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Atmospheric Chemistry and Physics
Discussions

Interactive comment on “Gasoline aromatic: a critical determinant of urban secondary organic aerosol formation” *by* Jianfei Peng et al.

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We thank the referee for his/her careful and critical review of our paper. The following are our responses to the referee's comments.

1. The paper by Peng et al. summarizes results of experiments on SOA formation in a smog chamber from exhaust of a PFI gasoline vehicle and two gasoline engines (PFI and GDI), running on fuel with different PAH contents. The results indicate significant SOA formation that is not reproduced by taking into account SOA formation yields and the measured single-ring aromatics; underestimation was more so with fuels of higher PAH content. The authors conclude that PAH components of gasoline are important contributors to urban SOA and their emission control can benefit local air quality. The

paper can benefit from a thorough edit as some sentences/words are not structured properly. The topic of the manuscript is of high interest in the community, but there's a major shortcoming (see my first comment below). Other comments are also highlighted.

Specific comments: 2. One major shortcoming of the paper is the limited characterization of gas phase SOA precursors (both alkanes and higher molecular weight PAHs). The authors should address this in the discussion of results to convince the readers that the increased SOA is truly from PAHs and not other, unspeciated species.

We agree with the referee that more information on the molecular level measurement of the SVOC and IVOC will benefit our study a lot. Unfortunately, in this study, we were only able to measure the VOCs (up to 11 carbons) and particulate organic matters (POM), with the semi-volatile species absent in the emission profile. However, since both the particle-phase PAHs (mostly 3-7 rings) and gas phase aromatic VOCs (one ring) exhibited much higher concentration using F3 fuel, it is reasonable to speculate higher emission of 2-3 ring PAHs in gas phase, which might contribute to the SOA formation. But this doesn't mean that other SVOC species didn't contribute to the increased SOA. We are not able to decide whether other unspeciated species contribute to the SOA enhancement. Regarding the referee's concern, we modified the relative expression at line 278 as “Since both gas-phase aromatic VOCs (one ring) and particle-phase PAHs (mostly 3-7 rings) exhibited much higher EFs using high-aromatic gasoline fuel, it is reasonable to speculate higher EFs of the semi-volatile PAHs (2-3 rings) in our experiments.” The relative expression in the abstract is also modified as “Considerably higher emission of aromatic volatile organic compounds (VOCs) using high-aromatic fuel plays an essential role in the SOA production enhancement, while the semi-VOCs (e.g., gas-phase PAHs) may also contribute to the higher SOA production.”

3. Line 68: what is meant by “strong oxidizability condition”? Is that conditions similar to PAM? Figure 1 indicates oxidation for both types of experiments was carried out in a smog chamber.

The referee is right that we conduced both engine and vehicle experiments in our outdoor chamber. In the engine exhaust experiment, however, the precursor (e.g., NOx, THC) concentrations were at least 1 order higher than in vehicle experiments and in ambient air. This led to faster photochemical reaction in engine experiments, representing by the high O3 inside the chamber (up to 2 ppm) (Du et al., 2017). To response to the referee's concern, we have changed the sentence at line as "SOA formation experiments from engine exhausts were carried out with relatively high OH exposure compared to ambient conditions to obtain the SOA production potential."

4. Line 84-86: what's the effect of dilution on re-partitioning of semivolatile species? Also, what is the temperature of the exhaust in the CSV? Since transfer lines aren't heated, could temperature differences affect equilibrium partitioning of the semivolatiles.

We agree with the referee that both the dilution and temperature drop in the CVS would influence the partitioning of SVOCs. It is difficult to precisely quantify the effect of both of them. However, as the dilution of exhaust in the CVS was similar with what happened in the ambient air, the partitioning in the CVS is considered also similar with that in ambient air. Besides, the dilution and temperature drop were the same for all experiments, which suggests that this would not influence our conclusion on fuel effects.

5. Line 106: please indicate the olefin content for comparison (rather than having to refer to the SI table)

The information of olefin content in each fuel has been provided as suggested by the referee.

6. Was zero air added to the chamber throughout the experiment, meaning the chamber was being diluted constantly?

Yes, it was. Our chamber is not expandable. During the experiments, we used zero air to make up the volume pulled out by the instruments. The flowrate of zero air was exactly equal to the total flowrate of instruments. This led to dilution of both gases and particles in the chamber by a factor of approximately 2 at the end of each experiment. The dilution factor was also estimated by the degradation of CO concentration and used to correct the SOA formation. We have modified the sentence at line 167 as "Zero airflow was connected to the chamber over entire experiment to make up the sampling volume by the instruments. To minimize the sampling volume by the instruments, all instruments except SMPS were connected with several three-way valves, which were successively switched between the ambient air and the chamber very 15 or 30 min.".

