

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 SO₂. Liu et al. find that the addition of SO₂ 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 $5.5 \pm 4.5 \mu\text{g m}^{-3}$ 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.

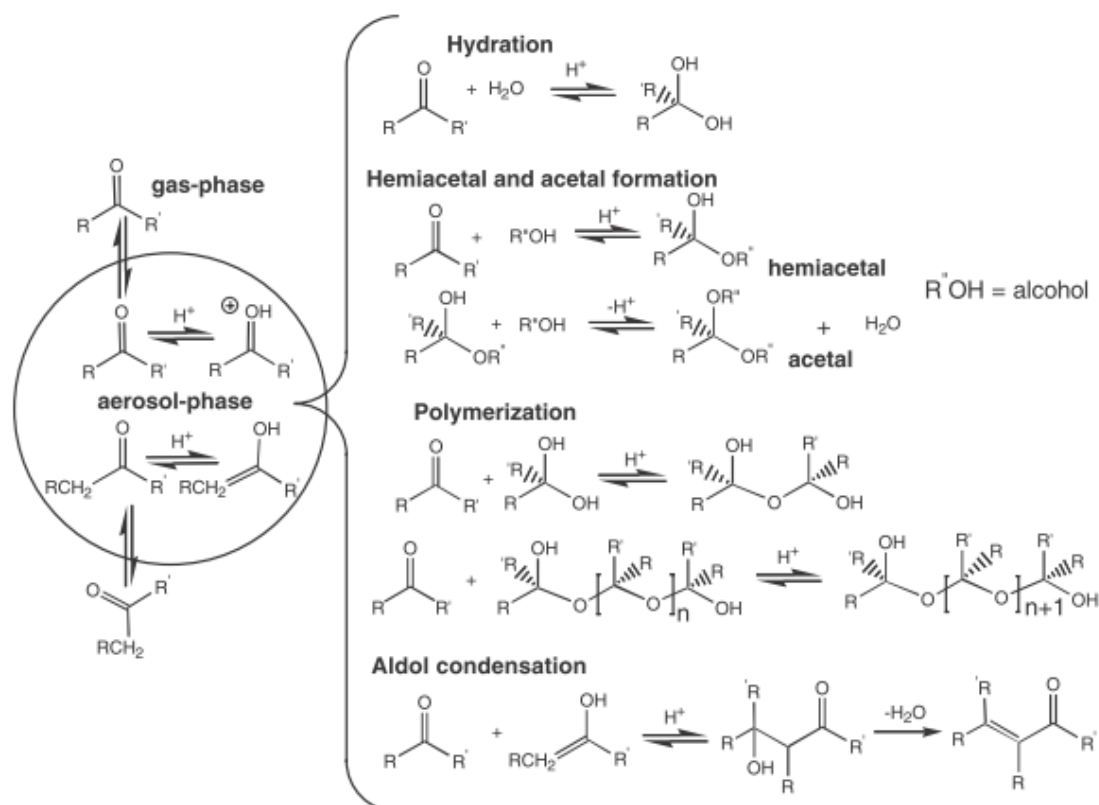


Figure 1. Acid-catalyzed heterogeneous reaction mechanisms of atmospheric carbonyls (derived from Jang et al. (2002)).

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 $5.5 \pm 4.5 \mu\text{g m}^{-3}$ 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 SO₂ oxidation applies to SOA precursors? Is there prior evidence for such?

Reply: SO₂ is readily oxidized by OH radical and sCIs in the gas-phase or by H₂O₂ and O₃ 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 SO₂ 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, CH₂OO and CH₃CHOO 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 ($53.3 \mu\text{g m}^{-3}$) 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 ($53.3 \mu\text{g m}^{-3}$) 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.”

Crige 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 SO₂? 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 SO₂/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 SO₂. 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 $10^6 \mu\text{g m}^{-3}$ 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 $100 \mu\text{g m}^{-3}$ 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 $10 \mu\text{g m}^{-3}$ would then be approximately 50% higher than that for C_i^* bin of $100 \mu\text{g m}^{-3}$ 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 $2.0 \times 10^{-5} \text{ s}^{-1}$, 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 $2.5 \times 10^{-4} \text{ s}^{-1}$, 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.

