xiao et al. (2009) and Zhang et al. (2011).

The following text has been added to the revised manuscript:

"The formation rate of sulfate was related to the concentrations of SO_2 and OH, which were respectively approximately 7 times higher and 2-16 times lower than those in the study of Xiao et al. (2009). Significant differences of sulfate formation rates between chamber and ambient observations could, however, indicate that there might be other processes dominating the oxidation of SO_2 rather than gas-phase oxidation by OH in this study."

Q7- Page 23625, lines 10-17: Given that there is routine analysis for calcium, magnesium, potassium, and sodium in motor vehicle exhaust (California Air Resources Board, 2011), how might the presence of these additional cations affect the H+ calculations? I do not think this will change the authors conclusions, but it may be worth noting that the reported values of H+ can be considered an upper bound.

Reply: As shown in Figure 1, the mass of primary particles was negligible compared with the formed secondary inorganic aerosols. This indicated that other ions (i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+), only part of the primary particles, had negligible influence on the aerosol acidity. But we agree with the referee that the reported values of H^+ are upper bounds.

The following text has been added to the revised manuscript.

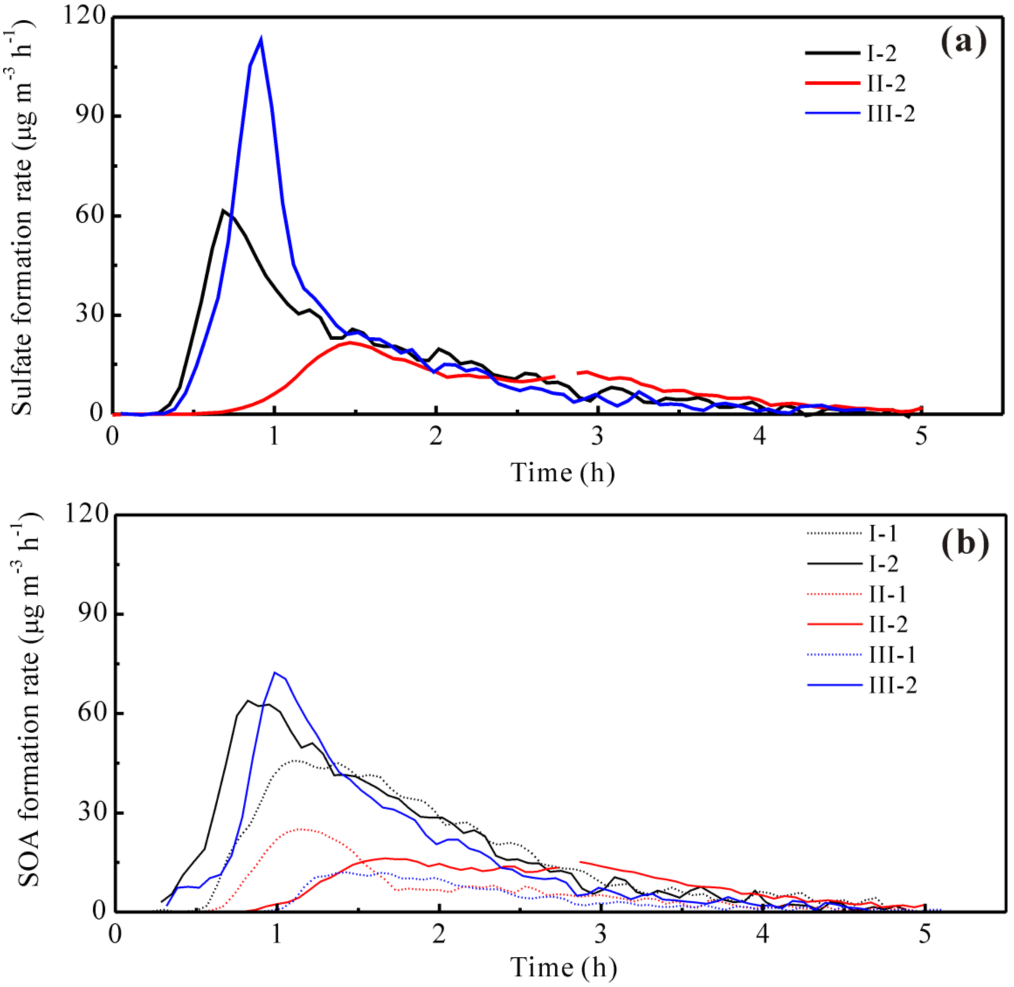
"SO_4^{2-}, NH_4^+ and NO_3^- contributed virtually all of the aerosol phase ions mass in this study, thus determining the aerosol acidity. Though other ions (i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+) had negligible influence on the aerosol acidity, it is worth noting that the reported values of H^+ may be the upper bound."

Q8- Figures 1-4: Presumably, particle concentrations are wall-loss-corrected. It may be worth explicitly stating this in the caption.

Reply: The concentrations of particle-phase species are wall-loss corrected. This has been clarified in the revised manuscript.

Q9- Figure 5: I would recommend using the same y-axis scale for both figures. This can facilitate direct comparisons between the time series of sulfate and SOA production rates.

Reply: Revised as suggested.



Q10- Figure 6: Maybe this is discussed in the text, and I have missed it, but why is there a large difference between the total loss rate and the sum of sCI and OH oxidation for vehicle II? The results for this vehicle are more drastic than the two others. Could the authors use the results from He et al. (2014) to estimate surface reactions on particles for the present study?

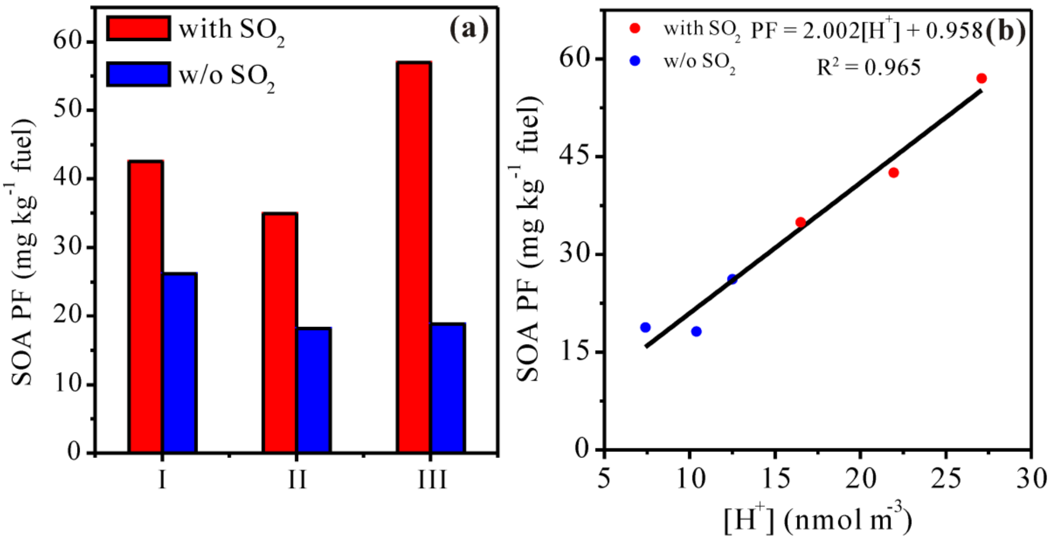
Reply: The difference between the total loss rate and the sum of sCIs and OH oxidation for vehicle II indicated that there might be other oxidation pathways for SO_2. As discussed in the manuscript, the reaction between SO_2 and NO_2 on the surface of existed aerosols might be an explanation. As shown in Fig. 5 in the revised manuscript, the initial particle number for vehicle II was approximately 5000 cm^{-3}, nearly 40-50 times higher than those for vehicle I and III, providing larger aerosol surface areas for the oxidation of SO_2 by NO_2. However, quantification of SO_2 oxidation by NO_2 on the surface of existing aerosols is difficult due to the lack of reaction rate constant (He et al., 2014). Thus we speculate that the reaction between SO_2 and NO_2 on the surface of existing aerosols might explain the difference between the total loss rate of SO_2 and the sum of sCIs and OH oxidation for vehicle II.

The sentence "*In this study, the reaction between SO_2 and NO_2 on the surface of existed aerosols might be a pathway to lead to the formation of sulfate.*" has been revised and now reads:

"As shown in Fig. 5, the initial particle number for vehicle II was approximately 5000 cm^{-3}, nearly 40-50 times higher than those for vehicle I and III, providing larger aerosol surface areas for the oxidation of SO_2 by NO_2. However, quantification of SO_2 oxidation by NO_2 on the surface of existing aerosols is difficult due to the lack of reaction rate constant (He et al., 2014). We speculate that the reaction between SO_2 and NO_2 on the surface of existing aerosols might explain the difference between the total loss rate of SO_2 and the sum of sCIs and OH oxidation for vehicle II."

Q11- Figure 7b: It may be worthwhile to color the markers in this figure to be consistent with the bar colors in Figure 7a in order to distinguish between "with SO_2" and "w/o SO_2". This should be obvious to the reader, but it will really drive the point home.

Reply: Revised as suggested.



Q12-Figure 9: If I understand this correctly, these figures are discrete points corresponding to data selected from Figure 5? I would recommend some clarification of this in the text. Furthermore, can the authors explain why the slopes are vastly different (i.e., ~4 vs. ~1 vs. ~3)? Given that the initial conditions were largely similar (i.e., Table 2), why might the results be the way that they are? Could this be a function of alkene abundance, or might some other factor play a role?

Reply: Yes, these discrete points are corresponding to data selected from Figure 5. This has been clarified in the revised manuscript. The difference in slopes suggested that there were some other factors influencing the SOA formation rate. We agree with the referee that the alkene abundance might play an important role. The initial concentration of alkenes for experiments I-2, II-2 and III-2 was 547 ppb, 248 ppb and 353 ppb, respectively, consistent with the variation of the slopes. Higher alkene content would increase the formation rate of sCIs, which could rapidly oxidize SO_2 to sulfate and thus influence the aerosol acidity.

The sentence "*Significant linear correlations (P<0.05, R^2>0.88) between SOA formation rate and particle acidity (Fig. 9) during this stage for experiments with SO_2 suggest that acid-catalyzed heterogeneous reactions might play an important role on the fast formation of SOA (Jang et al., 2002)*" has been revised and now reads:

"Fig. 10 shows the correlation between SOA formation rate and particle acidity. Plotted data corresponded to data selected from Fig. 6 when SOA formation rate was higher than zero to when the rate reached the maximum value. Significant linear correlations ($P<0.05$, $R^2>0.88$) between SOA formation rate and particle acidity during this stage for experiments with SO_2 suggest that acid-catalyzed heterogeneous reactions might play an important role in the rapid formation of SOA (Jang et al., 2002)"

The following text has been added to the revised manuscript.

"The fitted slopes for vehicle I, II and III were 3.96, 0.82 and 3.14, respectively, suggesting other factors, including alkene abundance, may influence the SOA formation rate. The initial concentration of alkenes for experiments I-2, II-2 and III-2 was 547 ppb, 248 ppb and 353 ppb, respectively, consistent with the variation of the slopes. Higher alkene content would increase the formation rate of sCIs, which could rapidly oxidize SO_2 to sulfuric acid, thus influence the aerosol acidity."

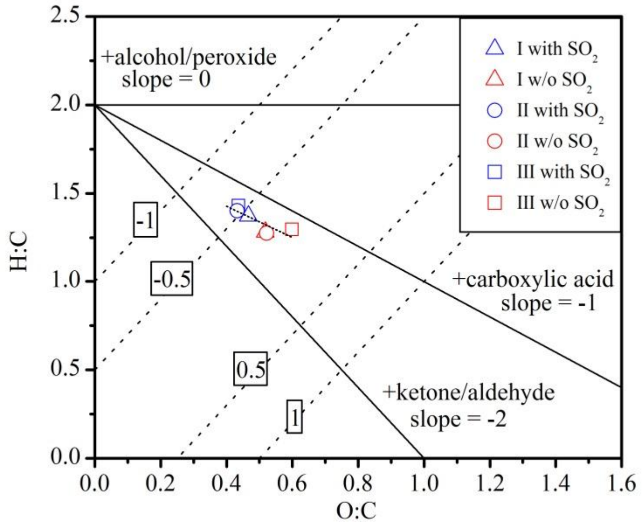
Q13- Figure 10: Do the authors have sufficient signal in the AMS results to calculate an initial H:C and O:C? These may be uncertain because POA concentrations were low. Based on the figure, it appears that the six data points have a slope of -1 and a y-intercept of roughly 1.8, so I am curious for this reason.

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 exhaust 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 exhaust 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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Liu, T., Wang, X., Deng, W., Hu, Q., Ding, X., Zhang, Y., He, Q., Zhang, Z., Lü, S., Bi, X., Chen, J., and Yu, J.: Secondary organic aerosol formation from photochemical aging of light-duty gasoline vehicle exhausts in a smog chamber, Atmos. Chem. Phys., 15, 9049-9062, 10.5194/acp-15-9049-2015, 2015.

Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11, 6465-6474, 10.5194/acp-11-6465-2011, 2011.

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Xiao, R., Takegawa, N., Kondo, Y., Miyazaki, Y., Miyakawa, T., Hu, M., Shao, M., Zeng, L. M., Hofzumahaus, A., Holland, F., Lu, K., Sugimoto, N., Zhao, Y., and Zhang, Y. H.: Formation of submicron sulfate and organic aerosols in the outflow from the urban region of the Pearl River Delta in China, Atmos. Environ., 43, 3754-3763, http://dx.doi.org/10.1016/j.atmosenv.2009.04.028, 2009.

Zhang, Y. M., Zhang, X. Y., Sun, J. Y., Lin, W. L., Gong, S. L., Shen, X. J., and Yang, S.: Characterization of new particle and secondary aerosol formation during summertime in Beijing, China, Tellus B, 63, 10.3402/tellusb.v63i3.16221, 2011.

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).

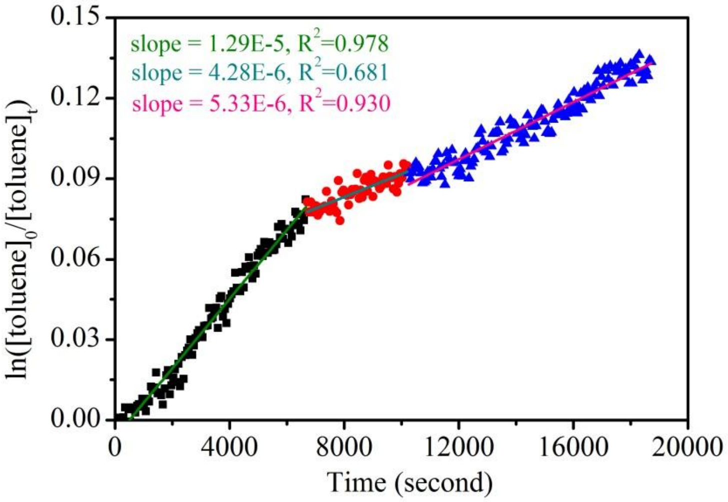
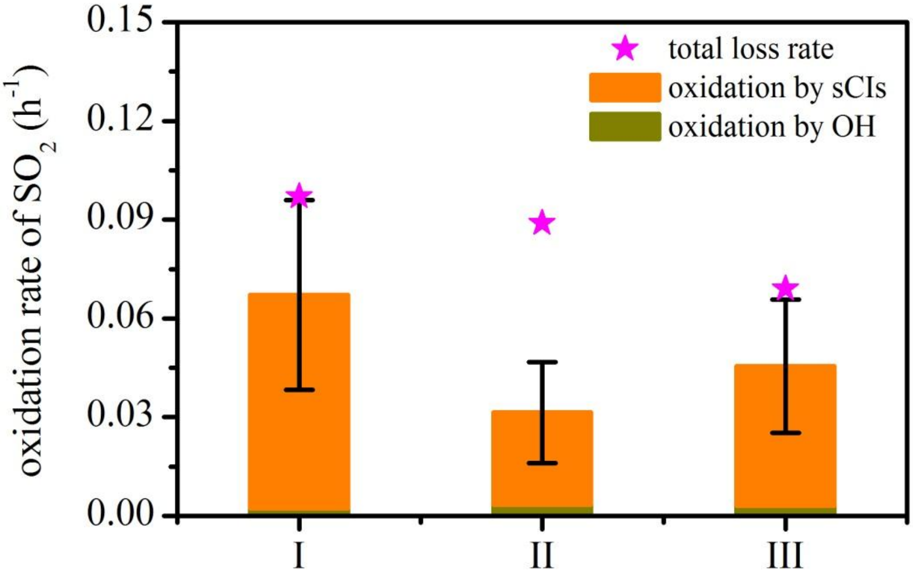


Figure 1. *ln*($[toluene]_0/[toluene]_t$) versus time t.

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

Exp #	Time period (h)	OH ($\times 10^6$ 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.