7. It is unclear how H2O2 photolysis leads to NO2 formation. I believe HO2/RO2+NO reactions predominantly form NO2. Please clarify.

The referee is right that reaction with HO2/RO2 is the predominant way for NO to form NO2. We have modified the sentence as "After the chamber was exposed to the sunlight, 99% of NO was converted to NO2 within the first 10 min. This is because the fast photolysis of H2O2 produced large amount of OH radical and further HO2/RO2 radicals inside the chamber, which reacted with NO to form NO2 (Seinfeld and Pandis, 2006)."

8. Why was OH assumed to be 1.6e6 molecule/cm3 rather than using the calculated OH values based on the toluene/benzene?

The OH in the chamber is calculated based on the toluene / benzene ratio. The value of 1.6e6 molecule/cm3 is the assumed ambient OH concentration rather than OH inside the chamber. The reason we apply this value is to compare our chamber results to field measurement. However, since this confused the referee, we modified the relative expression beginning in line 183 to make this clear. "Aerosol evolution is always characterized by a photochemical-age-based parameterization method in ambient measurements as well as chamber experiments (Hu et al., 2013; de Gouw et al., 2005; Peng et al., 2016a). Therefore, in order to compare our SOA productions in different experiments (in which solar flux were different), OH exposures were calculated based on the ratios of benzene and toluene concentrations, which reacted at different rates with OH radical (de Gouw et al., 2005). Besides, to compare the OH exposure in our chamber experiments with the previous ambient measurements, the OH concentration in the ambient air was assumed as 1.6 × 106 molec cm-3 (Hu et al., 2013; Peng et al., 2016a), and the equivalent photochemical ages of chamber experiments were then estimated by the ratio of OH exposure in the chamber to the assumed OH concentration in the ambient air."

9. Line 166: Was POA removed from the exhaust before introduction in the chamber? What was the mass of POA?

The POA was removed from the exhaust before introduction in the chamber. The emission factor of POA in this study was measured by a filter-based sampler. The sampling inlet was placed inside the tubing of CVS system. We have added the following statement to make this clear. Line 100, "Besides, a filter based sampler (AVL SPC 472) was used to sample primary particles from gasoline vehicles for chemical composition analysis." Line 113, "Primary particles were sampled a filter based sampler (AVL SPC 472) and particulate chemical compositions, i.e., ions, EC, OC and polar and nonpolar organic species, were analyzed using ion chromatography, EC/OC analyzer (SUNSET Laboratory Inc.) and gas chromatography mass spectrometry (GC-MS) (Guo et al., 2013), respectively."

10. Line 186: the size distributions during wall loss experiments are very different from the size distribution of the actual chamber oxidation runs. Coagulation rates and losses are size dependent- how does this discrepancy affect the results?

The peak diameter of particles in wall loss experiment was about 90 nm, a little larger than the particles in vehicle experiments, which ranged from 50 to 100 nm at the end of experiments. However, in our wall-loss experiment, we found that the particles with size between 60 to 180 nm lost had the similar rate (with less than 20% difference).

Additionally , the particles in the chamber grew to more than 50 nm very fast. Thus, the calculated wall loss correction factor can be adapted to our vehicle experiments. Nevertheless, there was definitely uncertainty in the wall loss correction.

11. Line 208-209: I think this conclusion is a bit out of place- just because formation of SOA from the PFI engine was high, it doesn't mean it can represent SOA production from vehicles with low after-treatment technologies.

We are sorry for the confusion. The reason of which the PFI engine emission can represent vehicle with low after-treatment technologies is that the PFI engine used in our study is an experimental one with an old three-way catalyst (TWC). In our experiment, we measured the VOCs emission before and after the TWC and found that the deduction rate for VOCs in the TWC is only about 80% for the PFI engine, which was much lower than another GDI engine with new after-treatment (above 99%) and vehicles we used in the study. Therefore, we identified the PFI engine emission as a representative of high emission vehicles. We have added the following sentence in the manuscript to prevent this confusion. Line 104, "The PFI engine used in this study was an experimental one with an old three-way catalyst (TWC), while the GDI engine was a commercial one designed for vehicles meeting the national âĚč emission standard.". Besides, we have modified the following sentence in the discussion part. Line 327, "This enhancement of SOA formation, meanwhile, was found using not only a new vehicle meeting China IV emission standard, operated at a representative cycle condition in Beijing, but also an experimental engine which emitted more gaseous pollutants and was operated at steady state, suggesting the extensive applicability of our results."

