Response to Referee #1:

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. This study investigates the effect of aromatic content on the secondary aerosol production from photochemical processing of gasoline vehicle exhaust. The authors observed a large increase in the SOA production when fuel with higher aromatic content is used. In view of this, the authors suggest that regulations on the gasoline aromatic content would introduce 'unexpected benefit on air quality in urban area'. As such suggestions might help to develop and implement future regulatory plans, it is necessary to take both environmental consequences and economic factors into account. That is, for the different types of fuels used, are they producing the same amount of energy or driving distance? The authors are suggested to normalize the reported SOA yields values by the total driving mileage during one test cycle, to be more illustrative to evaluate the influence of aromatic content in the fuel on the PM emissions.

Response: the referee made an important point here. During our vehicle experiments, the same vehicle using different fuels were performed on the chassis dynamometer to run the same driving cycle (with the same distance). The average fuel consumption per unit distance using F1, F2 and F3 fuels were 0.113, 0.112 and 0.113 L km^{-1}, respectively, indicating no difference in fuel economy among the three fuels. The SOA production per unit distance were for 6.3 mg km^{-1} and 2.1 mg km^{-1} for F3 and F2 fuel, respectively, when OH exposure was 12 equivalent photochemical hours. These values have been added in the manuscript at line 201 "The average fuel consumption per unit distance using F1, F2 and F3 fuels were 0.113, 0.112 and 0.113 L km^{-1}, indicating no difference in fuel economy among the three fuels", and at line 209 "The average SOA production at 12 equivalent photochemical-hours using F3 fuel was 76 mg kg-fuel^{-1} (6.3 mg km^{-1}), equivalent to 3 times of that using F2 fuel (25 mg kg-fuel^{-1}, 2.1 mg km^{-1})."

2. The SOA formation potential and OH reactivity of aromatic compounds are among the highest achieved in chamber experiments simulating SOA production from a variety of anthropogenic and biogenic precursors. The authors may refer to any global SOA production models, like CMAQ, for the SOA yields used from a selection of VOCs in the model mechanism. It is not surprising that increasing the aromatic content leads to enhanced SOA production from gasoline exhaust. My concern is that the authors did not provide sufficient evidence to support the causal relationship between the observed increase in SOA yield and the increasing amount of aromatic content. As shown in Table S3 in the supplementary materials, less than 50% fraction of the gasoline has been identified, including mostly olefin and aromatics. What if the unidentified carbon mass really contributes to the SOA production, and variations in the recipe of these unknown species in different types of fuel are the main drivers to the observed changes in SOA production? These unresolved carbons might include long-chain alkanes and alkenes that have been demonstrated to constitute a large fraction of gasoline emissions (Gentner et al. PNAS, 2012). The authors need to ensure that for the three types of fuels tused, the aromatic content is the only variable and the rest of the carbon mass *stays constant. This is the prerequisite for the further examination on the contribution of aromatics in gasoline fuels to SOA production.*

We agree with the referee that it is important to make sure that aromatic content is the only difference for F2 and F3 fuels. This is why we used F2 fuel to blend F3 fuel. As discussed in part 2.2 of manuscript, F3 fuel was blended from 80% of F2 fuel, 15–20% of refinery reformate stream with high aromatic content and very small amount of o-octane and n-heptane to keep the same octane level. This means that at least 80% of the mass was the same for F2 and F3 fuel. Besides, to response to the referee's concern, we have added the molecular information for all three fuels the as Table S4, which clearly exhibits that the concentrations of most long-chain alkanes and alkenes in F2 fuel were higher than those in F3 fuel, but the concentrations of aromatics were much higher in F3 fuel. Thus, if the long-chain alkanes and alkenes in gasoline fuel were more important than the aromatics on SOA formation, the SOA using F2 fuel should be higher than using F3 fuel. In contrary, we found SOA were much more using F3 fuel, which could only be explained by the higher SOA formation efficiency for fuel aromatics.

Minor comments

3. Page 2, Line 49: The vapor pressure of benzoic acid falls into the semi-volatility range. The authors may refer to Schwantes et al. ACP (2017) for an example.