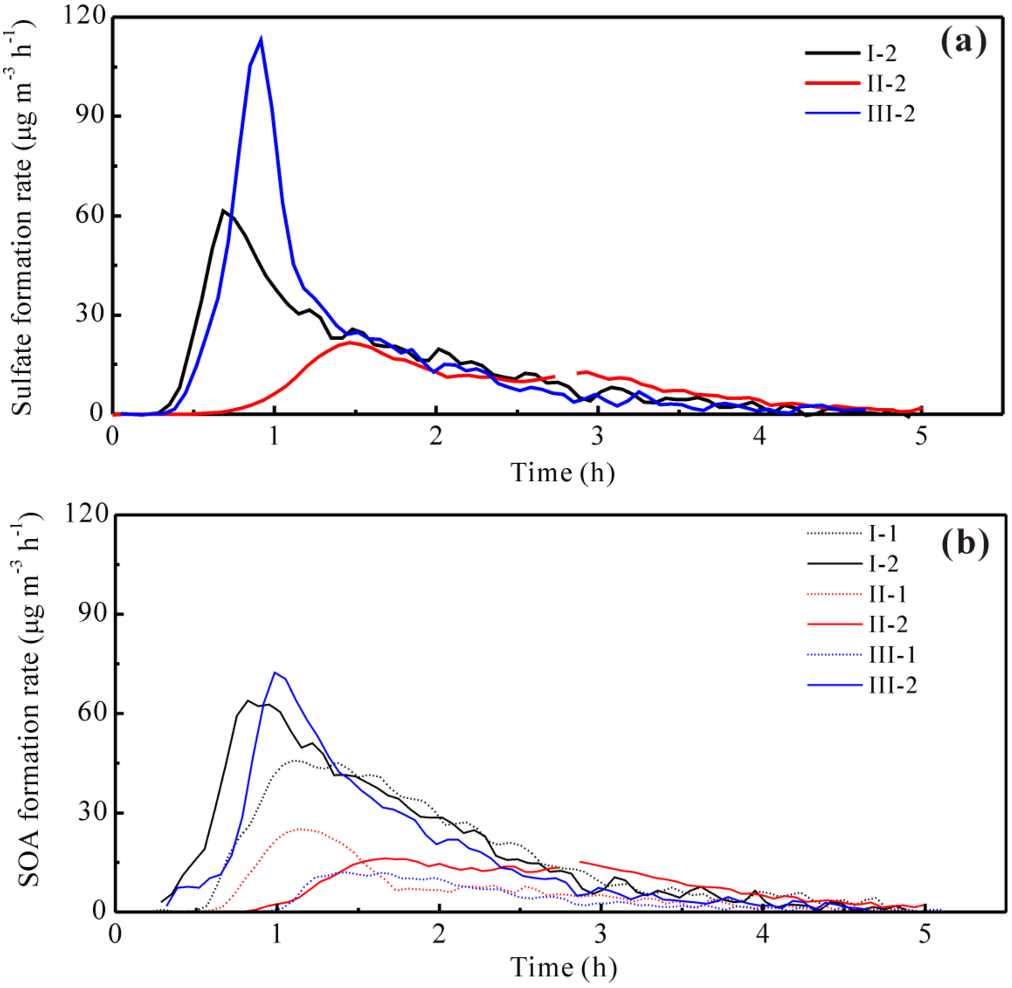
Reply: This issue has been addressed in Q3 and Q4.

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.

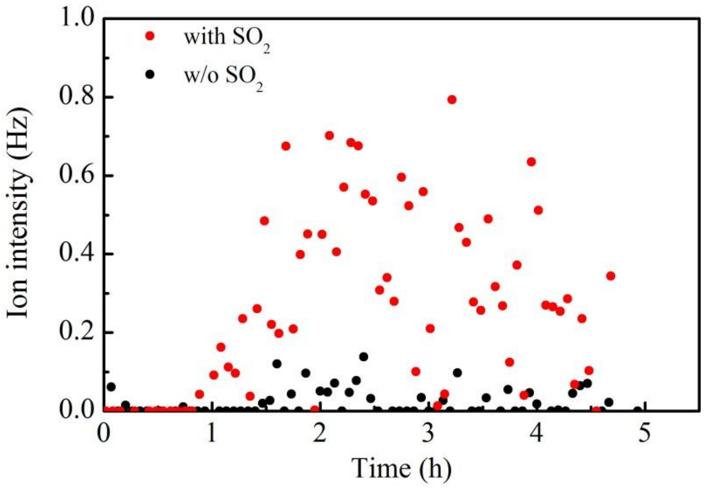
"The S-bearing organic fragments $C_xH_yO_zS$ determined by HR-TOF-AMS can be used as marker ions to quantify organosulfates (Huang et al., 2015). In this study the fragments $C_xH_yO_zS$ were almost not appreciable. Using the methods of Huang et al. (2015), we estimated the mass ratio of organosulfates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

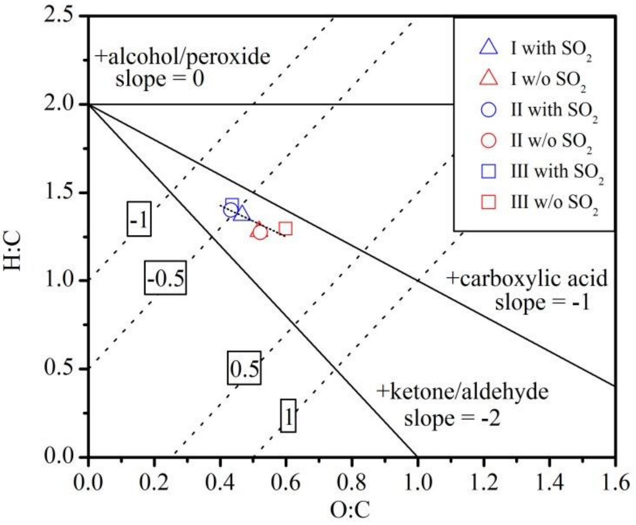
Q13- Fig 10 should include the composition of the POA.

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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Seinfeld, J. and Pandis, S. N.: From air pollution to climate change, Atmospheric Chemistry and Physics, 2nd Edn., p. 208, 1998.

A list of relevant changes

Line 2–Change "exhausts" in the title to "exhaust"

Line 29–Change "exhausts" to "exhaust"

Line 29-30–Change "is still poorly understood" to "remains uncertain"

Line 30-31–Change "Here we directly co-introduced gasoline vehicles exhausts" to "Gasoline vehicle exhaust"

Line 31-32–Add "are directly co-introduced" after "a typical pollutant from coal burning,"

Line 32–Add ", in this study," after "a smog chamber"

Line 33-35–Change "In the presence of high concentration of SO_2, new particle formation was enhanced while substantial sulfate was formed through the oxidation of SO_2." to "New particle formation was enhanced while substantial sulfate was formed through the oxidation of SO_2 in the presence of high concentration of SO_2."

Line 36–Change "The homogenous" to "Homogenous"

Line 41-42–Change "This increase could largely be attributed to acid-catalyzed SOA formation, which was…" to "The increase could principally be attributed to acid-catalyzed SOA formation as…"

Line 46–Add "(0.44 ±0.02)" after "(O:C)"

Line 46–Add "(1.40 ±0.03)" after "(H:C)"

Line 47–Change "much" to "significantly"

Line 48 –Delete "that of"

Line 49-50–Change "the major reason for the lower oxidation degree of SOA" to "a significant explanation for the lower SOA oxidation degree"

Line 52-55–Change "As main components of fine particles or $PM_{2.5}$, sulfate and organic aerosols (OA) can lead to serious and complex air pollution (Parrish and Zhu, 2009) and have negative effects on human health (Nel, 2005)." to "Sulfate and organic aerosols (OA) can lead to serious and complex air pollution (Parrish and Zhu, 2009) as the main components of fine particles or $PM_{2.5}$, conveying negative effects on human health (Nel, 2005).”

Line 55-56–Change “Furthermore, sulfate and OA affect radiative forcing on global scale (Andreae et al., 2005; Shindell et al., 2009).” to “Sulfate and OA additionally affect radiative forcing on a global scale (Andreae et al., 2005; Shindell et al., 2009).”

Line 56–Change “A” to “Thus, a”

Line 58 –Delete “therefore”

Line 58–Add “and” after “to”

Line 59–Change “, yet this attempt is often complicated” to “Complications often arise”

Line 60 –Delete “the”

Line 61–Delete “which is”

Line 63–Change “which account” to “accounting”

Line 65-77–Change “SO_2, mainly emitted from coal-fired power plants and coal-burning boilers, when mixed with gasoline vehicle exhausts containing a plenty of NO_x and aromatics that provide precursors for the formation of secondary nitrates and organic aerosols, might react with each other and make the formation of sulfate and SOA complicated.” to “Recent smog chamber studies have demonstrated that the amount of SOA formed from dilute gasoline vehicle exhaust often exceeds primary OA (POA) (Nordin et al., 2013; Platt et al., 2013; Gordon et al., 2014; Liu et al., 2015). Aromatic hydrocarbons were found to be vital SOA precursors in gasoline vehicle exhaust. Up to 90% of SOA from idling Euro 1–4 vehicle exhaust could be attributed to aromatics (Nordin et al., 2013; Liu et al., 2015). Gordon et al. (2014) concluded that traditional precursors could fully explain the SOA production from old vehicles with model years prior to 1995. Emitted primarily from coal-fired power plants and coal-burning boilers, SO_2, when mixed with gasoline vehicle exhausts containing the precursors for secondary nitrates and organic aerosols, NO_x and aromatics, may react, complicating the formation of sulfate and SOA”

Line 77–Change “The alkenes” to “alkenes”

Line 78–Change “exhausts” to “exhaust”

Line 78–Change “CIs” to “sCIs”

Line 78–Delete “which were”

Line 79-80–Change “thus influence the formation of sulfate” to “influence sulfate formation”

Line 81–Delete “the”

Line 85–Change “is still” to “still remains”

Line 85-88–Change “In addition, these combinations of several pure chemicals could not well represent the mixing of SO_2 with vehicle exhausts brimming with…” to “Combinations of several pure chemicals, additionally, are not fully representative of SO_2 mixing with vehicle exhausts containing…”

Line 91–Change “the formation of secondary aerosols” to “secondary aerosol formation”

Line 92–Change “exhausts” to “exhaust”

Line 93–Change “exhausts” to “exhaust”

Line 95–Change “exhausts” to “exhaust”

Line 96–Change “the oxidation of SO_2” to “SO_2 oxidation”

Line 97–Change “the formation of SOA” to “SOA formation”

Line 97–Change “exhausts” to “exhaust”

Line 100-103–Add “In Europe, vehicle emissions are classified by “Euro Standards”, currently ranging from Euro 1 to Euro 6. China implemented the Euro 1, Euro 2, Euro 3 and Euro 4 emission standards in 2000, 2004, 2007 and 2012 for LDGVs and the Euro 5 standard will be implemented in 2018.” before “Three LDGVs…”

Line 103–Change “used” to “utilized”

Line 105–Change “More details of the individual vehicles” to “Further vehicle details”

Line 106 –Delete “the”

Line 110–Change “of” to “with”

Line 111–Change “in” to “at”

Line 112–Change "The details" to "Details"

Line 114–Add "the" after "used as"

Line 116–Change "well" to "thorough"

Line 117–Change "In this study the temperature" to "Temperature"

Line 118–Change "around" to "approximately"

Line 118–Add "A schematic of the experiment setup is presented in Fig. 1. Eight thermocouples are placed between the enclosure and the reactor walls to control the temperature. The temperature inside the reactor (T9) was measured by Siemens QFM2160 (Siemens AG, Germany)." after "respectively."

Line 121-124–Change "Before the introduction of vehicle exhaust, the vehicles were running on-road for at least half an hour to warm up the three-way catalysts, and then the idling vehicle exhaust was introduced directly…" to "Vehicles were first operated on-road to warm up the three-way catalysts for a minimal half an hour prior to introducing the vehicle exhaust. Idling vehicle exhaust was then introduced directly…"

Line 130–Change "at least" to "a minimal"

Line 133-138–Change "After the introduction of exhaust, SO_2 was injected by a gas-tight syringe to make the mixing ratio of SO_2 in the reactor around 150 ppb during three experiments using the three vehicles. For comparison, experiments without additional SO_2 were also conducted for each vehicle. Additional NO was added to adjust the VOC/NO_x ratios to between 4.9 and 10.8 (Table 2)." to "SO_2 was injected by a gas-tight syringe following introduction of exhaust to create a mixing ratio of SO_2 in the reactor of approximately 150 ppb during three experiments with the three vehicles. Experiments without additional SO_2 were also conducted for each vehicle to compare and additional NO was added to adjust the VOC/NO_x ratios (ppb/ppb) to between 4.9 and 10.8 (Table 2)."

Line 139–Change ". Initial" to "with initial"

Line 140–Change "ranged" to "ranging"

Line 142-145–Change "After the black lamps were switched off, the formed SOA was characterized for another 2 to 3 h to correct the particles wall loss. In this study, no OH precursor and seed particles were introduced." to "The formed SOA was characterized for another 2 to 3 h after the black lamps were switched off to correct the particles wall loss. OH precursor and seed particles were not introduced in this study.”

Line 174–Change “like” to “including”

Line 176–Change “using the” to “with”

Line 180–Change “span” to “spans”

Line 180 –Delete “those”

Line 181–Change “Primary OA (POA)” to “POA”

Line 182–Change “, which” to “and”

Line 185-192–Change “Though initial NMHCs, NO_x and average OH concentrations are different from typical urban conditions, we tried to maintain the initial concentrations of the reactants as similar as possible for the same vehicle, so that all the changes in the SOA mass could be attributed to the effects of SO_2.” to “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). Initial concentrations of the reactants were maintained as similar as possible for the same vehicle, though initial NMHCs, NO_x and average OH concentrations are different from typical urban conditions, so all changes in SOA mass could be attributed to the effects of SO_2.”

Line 200-202–Change “The total hydrocarbons measured in this study include methane and C_2-C_{12} hydrocarbons.” to “Total hydrocarbons measured in this study include methane and C_2-C_{12} hydrocarbons. The carbon content of each hydrocarbon was respectively calculated and then summed in Eq. (1)”

Line 208-210–Add “The value of *k* is obtained from the Master Chemical Mechanism version 3.3 or MCM v3.3 (http://www.chem.leeds.ac.uk/MCM) (Jenkin et al., 2003).” after “…toluene and OH radical.”

Line 214–Change “therefore” to “then”

Line 216-220–Add “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.” after “Eq. (4)”

Line 221–Change “stabilized CIs” to “sCIs”

Line 222-226–Change "The production of sCIs in the atmosphere is dominated by ozonolysis of alkenes (Heard et al., 2004)." to "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)."

Line 227–Reaction (1) is revised as:

$$\text{alkene} + O_3 \longrightarrow \phi \text{sCIs} + \text{products}$$

Line 228–Add "where ϕ represents the yield of sCIs from ozonolysis of alkenes." before "The four main losses…"

Line 230-233–Reactions (2-5) are revised as follows:

$$\text{sCIs} + H_2O \longrightarrow \text{products} \qquad \text{(R2)}$$

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

$$\text{sCIs} + NO_2 \longrightarrow \text{products} \qquad \text{(R4)}$$

$$\text{sCIs} \longrightarrow \text{products} \qquad \text{(R5)}$$

Line 234–Change "CIs" to "sCIs"

Line 236-239–Add "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. This equation was widely used to predict the steady state concentration of sCIs in the atmosphere (Welz et al., 2012; Newland et al., 2015)." after "Eq. (5)"

Line 240-250–Change "In this study, we estimated the steady state concentration of stabilized CIs throughout the whole experiment. The production rate of stabilized CIs depended on both the concentrations and composition of alkenes in the exhausts. Detailed gas-phase mechanisms of alkenes from the Master Chemical Mechanism version 3.3 or MCM v3.3 (http://www.chem.leeds.ac.uk/MCM) were run to determine the time-resolved concentrations of stabilized CIs in the experiments." to "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 exhaust. 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%."

Line 251–Change "the measured" to "measured"

Line 252-254–Add "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." after "…concentrations"

Line 255–Change "Table 4" to "Table 5"

Line 255-260–Change "The rate coefficients for other stabilized CIs reacted with H_2O, SO_2, NO_2 and their unimolecular decomposition were assumed to be same as CH_2OO." to "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."

Line 262–Change "respectively. Yields of other stabilized CIs were assumed to be same as" to "respectively, while yields of other sCIs were assumed to be same as"

Line 265–Change "has to" to "must"

Line 273–Change "the wall" to "wall"

Line 274–Change "correction of particles" to "correction of the particles"

Line 275–Add "a" after "in"

Line 276-279–Change "In this study, the impact of the nucleation event on wall-loss estimate is considered to be negligible for only less than 5% of the particle mass is in the nucleation mode twenty minutes after nucleation for all the experiments." to "The impact of the nucleation event on wall-loss estimate is considered to be negligible as less than 5% of the particle mass is in the nucleation mode twenty minutes after nucleation for all experiments in this study."

Line 281-283–Change "It is recently established that wall deposition of a compound is related with…" to "Wall deposition of a compound has recently been established as related with…"

Line 290-292–Change "The ratio of…" to "The emission of black carbon (BC) from LDGVs was negligible according to a previous study (Liu et al., 2015), thus the ratio of…"

Line 297–Change "Fig. 1" to "Fig. 2"

Line 300-311–Change "After the black lamps were turned on, NO was fast oxidized in less than 1 h. With or without SO_2, mass concentrations of secondary aerosols started to climb rapidly after photooxidation for about 1 h, and became stabilized after about 4 h photooxidation (Figs 1, 2, and 3). For experiments with SO_2, substantial sulfate was formed synchronously with OA. The maximum particle number concentrations with SO_2 were 5.4–48 times of those without SO_2 (Table 1, Fig .4), indicating enhanced new particle formation (NPF) when adding SO_2. As the precursor of sulfuric acid (H_2SO_4), SO_2 at higher concentrations would lead to more H_2SO_4 formed, and thereby increase the nucleation rates and total particle number concentrations (Sipila et al., 2010)." to "After the black lamps were switched on, NO was rapidly consumed in less than 1 h. Mass concentrations of secondary aerosols rapidly ascended following photooxidation with or without SO_2 for approximately 1 h, stabilizing after approximately 4 h of photo-oxidation (Figs. 2, 3, and 4). Substantial sulfate was formed synchronously with OA for experiments with SO_2 with the maximum particle number concentrations at 5.4–48 times of those without SO_2 (Table 1, Fig. 5), indicating enhanced new particle formation (NPF) when adding SO_2. As the precursor of sulfuric acid (H_2SO_4), SO_2 at higher concentrations would lead to additional formation of H_2SO_4, thereby increasing the nucleation rates and total particle number concentrations (Sipila et al., 2010)."