12. Line 218-219: how did the total aerosol mass in between experiments compare? If total mass was comparable, at least the effect on partitioning would be similar in the experiments with different fuel types, but if not, that adds another level of variability ot the results that needs to be considered.

We thank the referee for pointing out this. The parameter we compared between experiments was total SOA production in the chamber, which was corrected by the diffusion factor and wall loss. We agree with the referee that the partitioning may influence the SOA mass in the chamber. There are two aspects that we deal with this partitioning issue in the vehicle experiments. First, the exhaust was diluted by a factor of 200 in the CVS and chamber. As a result, the gas concentrations (e.g., NOx and toluene) were comparable with those in the ambient air during severe polluted episode. Therefore, the partitioning of organics in the chamber would be similar with that in the ambient air (if not exact the same). Second, in each experiment, the exhaust volume into the chamber was controlled nearly the same. Thus, the difference in gas concentration and SOA formation in the chamber between different fuel experiments was about a factor of 2-3. Such difference in concentration might lead to different partitioning in the chamber, but the influence won't be significant. Nevertheless, we have added the following discussion in the manuscript. Line 238, "It is worth to mention that as the concentrations of gas pollutants and formed SOA in the chamber using F3 fuel were 2-3 folders of those fusing F2 fuel, the partitioning of SVOCs in the experiments using F3 fuel might slightly benefit the SOA formation. This partitioning, however, would not qualitatively change the experimental conclusion that higher fuel aromatics led to higher SOA production."

13. Line 224: is EFs of PM referring to primary PM? Please clarify

Yes. We have added "primary" before "PM" here.

14. Line228: how were PAHs in the aerosol phase determined?

The PAHs in the aerosol phase were measured by GC-MS. We have added the sentence "Primary particles were sampled a filter based sampler (AVL SPC 472) and particulate chemical compositions, i.e., ions, EC, OC and polar and nonpolar organic species, were analyzed using ion chromatography, EC/OC analyzer (SUNSET Laboratory Inc.) and gas chromatography mass spectrometry (GC-MS) (Guo et al., 2013), respectively" at line 113 in the manuscript.

15. Line241-242: Is addition of acetylene or ethylene to PAHs reversible? I'm still confused how the PAH content and acetylene/ethylene concentrations are related.

In the engine, a large amount of acetylene or ethylene come from the complex reaction of larger organics, e.g., toluene. On the other hand, the addition reaction of acetylene and ethylene can also occur in the exhaust pipe as soon as they leave the engine. This reaction can lead to the formation of aromatic VOCs and PAHs. We have modified this part as "Aromatic components in the exhaust mainly come from two routes, which are the survival of fuel aromatic contents and the combustion-derived formation in the engine. Ethylene and acetylene are the key species for the combustion-derived aromatics. High concentrations of ethylene and acetylene accelerate the acetylene addition reaction, which generates light aromatic VOC as well as PAHs in the engine (Wang and Frenklach, 1997; Frenklach, 2002). In this study, when the high-aromatic fuel was used, the concentrations of ethylene and acetylene from GDI engine were enhanced by a factor of 3.3 and 2.7, respectively, indicating that more aromatics were formed through the addition reaction of acetylene and ethylene in the engine."

16. Alkanes are known to form SOA as well. Why aren't they considered the SOA budget of these experiments and assumed to be not important?

We apologize for such misleading. We understand that alkenes and alkanes can be important SOA precursors in the atmosphere. Here, we want to express that based on our VOCs measurement (up to 11 carbon), the reacted alkenes and alkanes with more than 7 carbons were much lower compared with aromatic VOCs over the experimental period. Therefore, their contribution to SOA were relatively small in our SOA prediction. We have modified the paragraph as "The SOA precursors here included benzene, toluene, C8-aromatics, C9-aromatics and styrene, which were all measured by PTR-MS during each experiment. The contributions of the alkenes and alkanes (7-11 carbons) to SOA formation in our experiments were also estimated using Equ 1 based on the off-line GC-MS measurement. Results showed that the measured alkenes and alkanes (7-11 carbons) only accounted for approximately 4% of the total predicted SOA concentration (Fig. S6) duo to the low emission factors as well as the small reacted proportion of these species inside the chamber." Additionally, we have provided more information on the SOA formation estimation in the Supplementary information (Fig. S6) to avoid this misleading.

