

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.

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 epoxydiols¹ 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?
- (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?
- (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).

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?

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.² and structure as shown by Matsunaga and Ziemann³). 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.² to the calculated particle surface areas observed in this work; see Figure 2C in Zhang et al.². 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.

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.

Minor Comments

1. 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'.
2. 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.⁴ and Nordin et al.⁵. 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.

3. 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.
4. Can the authors offer a schematic of the experimental setup that detail the instrumentation and hardware used?
5. How was the exhaust transferred to the chamber? Through a vacuum on the chamber or was it passed through the pump?
6. 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.
7. 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?
8. 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?
9. 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 ($\sim 0.1 \Delta_{\text{O:C}}$ for $\sim 50 \mu\text{g}/\text{m}^3 \Delta_{\text{OA}}$) based on historical data.
10. It might be helpful to provide the relevant O:C values in the abstract in addition to the oxidation state.
11. What are the units of VOC/NO_x? In my experience, this is usually expressed as ppbC/ppb.
12. 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?
13. What is the intent of Figure 8? In the manuscript, Figure 8 gets a one-sentence mention.

References

- 1 Paulot, F. *et al.* Unexpected epoxide formation in the gas-phase photooxidation of isoprene. *Science* **325**, 730-733 (2009).
- 2 Zhang, X. *et al.* Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol. *Proceedings of the National Academy of Sciences* **111**, 5802-5807 (2014).
- 3 Matsunaga, A. & Ziemann, P. J. Gas-wall partitioning of organic compounds in a Teflon film chamber and potential effects on reaction product and aerosol yield measurements. *Aerosol Science and Technology* **44**, 881-892 (2010).
- 4 Platt, S. *et al.* Secondary organic aerosol formation from gasoline vehicle emissions in a new mobile environmental reaction chamber. *Atmospheric Chemistry and Physics* **13**, 9141-9158 (2013).
- 5 Nordin, E. *et al.* Secondary organic aerosol formation from idling gasoline passenger vehicle emissions investigated in a smog chamber. *Atmospheric Chemistry and Physics* **13**, 6101-6116 (2013).