Line 311-332–Add "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.

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)." after "…particle number concentrations (Sipila et al., 2010)."

Line 333–Change "the formation" to "Formation"

Line 335–Change "started (Fig. 5a)" to "initiated (Fig. 6a)"

Line 342–Add "(Zhang et al., 2011)" after "in 2008"

Line 343-348–Add "The formation rate of sulfate was related to the concentrations of SO_2 and OH, which were respectively approximately 7 times higher and 2-16 times lower than those in the study of Xiao et al. (2009). Significant differences of sulfate formation rates between chamber and ambient observations could not be explained; however, indicating there might be other processes dominating the oxidation of SO_2 rather than gas-phase oxidation by OH in this study." after "…in 2008 (Zhang et al., 2011)."

Line 349–Change "Normally, SO_2 was deemed…" to "SO_2 was typically deemed…"

Line 352-353–Change "because of RH around 50%" to "due to RH of approximate 50%"

Line 355–Change "only accounting for" to "accounting for only"

Line 357–Change "this" to "the"

Line 358–Change "exhausts" to "exhaust"; Change "stabilized CIs" to "sCIs"

Line 359–delete "that"

Line 360-373–Change "The oxidation of SO_2 by stabilized CIs could be as important as that by OH radicals in the atmosphere. Here, we estimated the steady state concentrations of stabilized CIs throughout the whole experiments by running detailed gas-phase mechanisms of alkenes from the MCM v3.3. For experiments I-2 and III-2, the oxidation rate of SO_2 through the reactions with stabilized CIs was calculated to be 0.071 ± 0.033 h^{-1} and 0.045 ± 0.022 h^{-1} (Fig. 6), respectively, accounting for 73.6% and 65.1% of the total loss rate of SO_2. Considering the variability of stabilized CIs throughout the whole experiment, we concluded that stabilized CIs nearly took full responsibility for the oxidation of SO_2 in experiments I-2 and III-2. Whereas, the oxidation rate of SO_2 through the reactions with stabilized CIs for the experiment II-2 was estimated to be 0.030 ± 0.017 h^{-1}, contributing 33.1% of the total loss rate of SO_2." to "The oxidation of SO_2 by sCIs may be as significant as that by OH radicals in the atmosphere. The oxidation rate of SO_2 for experiments I-2 and III-2, through the reactions with sCIs, was calculated to be 0.065 ±0.029 h^{-1} and 0.042 ±0.020 h^{-1} (Fig. 7), respectively, accounting for 66.9% and 61.4% of the total loss rate of SO_2. Considering the variability of sCIs throughout the entire experiment, we concluded that sCIs were virtually responsible for the oxidation of SO_2 in experiments I-2 and III-2. The oxidation rate of SO_2 through the reactions with sCIs for the experiment II-2 was estimated to be 0.028 ±0.015 h^{-1}, contributing 31.5% of the total loss rate of SO_2."

Line 373–Change "due to the" to "a result of"

Line 374–Change "exhausts" to "exhaust"

Line 376-385–Change "In this study, the reaction between SO_2 and NO_2 on the surface of existed aerosols might be a pathway to lead to the formation of sulfate." to "As shown in Fig. 5, the initial particle number for vehicle II was approximately 5000 cm^{-3}, nearly 40-50 times higher than those for vehicle I and III, providing larger aerosol surface areas for the oxidation of SO_2 by NO_2. However, quantification of SO_2 oxidation by NO_2 on the surface of existing aerosols is difficult due to the lack of reaction rate constant (He et al., 2014). We speculate that the reaction between SO_2 and NO_2 on the surface of existing aerosols might explain the difference between the total loss rate of SO_2 and the sum of sCIs and OH oxidation for vehicle II."

Line 388–Change "exhausts" to "exhaust"

Line 390–Change "Fig. 7a" to "Fig. 8a"

Line 391-401–Change "Accordingly when adding SO_2, the in-situ particle acidities at the time when SOA formation rate peaks, calculated as H^+ concentrations based on AIM-II model H^+–NH_4^+–SO_4^{2-}–NO_3–H_2O with gas-aerosol partitioning disabled (http://www.aim.env.uea.ac.uk/aim/model2/model2a.php) (Clegg et al., 1998; Wexler and Clegg, 2002), were 1.6–3.7 times as high as those without adding SO_2 (Table 3)." to "The in-situ particle acidities at the time when SOA formation rate peaks were calculated as H^+ concentrations based on AIM-II model H^+–NH_4^+–SO_4^{2-}–NO_3^-–H_2O with gas-aerosol partitioning disabled (http://www.aim.env.uea.ac.uk/aim/model2/model2a.php) (Clegg et al., 1998; Wexler and Clegg, 2002). Inputs to the model include temperature, RH, $[SO_4^{2-}]$, $[NO_3^-]$, $[NH_4^+]$ and $[H^+]_{total}$, calculated based on ion balance. SO_4^{2-}, NH_4^+ and NO_3^- contributed virtually all of the aerosol phase ions mass in this study, thus determining the aerosol acidity. Though other ions (i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+) had negligible influence on the aerosol acidity, it is worth noting that the reported values of H^+ may be the upper bound. The in-situ particle acidities with the addition of SO_2 were 1.6–3.7 times as high as those without the addition of SO_2 (Table 3)."

Line 403–Change "exhausts" to "exhaust"

Line 404–Change “Fig. 7b” to “Fig. 8b”

Line 405–Change “important” to “vital”; Change “exhausts” to “exhaust”

Line 408–Change “greatly” to “significantly”

Line 410–Delete “as”

Line 410–Change “those” to “yields”

Line 412–Change “, which might be” to “possibly”

Line 413-414–Change “In this study, SOA production from gasoline vehicle exhaust was enhanced even at a low level of [H^+]…” to “SOA production from gasoline vehicle exhaust was enhanced in this study, even at a low level of [H^+]…”

Line 415–Change “exhausts” to “exhaust”

Line 416–Change “quickly” to “rapidly”

Line 418-452–Change “As shown in Fig. 8, the ion fragment m/z 88 that can only arise from a gloxyal 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.” to “Aerosol water is needed for the hydration of carbonyls and therefore it influences the acid-catalyzed reactions. Liquid water content (LWC) in this study was not measured but predicted by the AIM-II model, with an average value of 5.5±4.5 μg m^{-3} when SOA formation rate peaks, ensuring the occurrence of acid-catalyzed reactions. 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. A photo-oxidation experiment of exhaust from vehicle I in the presence of ammonium sulfate seeds (53.3 μg m^{-3}) with RH of 59% (Table 2) was conducted to explore the effect of sulfate on SOA formation as particle acidity is typically driven by sulfate. The SOA production factor was 22.2 mg kg^{-1} fuel, comparable with 26.2 mg kg^{-1} fuel for experiment I-1, indicating that sulfate may not directly influence SOA production. Thus, the SOA production was indeed dependent on the particle acidity.

The addition of SO_2 may vary the vapor wall loss rate and influence the estimation of SOA production. The wall accommodation coefficient ($\alpha_{w,i}$), governing the extent of wall deposition of a compound i, was observed to be inversely dependent on its effective saturation concentration C_i^* (X. Zhang et al., 2015). Partitioning coefficients for different C_i^* ranging from 0.01 to 10^6 µg m^{-3} were calculated using gas-particle partitioning theory (Donahue et al., 2006) (Table 6). Partitioning coefficients for experiments with and without the addition of SO_2 mainly exhibited big differences for C_i^* bins of 10 and 100 µg m^{-3} with $\alpha_{w,i}$ calculated to be 3.1×10^{-7} and 2.0×10^{-7}, respectively. The wall loss rate for C_i^* bin of 10 µg m^{-3} would then be approximately 50% higher than that for C_i^* bin of 100 µg m^{-3} assuming a linear relation between wall loss rate and $\alpha_{w,i}$ (X. Zhang et al., 2015). An increase of 50% in wall loss rate would lead to 11.5% higher vapor loss to walls when assuming the wall loss rate to be 2.0×10^{-5} s^{-1}, similar to a product of the photo-oxidation of toluene. Thus, biases of vapor wall loss rates due to the addition of SO_2 may have negligible influence on estimation of SOA production."

Line 455-461–Change "Therefore, the increase of condensation sinks due to the formation of sulfate with adding SO_2 might be another reason that caused the enhancement of SOA production." to "However, comparable SOA PFs for experiments with and without seed aerosols observed in this study indicated the negligible impact of seed aerosols on SOA production. Cocker III et al. (2001) also observed that the presence of ammonium sulfate seed aerosols had no impact on SOA formation from the photo-oxidation of m-xylene and 1,3,5-trimethylbenzene ."

Line 464–Change "Fig. 5b" to "Fig. 6b"

Line 468–Add "Fig. 10 shows the correlation between SOA formation rate and particle acidity. Plotted data corresponded to data selected from Fig. 6 when SOA formation rate was higher than zero to when the rate reached the maximum value." after "…haze (He et al., 2014)."

Line 472–Delete "(Fig. 9)"

Line 474–Change "on the fast" to "in the rapid"

Line 475-480–Add "The fitted slopes for vehicle I, II and III were 3.96, 0.82 and 3.14, respectively, suggesting other factors, including alkene abundance, may influence the SOA formation rate. The initial concentration of alkenes for experiments I-2, II-2 and III-2 was 547 ppb, 248 ppb and 353 ppb, respectively, consistent with the variation of the slopes. Higher alkene content would increase the formation rate of sCIs, which could rapidly oxidize SO_2 to sulfuric acid, thus influence the aerosol acidity." after "…(Jang et al., 2002)."

Line 484–Change "Fig. 10" to "Fig. 11"

Line 484-487–Add "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." after "…Fig.

11.”

Line 487–Add “(0.44±0.02)” after “O:C”

Line 487–Add “(1.40±0.03)” after “H:C”

Line 488–Change “exhausts” to “exhaust”

Line 491–Change “that averagely” to “an average”

Line 492–Change “exhausts” to “exhaust”

Line 493–Change “though they were” to “with”

Line 495-498–Change “As Loza et al. (2012) did not observed a difference in H:C and O:C for m-xylene SOA with neutral and acidic seed particles, acid-catalyzed heterogeneous reactions might not influence…” to “A difference in H:C and O:C for m-xylene SOA with neutral and acidic seed particles was not observed by Loza et al. (2012), thus acid-catalyzed heterogeneous reactions may not influence…”

Line 501–Change “the compounds” to “compounds”

Line 505–Change “might” to “may”

Line 506-518–Add “The O:C ratios were observed to decrease 0.1 with an increase of approximately 50 μg m^{-3} of OA concentrations for m-xylene and p-xylene (Kang et al., 2011). However, in this study the slope was 0.1 ΔO:C for approximately 26 μg m^{-3} ΔOA. The differences may be due to that some other precursors other than aromatics contributed to SOA formation from gasoline vehicle exhaust (Liu et al., 2015).
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.” after “…decrease the oxidation degree of OA.”

Line 520–Change “We reported a…” to “A…”

Line 521–Add “were conducted” after “vehicle exhaust”

Line 522-525–Change “The high content of alkenes in gasoline vehicle exhaust formed a plenty of stabilized CIs, which dominated the formation of sulfate. On the other hand, the elevated particle acidity due to the formation of sulfuric acid enhanced the SOA production from gasoline vehicle exhaust." to "The high content of alkenes in gasoline vehicle exhaust formed numerous sCIs, dominating the formation of sulfate while elevated particle acidity, resulting from the formation of sulfuric acid, enhanced SOA production from the gasoline vehicle exhaust."

Line 526–Change "exhausts" to "exhaust"

Line 527–Change "Consequently, high concentration…" to "High concentration…"

Line 528–Change "combined" to "together"; Change "heavy" to "heavily"

Line 529–Change "would make…" to "might consequently worsen…"; Change "worse if there were no" to "in the absence of "

Line 532–Delete "the"

Line 532–Change "not a good thing" to "damaging"

Line 535–Change "stabilized CIs" to "sCIs"; Change "which would facilitate" to "facilitating"

Line 536–Change "In China the" to "The"

Line 537–Add "in China" after "content"

Line 539–Change "is still quite" to "remains substantially"

Line 541–Change "would" to "might"

Line 578–Add the reference "Cocker III, D. R., Mader, B. T., Kalberer, M., Flagan, R. C., and Seinfeld, J. H.: The effect of water on gas–particle partitioning of secondary organic aerosol: II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems, Atmos. Environ., 35, 6073-6085, doi:10.1016/S1352-2310(01)00405-8, 2001."

Line 592–Add the reference "Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled Partitioning, Dilution, and Chemical Aging of Semivolatile Organics, Environ. Sci. Technol., 40, 2635-2643, doi:10.1021/es052297c, 2006."

Line 601–Add the reference "Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, P. Natl. Acad. Sci., 107, 6670-6675, doi:10.1073/pnas.0912340107, 2010."

Line 630–Add the reference "Huang, D. D., Li, Y. J., Lee, B. P., and Chan, C. K.: Analysis of Organic Sulfur Compounds in Atmospheric Aerosols at the HKUST Supersite in Hong Kong Using HR-ToF-AMS, Environ. Sci. Technol., 49, 3672-3679, doi:10.1021/es5056269, 2015."

Line 646–Add the reference "Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181-193, doi:10.5194/acp-3-181-2003, 2003."

Line 691–Add the reference "Liu, T. Y., Wang, X. M., Wang, B. G., Ding, X., Deng, W., Lü, S. J., and Zhang, Y. L.: Emission factor of ammonia (NH_3) from on-road vehicles in China: tunnel tests in urban Guangzhou, Environ. Res. Lett., 9, 064027, doi:10.1088/1748-9326/9/6/064027, 2014."

Line 721–Add the reference "Ng, N. L., Canagaratna, M. R., Jimenez, J. L., Chhabra, P. S., Seinfeld, J. H., and Worsnop, D. R.: Changes in organic aerosol composition with aging inferred from aerosol mass spectra, Atmos. Chem. Phys., 11, 6465-6474, doi:10.5194/acp-11-6465-2011, 2011."

Line 743–Add references "Platt, S. M., El Haddad, I., Zardini, A. A., Clairotte, M., Astorga, C., Wolf, R., Slowik, J. G., Temime-Roussel, B., Marchand, N., Ježek, I., Drinovec, L., Močnik, G., Möhler, O., Richter, R., Barmet, P., Bianchi, F., Baltensperger, U., and Prévôt, A. S. H.: Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber, Atmos. Chem. Phys., 13, 9141-9158, doi:10.5194/acp-13-9141-2013, 2013.

Presto, A. A., Gordon, T. D., and Robinson, A. L.: Primary to secondary organic aerosol: evolution of organic emissions from mobile combustion sources, Atmos. Chem. Phys., 14, 5015-5036, doi:10.5194/acp-14-5015-2014, 2014.

Sato, K., Takami, A., Isozaki, T., Hikida, T., Shimono, A., and Imamura, T.: Mass spectrometric study of secondary organic aerosol formed from the photo-oxidation of aromatic hydrocarbons, Atmos. Environ., 44, 1080-1087, doi:10.1016/j.atmosenv.2009.12.013, 2010.

Seinfeld, J. and Pandis, S. N.: From air pollution to climate change, Atmospheric Chemistry and Physics, 2nd Edn., p. 208, 1998."

Line 834–Add the reference "Zhang, Y. M., Zhang, X. Y., Sun, J. Y., Lin, W. L., Gong, S. L., Shen, X. J., and Yang, S.: Characterization of new particle and secondary aerosol formation during summertime in Beijing, China, Tellus B, 63, doi:10.3402/tellusb.v63i3.16221, 2011."

Table 2 was revised.

Table 2. Summary of the initial conditions during the photooxidation of LDGV

exhaust.

Exp #[a]	OH (×10^6 molecules cm^{-3})	T (℃)	RH (%)	VOC /NO_x	NMHCs (ppbv)	NO (ppbv)	NO_2 (ppbv)	SO_2 (ppbv)
I–1	0.88	25.0 ±0.8	52.9 ±2.0	9.3	2896	300.6	9.5	8.6
I–2	1.19	25.5 ±0.3	53.6 ±2.5	7.7	2323	281.4	19.5	151.8
I–3[b]	1.45	23.9 ±0.9	59.0 ±4.1	7.9	2447	300.0	10.2	8.9
II–1	1.29	24.6 ±0.5	52.5 ±1.7	10.8	4313	374	24.7	9
II–2	1.08	24.2 ±0.7	55.9 ±2.5	9	3220	356	2.6	151.9
III–1	0.73	24.1 ±0.6	57.0 ±2.0	6	2582	431	0.6	9.2
III–2	0.79	24.3 ±0.3	57.9 ±1.2	4.9	2243	454.6	3.9	154.1

[a] Photooxidation experiments of LDGV exhaust named with I, II and III refers to different vehicles.