$\log_{10} C_i^*$ ($\mu\text{g m}^{-3}$)	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 $10^6 \mu\text{g m}^{-3}$ 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 $100 \mu\text{g m}^{-3}$ 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 $10 \mu\text{g m}^{-3}$ would then be approximately 50% higher than that for C_i^* bin of $100 \mu\text{g m}^{-3}$ 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 $2.0 \times 10^{-5} \text{ s}^{-1}$, similar to a product of the photo-oxidation of toluene. Thus,

biases of vapor wall loss rates due to the addition of SO₂ 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 SO₂ 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 SO₂ and vehicle exhausts.”* has been revised and now reads:

“High concentration of SO₂ 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 SO₂ 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 (SO₂) (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 (SO₂) (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 (SO₂) (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."

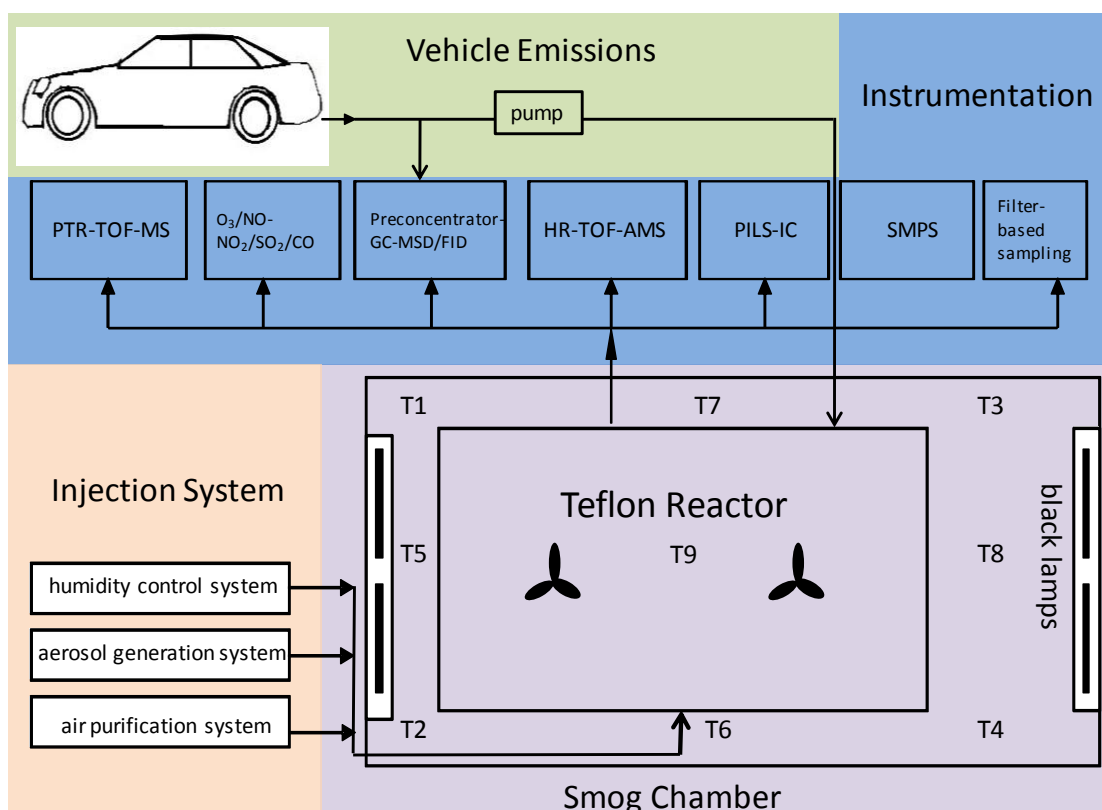
Q3- What do the Euro standards mean? A one sentence explanation of the Euro standard and its implication for vehicle emission standards and vehicle fleet globally would help put the choice of vehicles in context.

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 SO₂ 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 SO₂ 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, $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{NH}_4^+]$ and $[\text{H}^+]_{\text{total}}$, 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 $[\text{H}^+]_{\text{in-situ}}$ 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 $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ 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 $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ 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, $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{NH}_4^+]$ and $[\text{H}^+]_{\text{total}}$, 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 SO₂ suppressed the formation of ammonium nitrate in experiments with SO₂ as NH₃ 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 Δ OA. 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/NO_x? 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 SO₂.

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 SO₂ 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 SO₂, 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.”

References

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