17. Figures: Fig. 2, panel 2 and Fig. 5: why are there gaps in the measurements?

In our study, to reduce the dilution effect by the measurement volume, all instruments except SMPS were connected with several three-way valves, which were successively switched between ambient and chamber every 15 or 30 min. We have added the following sentence in part 2.3 as "To minimize the sampling volume by the instruments, all instruments except SMPS were connected with several three-way valves, which were successively switched between the ambient air and the chamber very 15 or 30 min."

18. Fig. 3: the x-axis in both plots should be similar for comparison

The OH exposure during engine experiments cannot be calculated because of the lack of VOCs measurements. Thus, Fig. 3B cannot be made with OH exposure as x-axis. Nevertheless, this does not influence our conclusion, because the SOA from engine experiments met the highest value within one hour and the difference in the SOA formation between using F2 and F3 fuel can be calculated without the information of OH exposure. Besides, we think it is unnecessary to compare engine experiments with vehicle experiment in our study, because they were conducted under totally different condition.

19. Fig. 3: it would be easier to read the plots if the legends appeared as legends rather than figure captions

We thank the referee for the suggestion. We have added the legends in the figure.

20. Fig. 4: why aren't values of aromatics and NMHCs from the PFI engine shown? Also, SOA GDI and PM-PFI are not included. If the plot gets too busy, possible a table

with all the values from the runs should be included. If the Is total PAH referring to the condensed phase PAH?

In this study, we focused on the fuel effect on SOA. Comparison of GDI and PFI SOA will be in our next paper. The VOCs data of PFI engine was not with high quality due to technical issue, so we did not put that information in the paper. The total PAHs was referring to the particles phase. A table containing all the data in Fig. 4 is added as table S6.

21. Fig. 4: there's no need to repeat the legends symbols in the caption.

Suggestion taken. Thank you very much!

Technical comments:

22. Line 17: consider rephrasing as "... potentially considerable impact on ..."

Suggestion taken. Thank you!

23. Line 17-19: the second part of the sentence needs to be rephrased

Thank you for pointing out this. The sentence has been revised as "Fuel composition has potentially considerable impact on gasoline SOA production, but the link between fuel components and SOA production is still poorly understood".

24. Line 20: consider "... through chamber oxidation approach."

Suggestion taken. Thank you!

25. Line 22: "Considerably higher content of both monocyclic and ..."

Thank you for the suggestion! We have however modified the sentence as "Considerably higher emission of aromatic volatile organic compounds (VOCs) using high-aromatic fuel plays an essential role in the SOA production enhancement, while the semi-VOCs (e.g., gas-phase PAHs) may also contribute to the higher SOA production."

26. Line 42: consider "...don't sufficiently take into account the impacts on SOA pro-

duction. This deficiency is mainly attributed..."

Thank you for pointing out this. The sentence has been revised as "…the impacts of fuel compositions on SOA production have not sufficiently been taken into account in current gasoline fuel standards. This deficiency is mainly attributed to…"

27. Line46: "...one benzene ring..." (not ring-like structure)

Revised. Thank you very much!

28. Line57: "However, until..."

Suggestion taken. Thank you!

29. Line74-76: unclear what 'different standard stage and working situation' means.

Thank you for pointing out this. The sentence has been revised as "A commercial PFI vehicle, an experimental PFI engine and a GDI engine were tested in this work."

30. Line 93: "... with 50% load."

Revised. Thank you very much!

31. Line 96: unclear what 'successively' means

Sorry for the confusing. We have modified the sentence as "During the injection, the engine exhaust steam was continuously introduced from the exhaust pipe into the chamber through a 1-meter-long tubing for 1 min."

32. Line 113-114: "...around 2010 and after 2013, respectively, in ..." (I believe respectively refers to the year of F2 and F3 fuel use and not the cities?)

Suggestion taken. Thank you very much!

33. Line 116: remove "were conducted"

We thank the referee for the suggestion. We have replaced the "conducted" by "utilized".

34. Line 128: remove 'to perform' and replace 'meanly' with "normally" and "moon" to "noon"

Suggestion taken. Thank you very much!