[b] Ammonium sulfate (53.3 µg m^{-3}) was introduced as seed aerosols.

The following Table was added as Table 4.

Table 4. 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

Table 4 was presented as Table 5.

Table 5. Summary of the final results during the photooxidation of LDGV exhaust.

Stabilized CIs	10^{15} K_{R2} (cm^3 molecule^{-1}s^{-1})	10^{11} K_{R3} (cm^3 molecule^{-1}s^{-1})	10^{12} K_{R4} (cm^3 molecule^{-1}s^{-1})	K_{R5} (s^{-1})
CH_2OO	0.025[a]	3.9[b]	7.0[b]	0[c]
CH_3CHOO	7.0[d]	4.55[d]	2.0[d]	67.5[e]
$(CH_3)_2COO$	2.1[c]	2.4[c]	2.0[c]	151[c]

[a] (Ouyang et al., 2013); [b] (Welz et al., 2012); [c] (Newland et al., 2015); [d] (Taatjes et al., 2013);

[e] Average of K_{R5} from Fenske et al. (2000) and Newland et al. (2015).

Table 6 was added.

Table 6. Partitioning coefficients for different C_i^* calculated using gas-particle partitioning theory.

$\log_{10}{}^{C_i*}$ (μg m^{-3})	I-1	I-2	II-1	II-2	III-1	III-3
-2	1.000	1.000	1.000	1.000	0.999	1.000
-1	0.999	0.999	0.997	0.997	0.994	0.999
0	0.987	0.989	0.968	0.974	0.946	0.987
1	0.886	0.901	0.754	0.789	0.638	0.885
2	0.437	0.477	0.235	0.272	0.150	0.435
3	0.072	0.084	0.030	0.036	0.017	0.071
4	0.008	0.009	0.003	0.004	0.002	0.008
5	0.001	0.001	0.000	0.000	0.000	0.001
6	0.000	0.000	0.000	0.000	0.000	0.000

The following figure was added as Fig. 1.

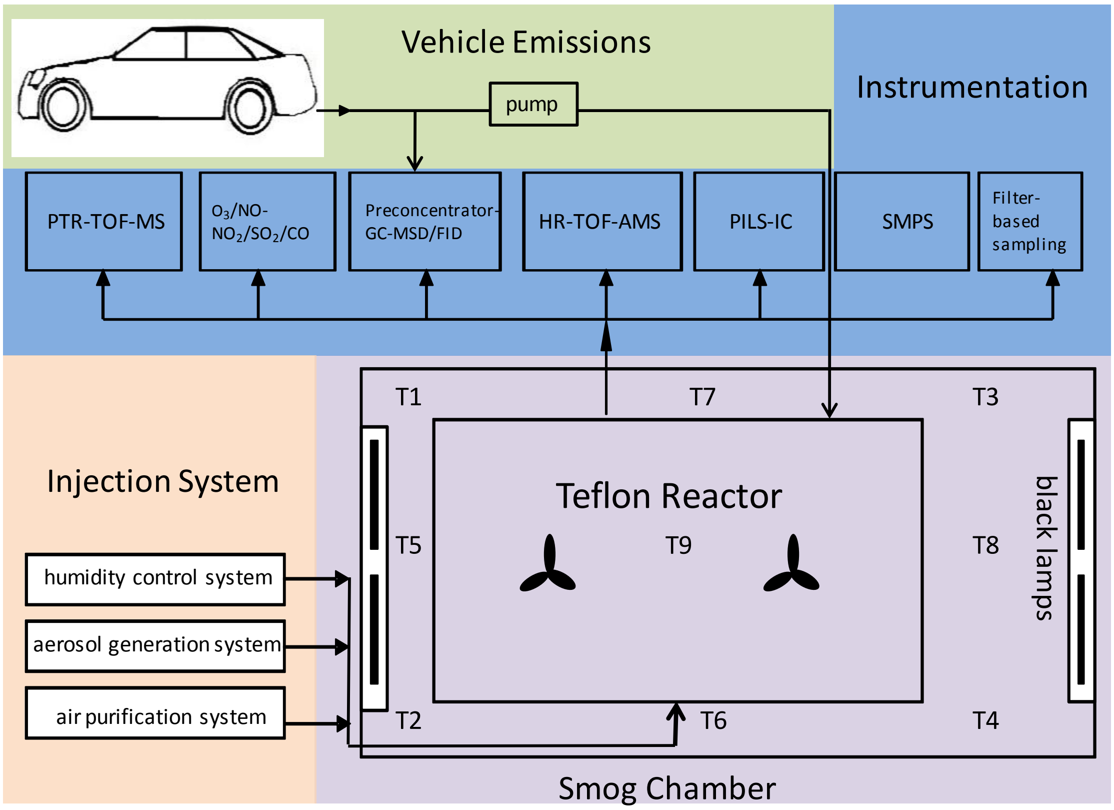

Fig. 1. Schematic of the GIG-CAS smog chamber facility and vehicle exhaust injection system.

The caption of **Fig. 1** was revised, now presented as **Fig. 2**.

Fig. 2. Concentration–time plots of NO (left-y axis) and particle–phase species (right-y axis) during the photochemical aging of emissions from vehicle III. (a) Without SO_2, and (b) with SO_2. The concentrations of particle-phase species are wall-loss corrected. At time =0 h, the black lamps were turned on.

The caption of **Fig. 2** was revised, now presented as **Fig. 3**.

Fig. 3. Concentration–time plots of NO (left-y axis) and particle–phase species (right-y axis) during the photochemical aging of emissions from vehicle I. (a) Without SO_2, and (b) with SO_2. The concentrations of particle-phase species are wall-loss corrected. At time =0 h, the black lamps were turned on.

The caption of **Fig. 3** was revised, now presented as **Fig. 4**.

Fig. 4. Concentration–time plots of NO (left-y axis) and particle–phase species (right-y axis) during the photochemical aging of emissions from vehicle II. (a) Without SO_2, and (b) with SO_2. The concentrations of particle-phase species are wall-loss corrected. At time =0 h, the black lamps were turned on.

Fig. 4 was now presented as **Fig. 5**.

Fig. 5 was revised and presented as **Fig. 6**.

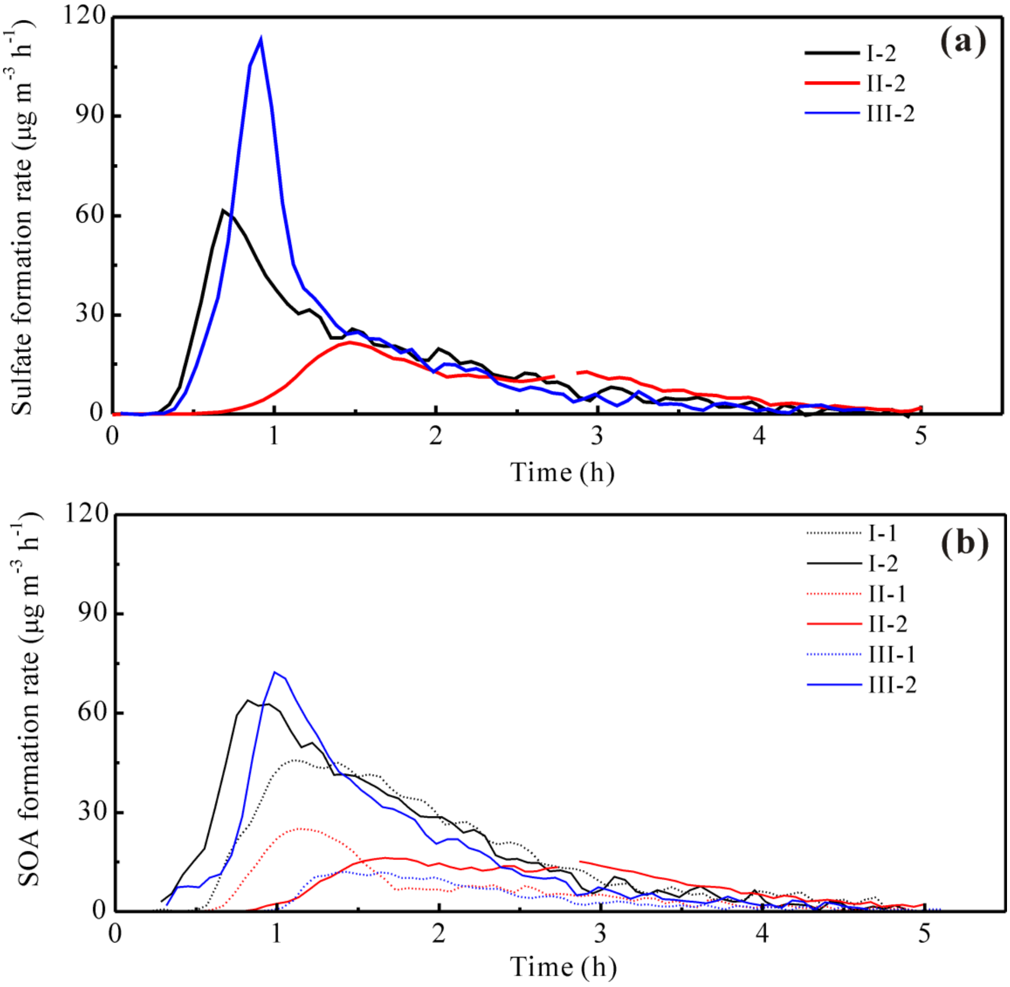

Fig. 6. Sulfate formation rates (**a**) and SOA formation rates (**b**) as a function of time during the photooxidation of LDGV exhausts.

Fig. 6 was revised and presented as **Fig. 7**.

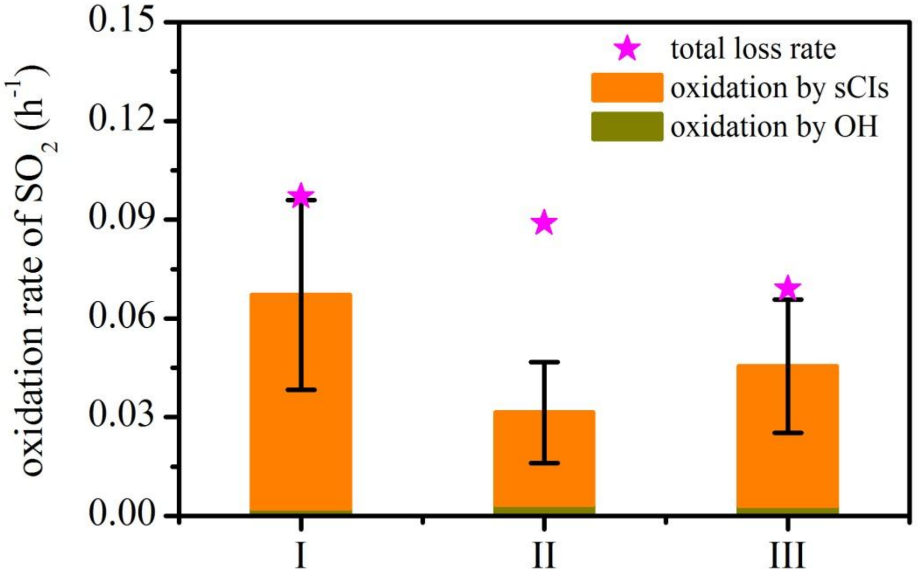

Fig. 7. The oxidation rate of SO_2 during the photooxidation of LDGV exhausts with SO_2. The loss rates of SO_2 reacting with OH radicals and sCIs were calculated by multiplying the reaction rate coefficients derived from the MCM v3.3 by the average OH concentration and estimated sCIs concentration, respectively. Error bars represent the standard derivation (1σ) of the oxidation rate of SO_2 by sCIs throughout the whole experiment.

Fig. 7 was revised and presented as **Fig. 8**.

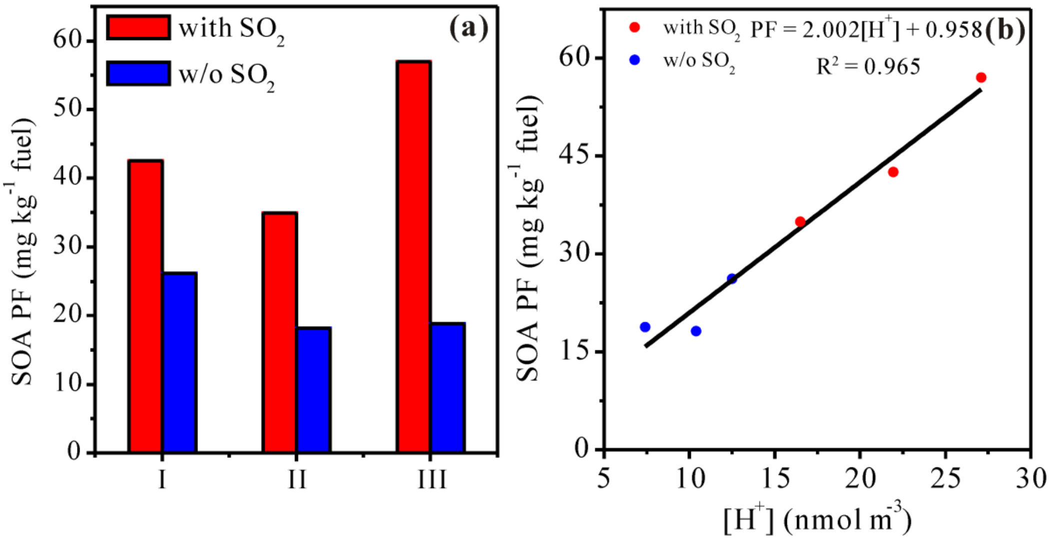

Fig. 7. SOA production factor (PF) and its relationship with particle acidity. (**a**) SOA PF after 5 h of photochemical aging of exhaust from different LDGVs with and

without additional SO_2. (**b**) SOA PF as a function of in-situ particle acidity. The concentration of H^+ in particle phase shown here was the value when the SOA formation rate reached the maximum during each experiment.

Fig. 8 was revised and presented as **Fig. 9**.

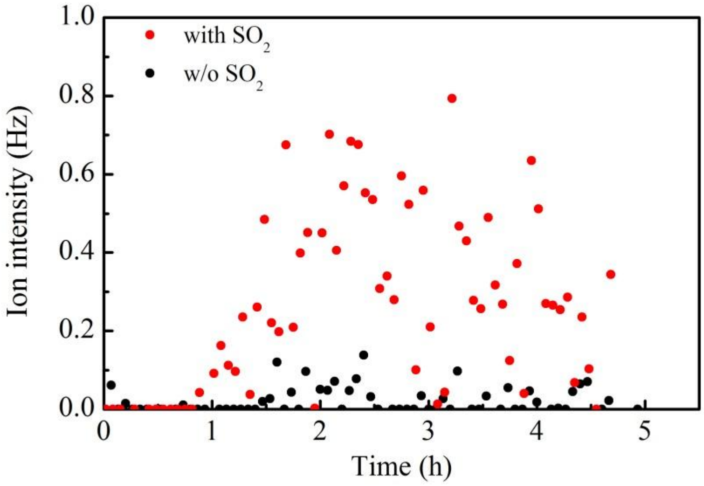

Fig. 9. Time evolution of m/z 88 during the aging of LDGV exhaust from vehicle III.

Fig. 9 was now presented as **Fig. 10**.

Fig. 10 was revised and presented as **Fig. 11**.

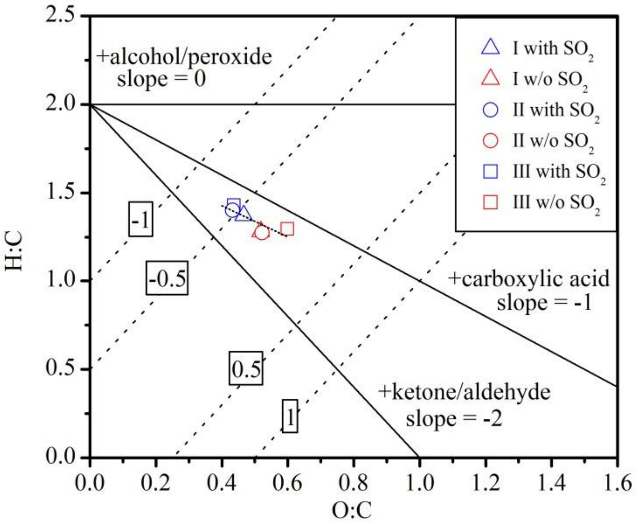

Fig. 11. O:C vs. H:C of SOA formed from LDGV exhaust with and without additional SO_2 at the end of each experiment. Blue and red symbols represent data with and

without additional SO_2, respectively. The dashed lines represent estimated average carbon oxidation states of -1, -0.5, 0.5 and 1 (Kroll et al., 2011). The black lines represent the addition of functional groups to an aliphatic carbon (Heald et al., 2010).

Formation of secondary aerosols from gasoline vehicle exhausts when mixing with SO_2

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Abstract

Sulfur dioxide (SO_2) can enhance the formation of secondary aerosols from biogenic volatile organic compounds (VOCs), but its influence on secondary aerosol formation from anthropogenic VOCs, particularly complex mixtures like vehicle exhaust~~s~~, ~~is still poorly understood~~remains uncertain.~~ Here we directly co-introduced gasoline~~ Gasoline vehicle~~s~~ exhaust~~s~~ (GVE) and SO_2, a typical pollutant from coal burning, are directly co-introduced into a smog chamber, in this study, to investigate the formation of secondary organic aerosols (SOA) and sulfate aerosols through photooxidation.~~ In the presence of high concentration of SO~~$_2$~~, new ~~New particle formation was enhanced while substantial sulfate was formed through the oxidation of SO_2 in the presence of high concentration of SO_2. ~~The h~~Homogenous oxidation by OH radicals contributed a negligible fraction to the conversion of SO_2 to sulfate, and instead the oxidation by stabilized Criegee intermediates (sCIs), formed from alkenes in the exhaust reacting with ozone, dominated the conversion of SO_2. After 5 h of photochemical aging, GVE's SOA production factor revealed an increase by 60–200% in the presence of high concentration of SO_2. ~~This ~~The increase could ~~largely ~~principally be attributed to acid-catalyzed SOA formation~~, which was~~ as evidenced by the strong positive linear correlation ($R^2 = 0.97$) between the SOA production factor and in-situ particle acidity calculated by AIM-II model. A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS) resolved OA's relatively lower oxygen-to-carbon (O:C) (0.44 ±0.02) and higher hydrogen-to-carbon (H:C) (1.40 ±0.03) molar ratios for the GVE/SO_2 mixture, with a ~~much ~~significantly lower estimated average carbon

oxidation state (OS_c) of -0.51±0.06 than ~~that of~~ -0.19±0.08 for GVE alone. The relative higher mass loading of OA in the experiments with SO_2 might be ~~the major reason~~a significant explanation for the lower SOA oxidation degree ~~of SOA~~.

1. Introduction

~~As main components of fine particles or PM$_{2.5}$, sulfate~~ Sulfate and organic aerosols (OA) can lead to serious and complex air pollution (Parrish and Zhu, 2009) as the main components of fine particles or PM$_{2.5}$, ~~and have~~conveying negative effects on human health (Nel, 2005). ~~Furthermore, s~~Sulfate and OA additionally affect radiative forcing on a global scale (Andreae et al., 2005; Shindell et al., 2009~~).~~). Thus, ~~A~~ a detailed understanding of the magnitude and formation pathways of sulfate and OA is ~~therefore~~ critical to formulate control strategies and to accurately estimate their impact on air quality and climate.~~,~~ ~~yet this attempt is often complicated~~Complications often arise due to~~ the~~ missing or underestimated oxidation pathways of sulfur dioxide (SO$_2$) (Berglen et al., 2004), ~~which is~~ the precursor of sulfate, and the unclear formation mechanisms of secondary organic aerosols (SOA) (de Gouw et al., 2005; Heald et al., 2005; Johnson et al., 2006; Volkamer et al., 2006), ~~which~~ accounting for a large fraction of OA (Zhang et al., 2007).

~~SO$_2$, mainly emitted~~ Recent smog chamber studies have demonstrated that the amount of SOA formed from dilute gasoline vehicle exhaust often exceeds primary OA (POA) (Nordin et al., 2013; Platt et al., 2013; Gordon et al., 2014; Liu et al., 2015). Aromatic hydrocarbons were found to be vital SOA precursors in gasoline vehicle exhaust. Up to 90% of SOA from idling Euro 1–4 vehicle exhaust could be attributed to aromatics (Nordin et al., 2013; Liu et al., 2015). Gordon et al. (2014) concluded that traditional precursors could fully explain the SOA production from old vehicles with model years prior to 1995. Emitted primarily from coal-fired power plants and coal-burning boilers, SO_2, when mixed with gasoline vehicle exhaust~~s~~ containing the precursors for secondary nitrates and organic aerosols, ~~a plenty of~~ NO_x and aromatics, ~~that provide precursors for the formation of secondary nitrates and organic aerosols, might~~ may react, ~~with each other and make~~complicating the formation of sulfate and SOA ~~complicated~~. ~~The a~~Alkenes present in gasoline vehicle exhaust~~s~~ can react with ozone to form stabilized Criegee intermediates (sCIs), ~~which were~~ recently considered to significantly oxidize SO_2 and ~~thus~~ influence ~~the~~ sulfate formation ~~of sulfate~~ (Mauldin et al., 2012; Welz et al., 2012). On the other hand, recent smog chamber simulations indicated that SO_2 could enhance ~~the~~ SOA formation from typical biogenic precursors, such as monoterpenes and isoprene through acid-catalyzed reactions (Edney et al., 2005; Kleindienst et al., 2006; Jaoui et al., 2008), but the influence of acid-catalyzed reactions on SOA formation from aromatics ~~is still~~still remains debatable (Cao and Jang, 2007; Ng et al., 2007). ~~In addition, these combinations~~ Combinations of several pure chemicals, additionally, are not fully representative ~~could not well represent the mixing~~ of SO_2 mixing with vehicle exhaust~~s~~ ~~brimming with~~containing thousands of gaseous and particle-phase components (Gordon et al., 2014) in the formation of secondary aerosols under real atmospheric conditions. Till present no reports are available about the influence of SO_2 on ~~the~~ secondary aerosol formation ~~of secondary aerosols~~ from complex vehicle exhaust~~s~~.

Here we directly introduced pipe exhaust~~s~~ from light-duty gasoline vehicles (LDGV) and SO_2 into a smog chamber with a 30 m^3 Teflon reactor (Wang et al., 2014), to study the production of secondary aerosols: the influence of LDGV exhaust~~s~~ on ~~the~~ SO_2 oxidation ~~of SO_2~~ to form sulfate aerosols and reciprocally that of SO_2 on ~~the~~ SOA formation ~~of SOA~~ from primary organics in LDGV exhaust~~s~~.

2. Materials and methods

2.1 Vehicles and fuel

In Europe, vehicle emissions are classified by “Euro Standards”, currently ranging from Euro 1 to Euro 6. China implemented the Euro 1, Euro 2, Euro 3 and Euro 4 emission standards in 2000, 2004, 2007 and 2012 for LDGVs and the Euro 5 standard will be implemented in 2018. Three LDGVs were ~~used~~ utilized in this study, one Euro 1 and two Euro 4 vehicles. They are all port fuel injected vehicles with model years ranging from 2002 to 2011. ~~More~~ Further vehicle details ~~of the individual vehicles~~ are listed in Table 1. All ~~the~~ vehicles were fueled with Grade 93# gasoline, which complies with the Euro III gasoline fuel standard. Details of the gasoline composition can be found elsewhere (Zhang et al., 2013).

2.2 Smog chamber experiments

Six photochemical experiments ~~of~~ with LDGV exhaust were conducted in a 30 m^3 indoor smog chamber ~~in~~ at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences (GIG-CAS). ~~The d~~Details of the smog chamber were described by Wang et al. (2014). Briefly, black lamps (1.2m-long, 60W Philips/10R BL, Royal Dutch Philips Electronics Ltd, The Netherlands) are used as a light source, providing a NO_2 photolysis rate of 0.49 min^{-1}. Two Teflon-coated fans are installed inside the reactor to guarantee ~~well~~ thorough mixing of the introduced gas species and particles within

120 seconds. ~~In this study the t~~ Temperature and relative humidity in the reactor were controlled at ~~around~~ approximately 25 ℃ and 50%, respectively. A schematic of the experiment setup is presented in Fig. 1. Eight thermocouples are placed between the enclosure and the reactor walls to control the temperature. The temperature inside the reactor (T9) was measured by Siemens QFM2160 (Siemens AG, Germany).~~Before the introduction of vehicle exhaust, the v~~Vehicles were first operated~~running~~ on-road to warm up the three-way catalysts for ~~at least~~a minimal half an hour prior to introducing the vehicle exhaust. ~~to warm up the three-way catalysts, and then the i~~ Idling vehicle exhaust was then introduced directly by two oil-free pumps (Gast Manufacturing, Inc, USA) into the reactor at a flow rate of 40 L min^{-1}. Losses of volatile organic compounds (VOCs) and particles in the transfer lines were estimated to be less than 5% (Liu et al., 2015). Prior to each experiment, the chamber was evacuated and filled with purified dry air for at least 5 times, then the reactor was flushed with purified dry air for ~~at least~~a minimal 48 h until no residual hydrocarbons, O_3, NO_x, or particles were detected in the reactor. The exhaust in the reactor was diluted by a factor of 13–94 compared to the tailpipe.

~~After the introduction of exhaust,~~ SO_2 was injected by a gas-tight syringe following introduction of exhaust to ~~make the~~create a mixing ratio of SO_2 in the reactor of ~~around~~ approximately 150 ppb during three experiments ~~using~~ with the three vehicles. ~~For comparison, e~~Experiments without additional SO_2 were also conducted for each vehicle to compare~~.~~ and ~~Additional~~ additional NO was added to adjust the VOC/NO_x ratios (ppb/ppb) to between 4.9 and 10.8 (Table 2). VOC/NO_x

ratios in experiments with the same vehicle were similar~~.~~ with ~~Initial~~ initial concentrations of NO$_x$ ~~ranged~~ ranging from 300.8 to 458.5 ppb. After more than half an hour of primary characterization, the exhaust was exposed to black light continuously for 5 h.~~After the black lamps were switched off,~~ ~~the~~ The formed SOA was characterized for another 2 to 3 h after the black lamps were switched off to correct the particles wall loss. ~~In this study, no~~ OH precursor and seed particles were not introduced in this study.

An array of instruments was used to characterize gas and particle phase compounds in the reactor. Gas phase NO$_x$, O$_3$ and SO$_2$ were measured with dedicated monitors (EC9810, 9841T, Ecotech, Australia, and Thermo Scientific Model 43iTLE, USA). The detection limit and accuracy of the SO$_2$ instrument are 0.2 ppb and ±1 %, respectively. Methane and CO concentrations were determined using a gas chromatography (Agilent 6980GC, USA) with a flame ionization detector and a packed column (5A Molecular Sieve 60/80 mesh, 3 m × 1/8 inch) (Zhang et al., 2012). CO$_2$ was analyzed with a HP 4890D gas chromatography (Yi et al., 2007). Gas phase organic species were measured with a Mode 7100 preconcentrator (Entech Instruments Inc., USA) coupled with an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector/electron capture detector (GC-MSD/FID, Agilent Technologies, USA) (Wang and Wu, 2008, Zhang et al., 2010, 2012, 2013) and a commercial proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, Model 2000, Ionicon Analytik GmbH, Austria) (Lindinger et al., 1998; Jordan et al., 2009). C$_2$-C$_3$ and C$_4$-C$_{12}$ hydrocarbons were measured by GC-FID and GC-MSD, respectively. PTR-TOF-MS was used to determine the time-resolved concentrations of VOCs such as aromatics. The decay curve of toluene was used to derive the average hydroxyl radical (OH) concentration during each experiment.

Particle number concentrations and size distributions were measured with a scanning mobility particle sizer (SMPS, TSI Incorporated, USA, classifier model 3080, CPC model 3775). An aerosol density of 1.4 g cm^{-3} was assumed to convert the particle volume concentration into the mass concentration (Zhang et al., 2005). A high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-MS, Aerodyne Research Incorporated, USA) was used to measure the particle chemical compositions and nonrefractory PM mass (Jayne et al., 2000; DeCarlo et al., 2006). The instrument was operated in the high sensitivity V-mode and high resolution W-mode alternatively every two minutes. The toolkit Squirrel 1.51H was used to obtain time series of various mass components (sulfate, nitrate, ammonium and organics). We used the toolkit Pika 1.1H to determine the average element ratios of organics, ~~like ~~including H:C, O:C, and N:C (Aiken et al., 2007, 2008). The contribution of gas-phase CO_2 to the m/z 44 signal was corrected ~~using the~~with measured CO_2 concentrations. The HR-TOF-MS was calibrated using 300 nm monodisperse ammonium nitrate particles.

A summary of initial experimental conditions and final results is presented in Table 2 and Table 3, respectively. Total wall-loss corrected OA varied from 17.8 to 91.4 μg m^{-3}, which spans the typical urban PM concentrations in ~~those ~~heavy polluted megacities with poor air quality. ~~Primary OA (~~POA~~)~~ concentrations of the experiments ranged from 0.13 to 0.31 μg m^{-3}~~, which~~ and are negligible compared with the formed SOA. Initial mixing ratios of non-methane hydrocarbons (NMHCs) in the reactor were between 2.2 and 4.3 ppm, much higher than typical urban conditions. 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).~~Though initial NMHCs, NO_x and average OH concentrations are different from typical urban conditions, we tried to maintain the initial~~ Initial concentrations of the reactants were maintained as similar as possible for the same vehicle, though initial NMHCs, NO_x and average OH concentrations are different from typical urban conditions, so ~~that~~ all ~~the~~ changes in ~~the~~ SOA mass could be attributed to the effects of SO_2.

2.3 SOA production factors

SOA production factor (PF) (mg kg^{-1}) is calculated on a fuel basis:

$$PF = 10^6 \cdot [SOA] \cdot \left(\frac{[\Delta CO_2]}{MW_{CO_2}} + \frac{[\Delta CO]}{MW_{CO}} + \frac{[\Delta HC]}{MW_{HC}}\right)^{-1} \cdot \frac{\omega_C}{MW_C} \qquad (1)$$

where [ΔCO_2], [ΔCO], and [ΔHC] are the background corrected concentrations of CO_2, CO and the total hydrocarbons in the reactor in μg m^{-3}; [SOA] is the concentration of wall-loss corrected SOA in μg m^{-3}; MW_{CO2}, MW_{CO}, MW_{HC}, and MW_C are the molecular weights of CO_2, CO, HC and C. ω_C (0.85) is the carbon intensity of the gasoline (Kirchstetter et al., 1999). ~~The t~~Total hydrocarbons measured in this study include methane and C_2-C_{12} hydrocarbons. The carbon content of each hydrocarbon was respectively calculated and then summed in Eq. (1).

2.4 Determination of OH concentration

Decay of toluene measured by PTR-TOF-MS is used to determine the average OH concentration during each experiment. Changes in the toluene concentration over time can be expressed as:

$$\frac{d[toluene]}{dt} = -k \cdot [OH] \cdot [toluene] \qquad (2)$$

where *k* is the rate constant for the reaction between toluene and OH radical. The value of *k* is obtained from the Master Chemical Mechanism version 3.3 or MCM v3.3 (http://www.chem.leeds.ac.uk/MCM) (Jenkin et al., 2003). Assuming a constant OH concentration during an experiment, we can integrate Eq. (2) to get Eq. (3):

$$\ln\left(\frac{[toluene]_0}{[toluene]_t}\right) = k \cdot [OH] \cdot t \qquad (3)$$

So by plotting *ln*([toluene]$_0$/[toluene]$_t$) versus time t, we can obtain a slope that equals $k \times [OH]$. The average OH concentration is ~~therefore~~ then calculated as:

$$[OH] = \frac{slope}{k} \qquad (4)$$

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.

2.5 Determination of the steady state concentration of ~~stabilized~~ sCIs

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). ~~The production of stabilized CIs in the atmosphere is dominated by ozonolysis of alkenes (Heard et al., 2004).~~

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

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.

$$\text{sCIs} + H_2O \longrightarrow \text{products} \qquad (R2)$$

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

$$\text{sCIs} + NO_2 \longrightarrow \text{products} \qquad (R4)$$

$$\text{sCIs} \longrightarrow \text{products} \qquad (R5)$$

The steady state concentration of sCIs will be

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

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. This equation was widely used to predict the steady state concentration of sCIs in the atmosphere (Welz et al., 2012; Newland et al., 2015).

~~In this study, we estimated t~~The steady state concentration of ~~stabilized~~ sCIs throughout the ~~whole~~ entire experiment was estimated in this study. The production rate of ~~stabilized~~ sCIs ~~depended~~ was dependent on both the concentrations and composition of alkenes in the exhaust~~s~~. Detailed gas-phase mechanisms of alkenes from the ~~Master Chemical Mechanism version 3.3 or~~ MCM v3.3 ~~(http://www.chem.leeds.ac.uk/MCM)~~ were run to determine the time-resolved concentrations of ~~stabilized~~ 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 ~~the ~~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 ~~4~~5. The rate coefficients for other ~~stabilized ~~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 ~~yields of other ~~stabilized ~~sCIs were assumed to be same as CH_2OO.

2.6 Wall loss corrections

The loss of particles and organic vapors onto the reactor walls ~~has to~~must be accounted for to accurately quantify the SOA production. A detailed discussion of these corrections can be found elsewhere (Liu et al., 2015). The loss of particles onto the walls was treated as a first-order process (McMurry and Grosjean, 1985). The wall-loss rate constant was determined separately for each experiment by fitting the SMPS and AMS data with first-order kinetics when UV lamps were switched off. By applying this rate to the entire experiment, we use the same method as Pathak et al. (2007) to correct the wall loss of the particles. The wall loss of particles is a size-dependent process, therefore, the presence of nucleation would influence ~~the~~ wall loss correction of the particles due to the rapid loss of nucleation mode particles. As shown in a previous study, particle wall loss rates could not be accurately quantified for the particles generated in the nucleation event (Keywood et al., 2004). ~~In this study, the~~ The impact of the nucleation event on wall-loss estimate is considered to be negligible ~~for~~ as ~~only~~ less than 5% of the particle mass is in the nucleation mode twenty minutes after nucleation for all ~~the~~ experiments in this study.

Wall deposition of organic vapors can lead to the underestimation of SOA production (Matsunaga and Ziemann, 2010; X. Zhang et al., 2014, 2015). ~~It is recently established that wall~~ Wall deposition of a compound has recently been established ~~is~~ as related with its volatility (Zhang et al., 2015). The extent that wall deposition of organic vapors impacts on SOA production depends on the competition of organic vapors depositing onto walls and suspended particles. Here, we assumed that gas-particle partitioning of organic vapors dominated their wall depositions and thus organic vapors were considered to only partition onto suspended particles.