35. Line 133-132: This first sentence seems to be repeat of what has already been mentioned in the last paragraph

We thank the referee for pointing out this mistake. The sentence has been deleted.

36. Line 136: "...composed of a ..."

Revised. Thank you very much!

37. Line 140: remove".... were continuously tracked..."

Revised. Thank you very much!

38. Line150-151: dilution factors have already been discussed before, consider removing this sentence.

We thank the referee for pointing out this mistake. The sentence has been deleted.

39. Line 155: "approximately"

Revised. Thank you very much!

40. Line 160: "..in order to compare..."

Revised. Thank you very much!

41. Line 170: consider using HR-ToF-AMS instead of the full name

Suggestion taken. Thank you very much!

42. Line 177: "...highly..."

Revised. Thank you very much!

43. Line 179: consider replacing “oxidized” with “formed”

Thank you for the suggestion. But we think “oxidized” may be more appropriate here, as there is another “formed” in this sentence.

44. Line 187: please include the exposure time at the end of experiment

We have added “after 3.5-hour aging” here.

45. Line 200: please indicate what the time period for this SOA production rate is/

Thank you for the suggestion. The sentence has been revised as “The average production rates of SOA were as high as 5-13 mg kg-1 h-1 over each experiment, . . .”.

46. Line 213: “..reproducibility...”

Revised. Thank you very much!

47. Line 226: unclear what ‘administration’ refers to

We are sorry for the carelessness here. There are two references added here, which are (EPA, 2013; Karavalakis et al., 2015).

48. Line 229: “... from the exhaust increased by 0.2 to ...”

The sentence has been revised as “The EFs of each aromatic VOCs from the exhaust experiment increased by a factor of 0.2 - 9.5 using high-aromatic gasoline fuel”.

49. Line 331: “... particle-phase PAHs was amplified by 1.8...”. Also mention what this comparison is against (F2 vs F3 or F1 vs F3).

The sentence has been revised as “the total particle-phase PAHs emission was amplified for 1.8 times using high-aromatic gasoline fuel (F3 vs F2)...”

50. Line 234: what is meant by “from one cycle to seven cycles?”

We are sorry for the confusing expression. It means aromatics with 1-7 rings. Regarding to referee’s comments, we have changed this sentence into “Since both gas-phase

aromatic VOCs (one ring) and particle-phase PAHs (mostly 3-7 rings) exhibited much higher EFs using high-aromatic gasoline fuel, it is reasonable to speculate higher EFs of the semi-volatile PAHs (2-3 rings) in our experiments.”

51. Line 235-236: This sentence is confusing

Sorry for the confusing. The sentence has been revised as “Aromatic components in the exhaust mainly come from two routes, which are the survival of fuel aromatic contents and the combustion-derived formation in the engine.”

52. Line 240-241 “.... three-way catalyst were enhanced by ...”

Revised. Thank you very much!

53. Line 243 “.... In the exhaust was estimated by ...”

Revised. Thank you very much!

54. Line 257: ‘....even higher (up to...”

Revised. Thank you very much!

55. Line 264: consider adding “likely a majority...” since there are not measured

Suggestion taken. Thank you very much!

56. Line 269: “.... High emission of single-ring aromatic VOC as well as SVOCs such as low molecular-weight PAHs.”

Revised. Thank you very much!

57. Line 272: “.... after treatment technology, operated at steady-state, suggesting the extensive applicability of our results.”

Revised. Thank you very much!

58. Line 278: “..continuously...”

Revised. Thank you very much!

59. Line 279: “...sulfur content have been sent and the oil...”

Revised. Thank you very much!

60. Line 284: “Neglecting the side effect of fuel standard change on SOA production may potentially ....”

Revised. Thank you very much!

61. Line 287: “... require...”

Revised. Thank you very much!

62. Line 287: what is meant by ‘catalytic reforming’?

The catalytic reforming is a chemical process used to convert petroleum refinery naphthas distilled from crude oil into high octane liquid products called reformates, which are premium blending stocks for high octane gasoline. It is a commonly adopted process in the petroleum refining procedure, in which large amount of aromatic contents could be produced. We have modified the sentence to make this clear. Line 347, “This may require more hydrogenation catalysis process in the petroleum refining procedure instead of catalytic reforming process, in which large amount of aromatic contents might be produced.”

63. Line 298: please include references for the range of PAH content of gasoline

Thanks for the suggestion. We have added the Table S7 and corresponding reference here to present the range of aromatic content in gasoline fuel standard in different countries.

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