As the collection efficiency of sulfate in the HR-TOF-AMS can vary due to the coating of OA onto sulfate, we used AMS data combined with SMPS data to derive the time-resolved concentrations of OA, sulfate, ammonium and nitrate. The emission of black carbon (BC) from LDGVs was negligible according to a previous study (Liu et al., 2015), thus ~~T~~the ratio of OA to inorganic aerosols from the AMS was used to split the total particle mass measured by SMPS into the mass of OA, sulfate, ammonium and nitrate (Gordon et al., 2014; Liu et al., 2015).

3. Results and discussion

3.1 Formation of sulfate

Fig. ~~1~~ 2 shows the temporal evolution of gas– and particle–phase species during the photochemical aging of emissions from vehicle III with and without adding SO_2. NO was injected to adjust the VOC/NO_x ratio at approximately time = -0.25 h for both experiments. After the black lamps were ~~turned~~ switched on, NO was ~~fast~~ rapidly ~~oxidized~~ consumed in less than 1 h. ~~With or without SO_2,~~ ~~mass~~ Mass concentrations of secondary aerosols ~~started to climb~~ rapidly ascended ~~after~~ following photooxidation with or without SO_2 for ~~about~~ approximately 1 h, ~~and became stabilized~~stabilizing after ~~about~~ approximately 4 h of photo-oxidation (Figs. ~~1~~2, ~~2~~3, and ~~3~~4). ~~For experiments with SO_2,~~ ~~substantial~~ Substantial sulfate was formed synchronously with OA for experiments with SO_2~~.~~ – with ~~The~~ the maximum particle number concentrations ~~with SO_2 were~~at 5.4–48 times of those without SO_2 (Table 1, Fig. ~~4~~5), indicating enhanced new particle formation (NPF) when adding SO_2. As the precursor of sulfuric acid (H_2SO_4), SO_2 at higher concentrations would lead to ~~more~~ additional formation of H_2SO_4 ~~formed~~, ~~and~~ thereby ~~increase~~ increasing the nucleation rates and total particle number concentrations (Sipila et al., 2010). 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.

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).

~~The f~~Formation rates of sulfate, derived from the differential of concentration-time plots of sulfate, exhibited burst increases at the initial stage of sulfate formation and then decreased to near zero 5 h after sulfate formation ~~started~~ initiated (Fig. ~~5a~~6a). The maximum formation rate of sulfate in experiments I–2, II–2 and III–2 was 61.5, 21.6 and 113 μg m^{-3} h^{-1}, respectively, extremely higher than the rate of 0.17–0.37 ppbv h^{-1} (0.73–1.59 μg m^{-3} h^{-1} under NTP condition) through gas-phase oxidation of SO_2 during the daytime in the Pearl River Delta (PRD) region of China in the summer of 2006 (Xiao et al., 2009), and also more than ten times higher than the maximum sulfate formation rate of 4.79 μg m^{-3} h^{-1} observed at an urban site in Beijing during the Beijing Olympic Games in 2008 (Zhang et al., 2011). The formation rate of sulfate was related to the concentrations of SO_2 and OH, which were respectively approximately 7 times higher and 2-16 times lower than those in the study of Xiao et al. (2009). Significant differences of sulfate formation rates between chamber and ambient observations could, however, indicate that there might be other processes dominating the oxidation of SO_2 rather than gas-phase oxidation by OH in this study.

~~Normally,~~ SO_2 was typically deemed to be oxidized by OH radicals through homogeneous reactions in gas-phase (Calvert et al., 1978), or by H_2O_2 and O_3 through in-cloud processes in aqueous-phase (Lelieveld and Heintzenberg, 1992) that, however, could be negligible in this study ~~because of~~due to RH of ~~around~~ approximate 50%. As shown in Fig. ~~6~~7, the loss rate of SO_2 through homogeneous reactions with OH radicals in the three experiments ranged from 0.0023 to 0.0034 h^{-1}, ~~only~~ accounting for only 2.4%–4.6% of the total loss rate of SO_2. The initial concentrations of alkenes in the experiments with SO_2 varied from 248 to 547 ppb, contributing 7.7%–23.5% of the total NMHCs. ~~This~~ The high content of alkenes in the exhaust~~s~~ might form a mass of ~~stabilized~~ sCIs through the reaction with ozone. Recent studies indicated ~~that~~ the rate coefficient of CH_2OO with SO_2 was 50 to 10000 times larger than that used in tropospheric models (Welz et al., 2012). The oxidation of SO_2 by ~~stabilized~~ sCIs ~~could~~ may be as ~~important~~ significant as that by OH radicals in the atmosphere. ~~Here, we estimated the steady state concentrations of stabilized CIs throughout the whole experiments by running detailed gas-phase mechanisms of alkenes from the MCM v3.3. For experiments I-2 and III-2, the~~ The oxidation rate of SO_2 for experiments I-2 and III-2, through the reactions with ~~stabilized~~ sCIs, was calculated to be 0.~~071~~065±0.~~033~~ 029 h^{-1} and 0.~~045~~042±0.~~022~~ 020 h^{-1} (Fig. ~~6~~7), respectively, accounting for ~~73.6~~66.9% and ~~65.1~~61.4% of the total loss rate of SO_2. Considering the variability of ~~stabilized~~ sCIs throughout the ~~whole~~ entire experiment, we concluded that ~~stabilized~~ sCIs ~~nearly took full responsibility~~were virtually responsible for the oxidation of SO_2 in experiments I-2 and III-2. ~~Whereas, t~~The oxidation rate of SO_2 through the reactions with ~~stabilized~~ sCIs for the experiment II-2 was estimated to be 0.~~030~~028±0.~~017~~ 015 h^{-1}, contributing ~~33.1~~31.5% of the total loss rate of SO_2. The unexplained loss of SO_2 might be ~~due to the~~a result of heterogeneous oxidation in the presence of LDGV exhaust~~s~~ containing massive aerosols and gaseous species. He et al. (2014) found that SO_2 could react with NO_2 on the surface of mineral dust to promote the conversion of SO_2 to sulfate. As shown in Fig. 5, the initial particle number for vehicle II was approximately 5000 cm^{-3}, nearly 40-50 times higher than those for vehicle I and III, providing larger aerosol surface areas for the oxidation of SO_2 by NO_2. However, quantification of SO_2 oxidation by NO_2 on the surface of existing aerosols is difficult due to the lack of reaction rate constant (He et al., 2014). We speculate that the reaction between SO_2 and NO_2 on the surface of existing aerosols might explain the difference between the total loss rate of SO_2 and the sum of sCIs and OH oxidation for vehicle II.~~In this study, the reaction between SO_2 and NO_2 on the surface of existed aerosols might be a pathway to lead to the formation of sulfate.~~

3.2 SOA production

Fuel-based SOA production factors (PF), expressed as SOA production in milligram (mg) after 5 h photooxidation of LDGV exhaust~~s~~ emitted when per kilogram (kg) gasoline was burned, all increased substantially when adding SO_2, 60%–200% above that without SO_2 (Fig. ~~7a~~8a), although the selected cars' emission standards varied from Euro-I to Euro-IV. ~~Accordingly when adding SO_2, the~~ The in-situ particle acidities at the time when SOA formation rate peaks~~, ~~ were calculated as H^+ concentrations based on AIM-II model H^+–NH_4^+–SO_4^{2-}–NO_3^-–H_2O with gas-aerosol partitioning disabled (http://www.aim.env.uea.ac.uk/aim/model2/model2a.php) (Clegg et al., 1998; Wexler and Clegg, 2002~~), ~~). Inputs to the model include temperature, RH, $[SO_4^{2-}]$, $[NO_3^-]$, $[NH_4^+]$ and $[H^+]_{total}$, calculated based on ion balance. SO_4^{2-}, NH_4^+ and NO_3^- contributed virtually all of the aerosol phase ions mass in this study, thus determining the aerosol acidity. Though other ions (i.e., Ca^{2+}, Mg^{2+}, K^+ and Na^+) had negligible influence on the aerosol acidity, it is worth noting that the reported values of H^+ may be the upper bound. The in-situ particle acidities with the addition of SO_2

were 1.6–3.7 times as high as those without ~~adding~~ the addition of SO_2 (Table 3). This elevated particle acidity could largely explain the higher PFs of SOA from LDGV exhaust~~s~~ with SO_2, supported by the strong positive linear correlations ($R^2 = 0.965$, $P<0.01$) between SOA PFs and the in-situ particle acidities (Fig. ~~7b~~8b). Aromatic hydrocarbons are ~~important~~ vital SOA precursors in gasoline vehicle exhaust~~s~~ (Nordin et al., 2013; Gordon et al., 2014; Liu et al., 2015). The influence of particle acidity on SOA formation from aromatics is still debatable. Cao and Jang (2007) found that the presence of acid seeds with [H^+] concentrations of 240-860 nmol m^{-3} ~~greatly~~ significantly increased the SOA yields from oxidation of toluene and 1,3,5-trimethylbenzene ~~as~~ compared with ~~those~~ yields using neutral seed aerosols. However, Ng et al. (2007) observed no influence of particle acidity on SOA yields from the aromatics~~, which might be~~ possibly due to the low content of aerosol water. ~~In this study,~~ SOA production from gasoline vehicle exhaust was enhanced in this study, even at a low level of [H^+] concentrations ranging from 7.4 to 27.1 nmol m^{-3}. Gas-phase oxidation products of aromatic hydrocarbons in the ~~exhausts~~exhaust, like multifunctional carbonyl glyoxal, would be transformed more ~~quickly~~ rapidly to low volatility products through acid-catalyzed heterogeneous reactions (Jang et al., 2002; Cao and Jang, 2007) and thus caused increasing SOA production. Aerosol water is needed for the hydration of carbonyls and therefore it influences the acid-catalyzed reactions. Liquid water content (LWC) in this study was not measured but predicted by the AIM-II model, with an average value of 5.5 ± 4.5 μg m^{-3} when SOA formation rate peaks, ensuring the occurrence of acid-catalyzed reactions. 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. A photo-oxidation experiment of exhaust from vehicle I in the presence of ammonium sulfate seeds (53.3 μg m^{-3}) with RH of 59% (Table 2) was conducted to explore the effect of sulfate on SOA formation as particle acidity is typically driven by sulfate. The SOA production factor was 22.2 mg kg^{-1} fuel, comparable with 26.2 mg kg^{-1} fuel for experiment I-1, indicating that sulfate may not directly influence SOA production. Thus, the SOA production was indeed dependent on the particle acidity.~~As shown in Fig. 8, the ion fragment m/z 88 that can only arise from a gloxyal 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.~~

The addition of SO_2 may vary the vapor wall loss rate and influence the estimation of SOA production. The wall accommodation coefficient ($\alpha_{w,i}$), governing the extent of wall deposition of a compound i, was observed to be inversely dependent on its effective saturation concentration C_i^* (X. Zhang et al., 2015). Partitioning coefficients for different C_i^* ranging from 0.01 to 10^6 μg m^{-3} were calculated using gas-particle partitioning theory (Donahue et al., 2006) (Table 6). Partitioning coefficients for experiments with and without the addition of SO_2 mainly exhibited big differences for C_i^* bins of 10 and 100 μg m^{-3} with $\alpha_{w,i}$ calculated to be 3.1×10^{-7} and 2.0×10^{-7}, respectively. The wall loss rate for C_i^* bin of 10 μg m^{-3} would then be approximately 50% higher than that for C_i^* bin of 100 μg m^{-3} assuming a linear relation between wall loss rate and $\alpha_{w,i}$ (X. Zhang et al., 2015). An increase of 50% in wall loss rate would lead to 11.5% higher vapor loss to walls when assuming the wall loss rate to be 2.0×10^{-5} s^{-1}, similar to a product of the photo-oxidation of toluene. Thus, biases of vapor wall loss rates due to the addition of SO_2 may have negligible influence on estimation of SOA production. Recent studies indicated that the presence of high concentrations of seed aerosols might decrease the loss of organic vapors to the walls and thus increase the SOA formation (Kroll et al., 2007; X. Zhang et al., 2014, 2015). However, comparable SOA PFs for experiments with and without seed aerosols observed in this study indicated the negligible impact of seed aerosols on SOA production. Cocker III et al. (2001) also observed that the presence of ammonium sulfate seed aerosols had no impact on SOA formation from the photo-oxidation of m-xylene and 1,3,5-trimethylbenzene .~~Therefore, the increase of condensation sinks due to the formation of sulfate with adding SO_2 might be another reason that caused the enhancement of SOA production.~~

SOA formation rates, derived from the differential of concentration-time plots of SOA, exhibited similar trends as sulfate with a burst increase at the initial stage of SOA formation (Fig. ~~5b~~6b). The average SOA formation rates for vehicles I, II and III with SO_2 were 1.1, 1.2 and 4.4 times as high as those without SO_2, respectively, although the maximum rate for vehicle II with SO_2 was lower. Here we particularly focused on the burst increase stage of SOA and sulfate, which may be related to fast increase of $PM_{2.5}$ and occurrence of haze (He et al., 2014). Fig. 10 shows the correlation between SOA formation rate and particle acidity. Plotted data corresponded to data selected from Fig. 6 when SOA formation rate was higher than zero to when the rate reached the maximum value. Significant linear correlations ($P<0.05$, $R^2>0.88$) between SOA formation rate and particle acidity ~~(Fig. 9)~~ during this stage for experiments with SO_2 suggest that acid-catalyzed heterogeneous reactions might play an important role ~~on~~ in the ~~fast~~ rapid formation of SOA (Jang et al., 2002). The fitted slopes for vehicle I, II and III were 3.96, 0.82 and 3.14, respectively, suggesting other factors, including alkene abundance, may influence the SOA formation rate. The initial concentration of alkenes for experiments I-2, II-2 and III-2 was 547 ppb, 248 ppb and 353 ppb, respectively, consistent with the variation of the slopes. Higher alkene content would increase the formation rate of sCIs, which could rapidly oxidize SO_2 to sulfuric acid, thus influence the aerosol acidity.

3.3 Oxidation state

After 5 h of photo-oxidation, SOA's molar ratios of oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) resolved by HR-TOF-AMS, were plotted on a Van Krevelen diagram (Heald et al., 2010) in Fig. ~~10~~11. 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. Relatively lower O:C (0.44±0.02) and higher H:C (1.40±0.03) for the mixture of SO_2 and exhaust~~s~~ were observed than those for exhaust~~s~~ alone. The oxidation state of carbon (OS_c), estimated from O:C and H:C, can be used to describe the chemistry and oxidative evolution of atmospheric organic aerosols (Kroll et al., 2011). Further calculated OS_c revealed ~~that averagely~~ an average lower level of -0.51 ±0.06 for SOA formed from LDGV exhaust~~s~~ with SO_2 when compared to that of -0.19 ±0.08 without SO_2, ~~though they were~~with all within or near the OS_c range of -0.5–0 for semi-volatile OOA (SV-OOA) (Aiken et al., 2008). The relatively lower OS_c with SO_2 indicated a lower oxidation degree of SOA. ~~As Loza et al. (2012) did not observed a~~ A difference in H:C and O:C for m-xylene SOA with neutral and acidic seed particles was not observed by Loza et al. (2012), thus acid-catalyzed heterogeneous reactions ~~might~~ may not influence the oxidation degree of SOA in this study. Shilling et al. (2009) observed a lower O:C of SOA formed from the dark ozonolysis of α-pinene at a higher mass loading of organic aerosols and suggested that ~~the~~ compounds partitioning into the particle phase at lower loadings were more oxygenated. Kang et al. (2011) also observed that the oxidation degree of OA decreased rapidly as the OA mass concentration increased for the same amount of OH exposure. Given that the average OH concentrations were similar for the same vehicle (Table 2), the relative higher mass loading of OA in the experiments with SO_2 ~~might~~ may lead to the lower O:C and thus decrease the oxidation degree of OA. The O:C ratios were observed to decrease 0.1 with an increase of approximately 50 μg m^{-3} of OA concentrations for m-xylene and p-xylene (Kang et al., 2011). However, in this study the slope was 0.1 ΔO:C for approximately 26 μg m^{-3} ΔOA. The differences may be due to that some other precursors other than aromatics contributed to SOA formation from gasoline vehicle exhaust (Liu et al., 2015).

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.

4. Conclusions

~~We reported a~~A series of chamber experiments investigating the formation of secondary aerosols from the mixture of SO_2 and gasoline vehicle exhaust were conducted. The high content of alkenes in gasoline vehicle exhaust formed ~~a plenty of~~numerous ~~stabilized~~ sCIs, ~~which dominated~~dominating the formation of sulfate~~. On the other hand, the~~ while elevated particle acidity, ~~due to~~resulting from the formation of sulfuric acid, enhanced ~~the~~ SOA production from the gasoline vehicle exhaust. We concluded that SO_2 and gasoline vehicle exhaust~~s~~ can enhance each other in forming secondary aerosols. ~~Consequently, h~~High concentration of SO_2 and high levels of aerosol acidity ~~together~~ combined with rapid increase of LDGVs in ~~heavy~~ heavily polluted cities such as Beijing (Pathak et al., 2009; He et al., 2014) ~~would~~ might consequently ~~make~~ worsen the air quality ~~worse if there were no~~in the absence of stricter control strategies on emissions of SO_2 and vehicle exhaust~~s~~. Previous studies indicated that ~~the~~ high content of alkenes in China's gasoline oil was ~~not a good~~

~~thing~~damaging for the control of ozone in ambient air (Y. Zhang et al., 2013, 2015). Our results suggested that the incomplete combustion of gasoline with high content of alkenes might also induce the formation of ~~stabilized~~ sCIs, ~~which would facilitate~~ facilitating the production of secondary aerosols. ~~In China the~~ The limit of alkenes content in China was lowered to 24% by volume in the newly established Level V gasoline fuel standard from 28% by volume in the Level IV gasoline fuel standard. This limit ~~is still quite~~remains substantially higher when compared to those in USA or in Europe, and in particular, 6 times that in California, USA. Thus, limiting the content of alkenes in China's gasoline ~~would~~ might benefit the control of both ozone and secondary aerosols.

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Table 1. Detailed information of the three LDGVs.

ID	Emission standard class	Vehicle	Model year	Mileage (km)	Displacement (cm^3)	Power (kW)	Weight (kg)
Ⅰ	Euro4	Golf	2011	25000	1598	77	1295
Ⅱ	Euro4	Sunny	2011	9448	1498	82	1069
Ⅲ	Euro1	Accord	2002	237984	2298	110	1423

Table 2. Summary of the initial conditions during the photooxidation of LDGV exhaust~~s~~.

Exp #[a]	OH ($\times 10^6$ molecules cm^{-3})	T (℃)	RH (%)	VOC /NO_x	NMHCs (ppbv)	NO (ppbv)	NO_2 (ppbv)	SO_2 (ppbv)
I–1	0.88	25.0 ±0.8	52.9 ±2.0	9.3	2896	300.6	9.5	8.6
I–2	1.19	25.5 ±0.3	53.6 ±2.5	7.7	2323	281.4	19.5	151.8
I–3[b]	1.45	23.9 ±0.9	59.0 ±4.1	7.9	2447	300.0	10.2	8.9
II–1	1.29	24.6 ±0.5	52.5 ±1.7	10.8	4313	374	24.7	9
II–2	1.08	24.2 ±0.7	55.9 ±2.5	9	3220	356	2.6	151.9
III–1	0.73	24.1 ±0.6	57.0 ±2.0	6	2582	431	0.6	9.2
III–2	0.79	24.3 ±0.3	57.9 ±1.2	4.9	2243	454.6	3.9	154.1

[a] Photooxidation experiments of LDGV exhaust~~s~~ named with I, II and III refers to different vehicles.

[b] Ammonium sulfate (53.3 µg m^{-3}) was introduced as seed aerosols.

Table 3. Summary of the final results during the photooxidation of LDGV exhaust~~s~~.

Exp #	POA (µg m^{-3})	SOA (µg m^{-3})	Sulfate (µg m^{-3})	Ammonium (µg m^{-3})	Nitrate (µg m^{-3})	Particle number (cm^{-3})[a]	[H$^+$][b] (nmol m^{-3})
I–1	0.31	77.6	0.7	17.1	65.9	85182	12.5
I–2	0.21	91.2	67.5	17.6	6.1	563705	21.9
II–1	0.28	30.7	-	2.6	5.6	7427	10.4
II–2	0.13	37.3	38.1	9.7	1.9	357673	16.5
III–1	0.17	17.6	-	0.1	0.7	116143	7.4
III–2	0.23	77	76.7	19.2	5.3	630620	27.1

[a] Maximum particle number concentrations were without wall loss corrections.

[b] The concentration of H$^+$ in particle phase shown here was the value when the SOA formation rate reached the maximum during each experiment.

Table 4. 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

Table ~~4~~5. Summary of the final results during the photooxidation of LDGV exhaust~~s~~.

Stabilized CIs	10^{15} K_{R2} (cm^3 $molecule^{-1}s^{-1}$)	10^{11} K_{R3} (cm^3 $molecule^{-1}s^{-1}$)	10^{12} K_{R4} (cm^3 $molecule^{-1}s^{-1}$)	K_{R5} (s^{-1})
CH_2OO	0.025[a]	3.9[b]	7.0[b]	0[c]
CH_3CHOO	7.0[d]	4.55[d]	2.0[d]	67.5[e]
$(CH_3)_2COO$	2.1[c]	2.4[c]	2.0[c]	151[c]

[a] (Ouyang et al., 2013); [b] (Welz et al., 2012); [c] (Newland et al., 2015); [d] (Taatjes et al., 2013);

[e] Average of K_{R5} from Fenske et al. (2000) and Newland et al. (2015).

Table 6. Partitioning coefficients for different C_i^* calculated using gas-particle partitioning theory.

$\log_{10}{C_i^*}$ (µg m^{-3})	I-1	I-2	II-1	II-2	III-1	III-3
-2	1.000	1.000	1.000	1.000	0.999	1.000
-1	0.999	0.999	0.997	0.997	0.994	0.999
0	0.987	0.989	0.968	0.974	0.946	0.987
1	0.886	0.901	0.754	0.789	0.638	0.885
2	0.437	0.477	0.235	0.272	0.150	0.435
3	0.072	0.084	0.030	0.036	0.017	0.071
4	0.008	0.009	0.003	0.004	0.002	0.008
5	0.001	0.001	0.000	0.000	0.000	0.001
6	0.000	0.000	0.000	0.000	0.000	0.000

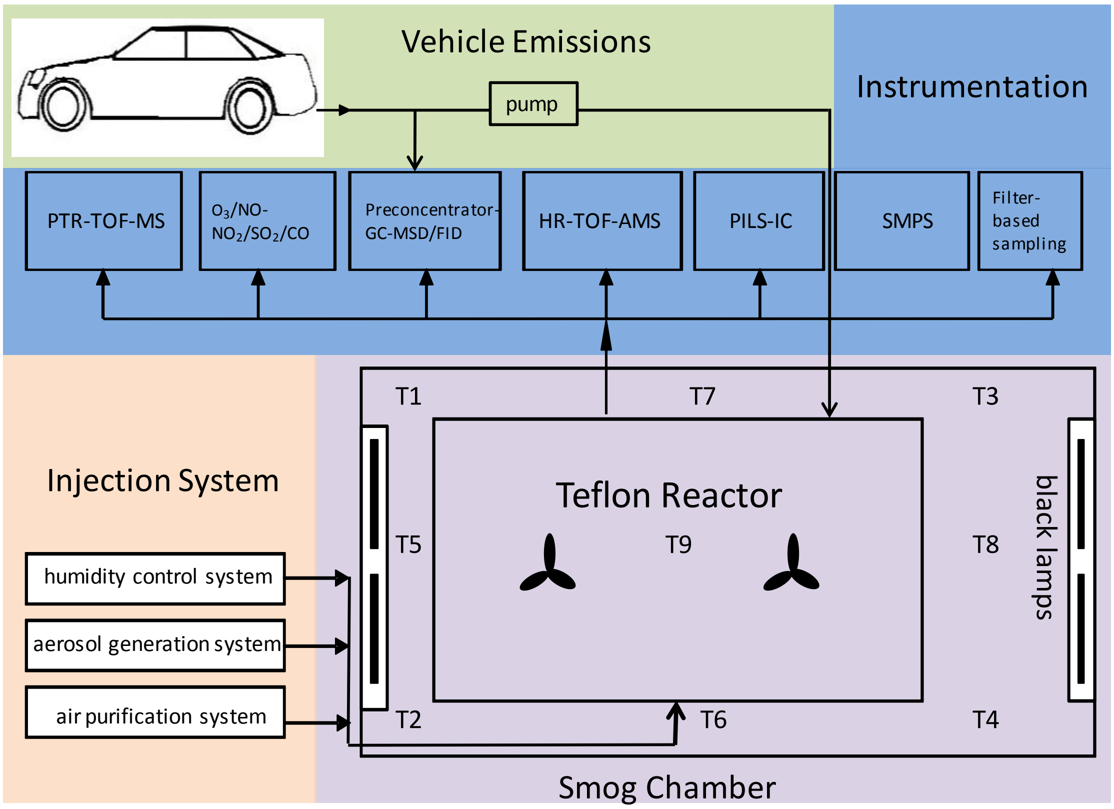

Fig. 1. Schematic of the GIG-CAS smog chamber facility and vehicle exhaust injection system.

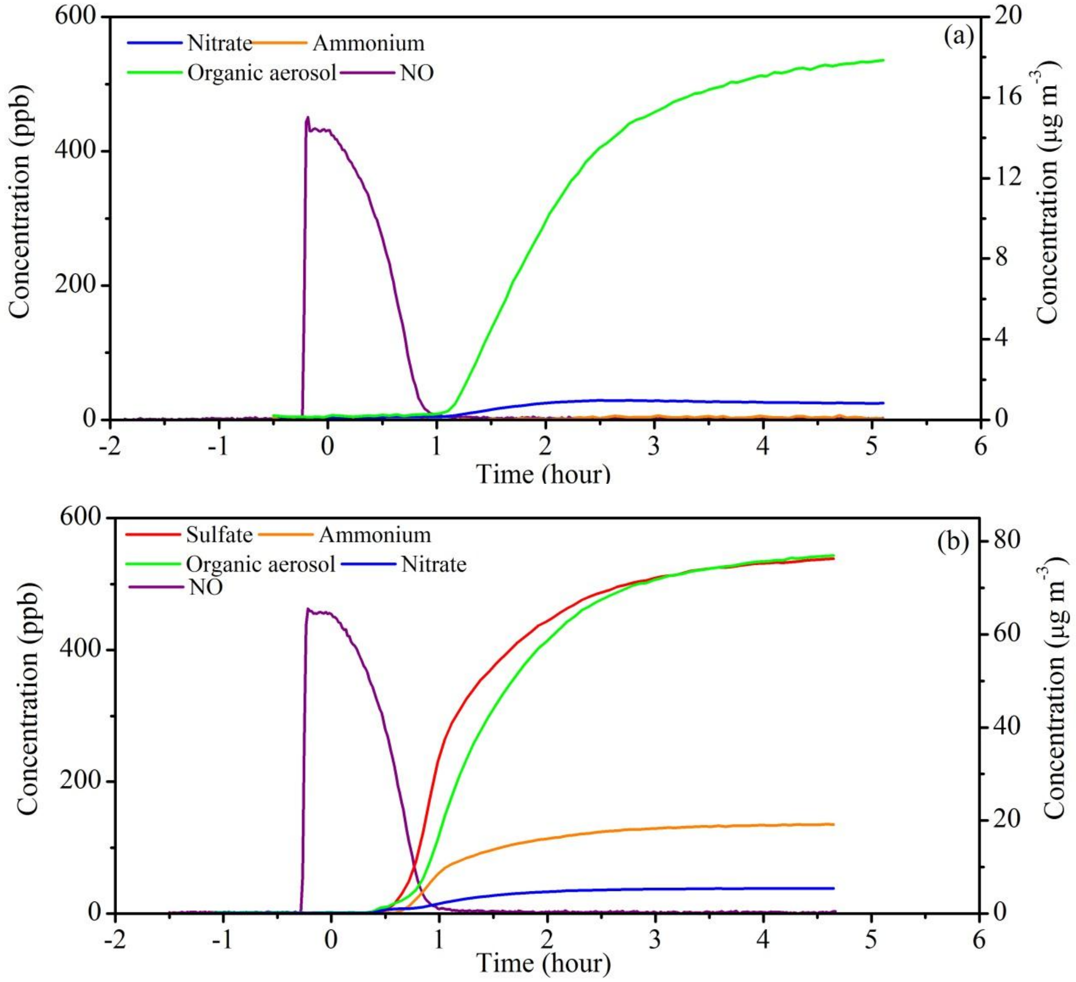

Fig. ~~1~~2. Concentration–time plots of NO (left-y axis) and particle–phase species (right-y axis) during the photochemical aging of emissions from vehicle III. (a) Without SO_2, and (b) with SO_2. The concentrations of particle-phase species are wall-loss corrected. At time =0 h, the black lamps were turned on.

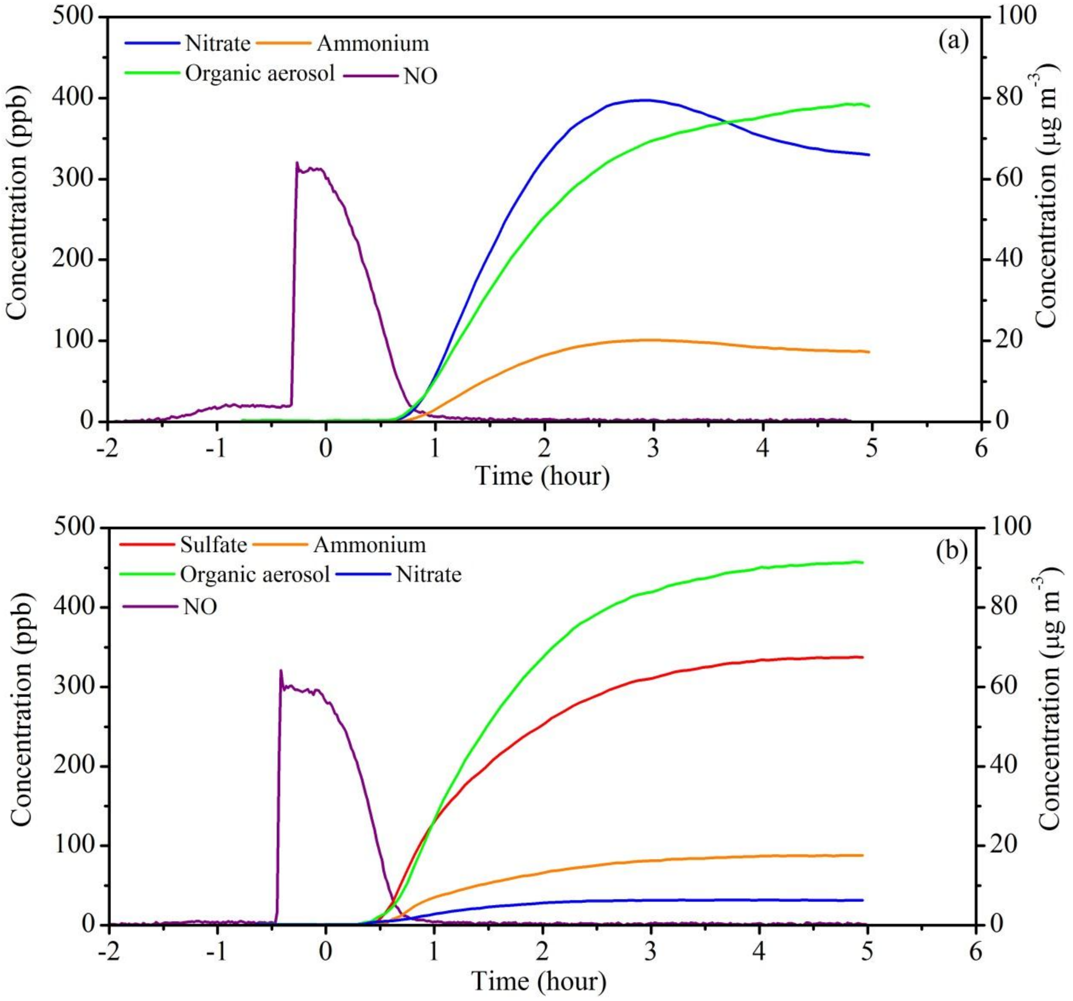

Fig. ~~2~~3. Concentration–time plots of NO (left-y axis) and particle–phase species (right-y axis) during the photochemical aging of emissions from vehicle I. (a) Without SO_2, and (b) with SO_2. The concentrations of particle-phase species are wall-loss corrected. At time =0 h, the black lamps were turned on.

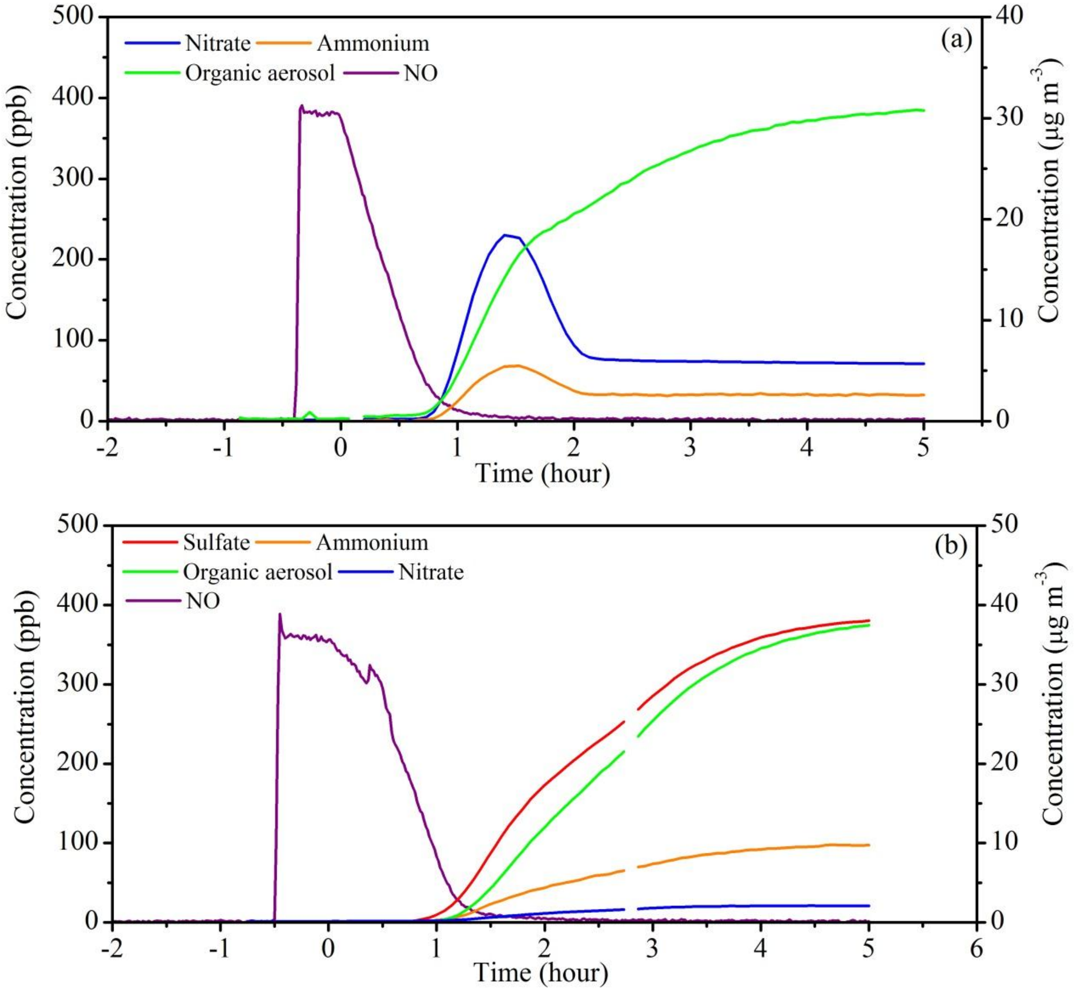

Fig. ~~3~~4. Concentration–time plots of NO (left-y axis) and particle–phase species (right-y axis) during the photochemical aging of emissions from vehicle II. (a) Without SO_2, and (b) with SO_2. The concentrations of particle-phase species are wall-loss corrected. At time =0 h, the black lamps were turned on.

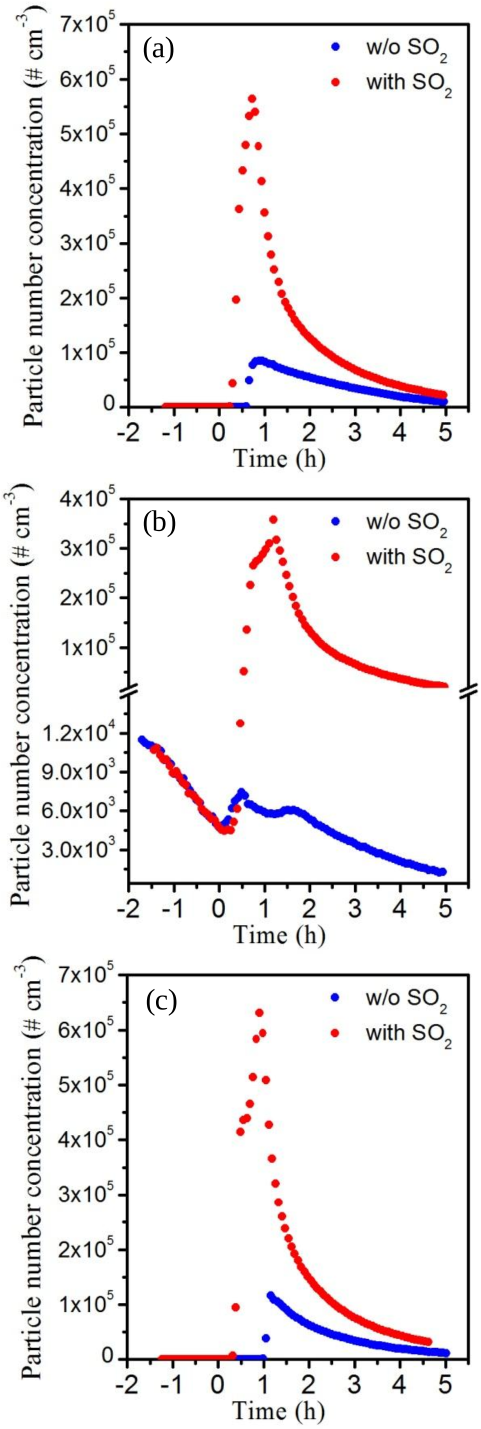

Fig. 45. Evolution of particle number concentrations during the aging experiments of LDGV exhaust for vehicle I (a), II (b) and III (c). At time =0 h, the black lamps were turned on. W/o SO_2 and with SO_2 in the figures represent experiments without and with adding SO_2, respectively.

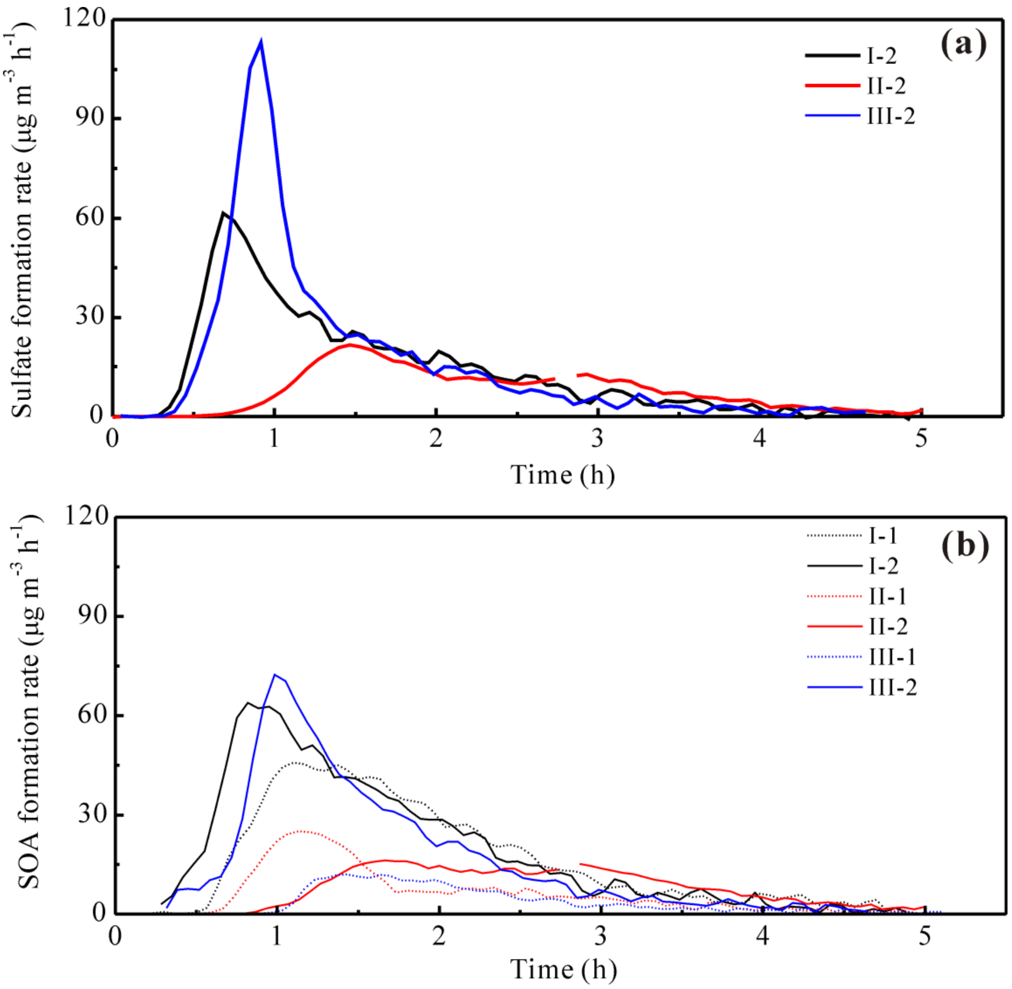

Fig. ~~5~~6. Sulfate formation rates (**a**) and SOA formation rates (**b**) as a function of time during the photooxidation of LDGV exhaust~~s~~.

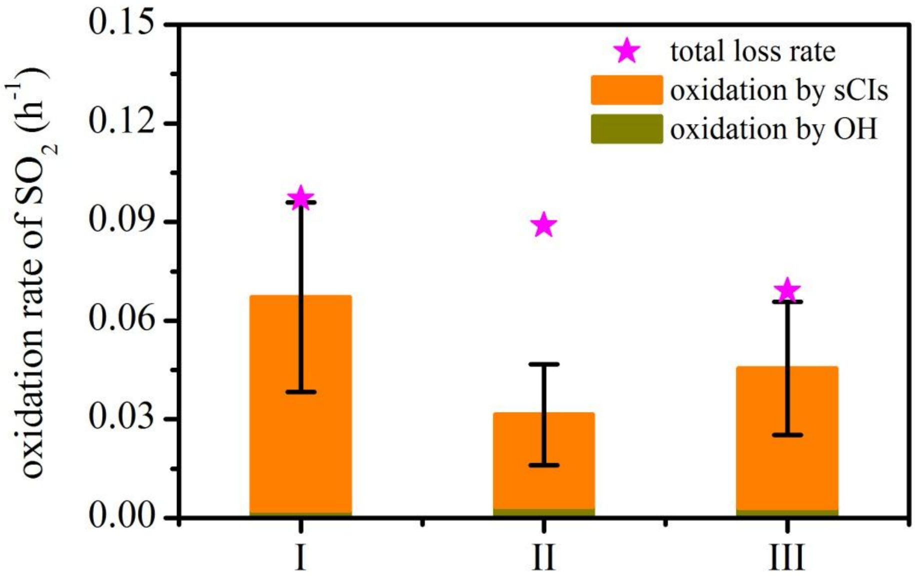

Fig. ~~6~~7. The oxidation rate of SO_2 during the photooxidation of LDGV exhaust~~s~~ with SO_2. The loss rates of SO_2 reacting with OH radicals and ~~stabilized~~ sCIs were calculated by multiplying the reaction rate coefficients derived from the MCM v3.3 by the average OH concentration and estimated ~~stabilized~~ sCIs concentration, respectively. Error bars represent the standard derivation (1σ) of the oxidation rate of SO_2 by ~~stabilized~~ sCIs throughout the whole experiment.

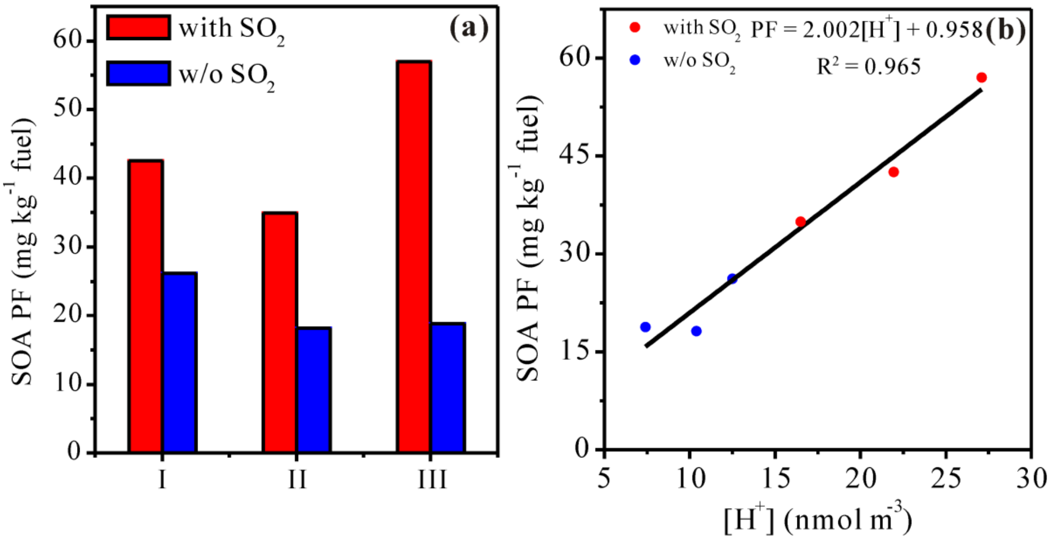

Fig. ~~7~~8. SOA production factor (PF) and its relationship with particle acidity. (**a**) SOA PF after 5 h of photochemical aging of exhaust~~s~~ from different LDGVs with and without additional SO_2. (**b**) SOA PF as a function of in-situ particle acidity. The concentration of H^+ in particle phase shown here was the value when the SOA formation rate reached the maximum during each experiment.

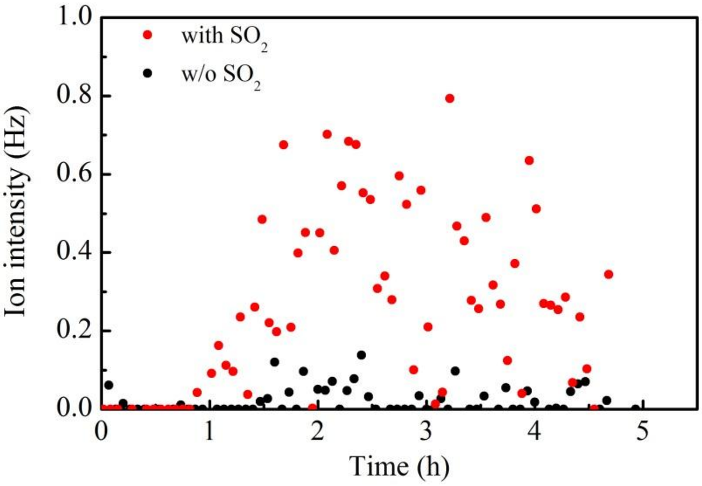

Fig. ~~8~~9. Time evolution of m/z 88 during the aging of LDGV exhaust from vehicle III.

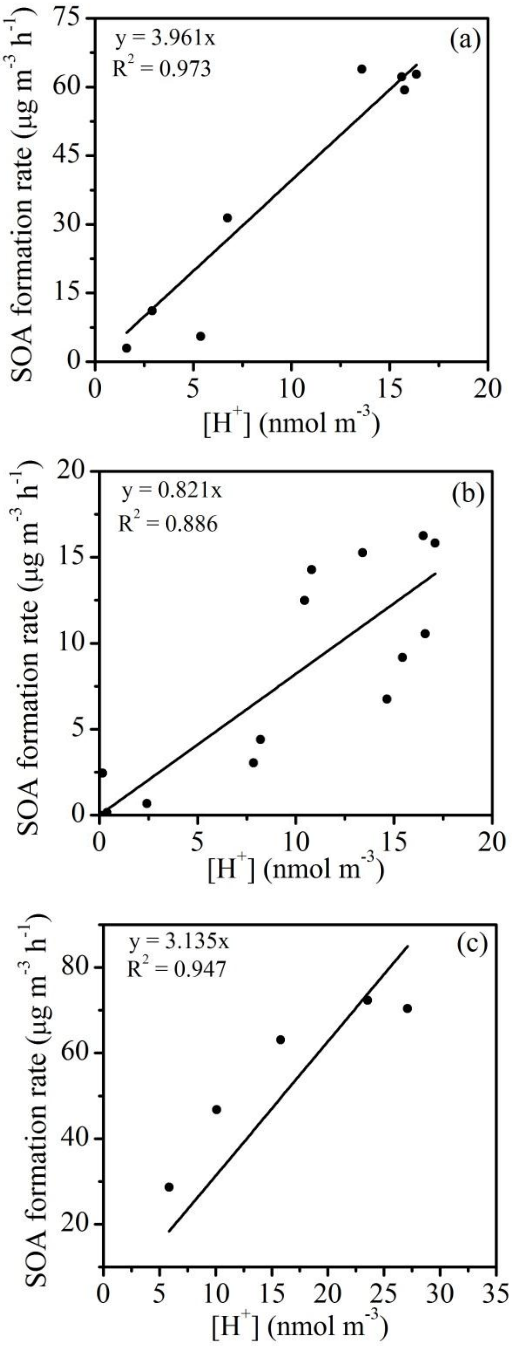

Fig. ~~9~~10. SOA formation rate as a function of in-situ particle acidity ([H$^+$]) for vehicle I (a), vehicle II (b) and vehicle III (c) with adding SO_2. Plotted data were selected from when SOA formation rate was higher than zero to when the rate reached the maximum value.

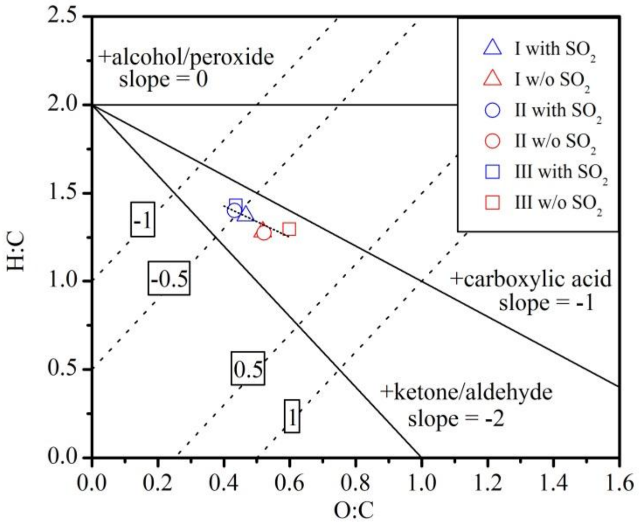

Fig. ~~10~~11. O:C vs. H:C of SOA formed from LDGV exhaust with and without additional SO_2 at the end of each experiment. Blue and red symbols represent data with and without additional SO_2, respectively. The dashed lines represent estimated average carbon oxidation states of -1, -0.5, 0.5 and 1 (Kroll et al., 2011). The black lines represent the addition of functional groups to an aliphatic carbon (Heald et al., 2010).