We thank the reviewer for reminding this. The sentence has been revised as "… leading to the formation of a variety of semi- or low-volatile species (e.g., benzoic acid) (Zhang et al., 2015; Schwantes et al., 2017)"

4. Page 2, Line 51: Please change 'exhibited' to 'shown'.

Thanks. It has been revised.

5. Page 3, Line 64-70: Please change 'underwent' to 'subject to'. Change to 'condition' to 'conditions'. Change 'under strong oxidizability conditions' to 'with high OH exposure'. The oxidation capacity in this study equals to one or two days of ambient OH exposure and does not necessary represent the high OH exposure cases that were reported in literatures (e.g., Lambe et al., ACP, 2015).

We thank the referee for pointing out these mistakes. They have been corrected. Also, to response to the referee's concern, we changed the sentence 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."

6. Page 3, Line 75: Change 'emission' to 'emissions'.

Thanks. It has been corrected.

7. Page 4, Line 116: Delete 'were conducted'.

Thanks. It has been deleted.

8. Page 5, line 129: Delete 'of' in front of 'relative humidity'.

Thanks. It has been deleted.

9. Page 5, Line 140: Delete 'continually tracked'.

Thanks. It has been deleted.

10. Page 6, Line 164: the OH concentration unite should be 'molec cm-3' or 'molecule cm-3'.

Thanks. It has been corrected.

11. Page 8, Line 226: 'Administration.'? References need to be cited here.

References have been added here.

12. Page 8, Line 213: Change 'reproducible' to 'reproducibility'.

Thanks. It has been corrected.

13. Page 9, Line 247: Please provide evidence for the conclusion that 'SOA formation from C10-aromatics, alkenes and alkanes is found to be negligible'. In contrast, there have been a number of studies showing significant SOA production from photooxidation of alkanes and alkenes (e.g., Loza et al., ACP, 2014; Matsunaga and Ziemann, 2010).

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, the reacted alkenes and alkanes with more than 7 carbons were much lower compared with aromatic VOCs over the experimental period. We have modified the paragraph as "The SOA precursors here included benzene, toluene, C8-aromatics, C9-aromatics and styrene, which were 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.

14. Page 10, Line 271: Change 'with not' to 'without'.

Thanks. It has been corrected.

15. Page 10, Line 278: Change 'continuous' to 'continuously'.

Thanks. It has been corrected.

16. Page 17, Figure 1: The unite for OH exposure should be 'molec cm-3 hr'.

We thank the reviewer for pointing out this mistake. The figure has been revised.

17. Page 18, Figure 2: SOA production from F1 is missing in subfigure (b).

In this study, we focus on the effect of gasoline aromatics on SOA production. This effect can be clearly found by the usage of F2 and F3 fuels, which show similar features between each other except aromatic contents. Therefore, we did not conduct any engine exhaust experiments using the F1 fuel. That's why there is no F1 fuel in Fig. 2b

18. Page 19: Figure 4: Please provide the data source for the emission factors for total hydrocarbon and total other NMHCs. Are they direct measurements from experiments? If so, instruments and methods for these measurements need to be given. It is difficult to differentiate these different hues of green color. Suggest to revise this figure for better visualization.

We thank the referee for the suggestion. The figure is revised. Also, we have added the following sentence "The total hydrocarbons (THC) were measured by vehicle emissions testing system, HORIBA, Ltd.), and the total aromatics and non-methane hydrocarbons (NMHCs) were measured by offline GC-MS" in the figure capture.

Response to *Referee #2:*

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 NO_2 within the first 10 min. This is because the fast photolysis of H_2O_2 produced large amount of OH radical and further HO_2/RO_2 radicals inside the chamber, which reacted with NO to form NO_2 (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 1.6×10^6 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 IV 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 production. 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.

Response to the short comment from G.Tang:

The authors presented the contribution of gasoline vehicle exhaust to SOA formation in urban atmosphere. The manuscript indicated the importance of the vehicular gasoline compositions and clarified the principal problem of vehicular emissions for haze pollution in China. However, in your literature review, the authors missed some new findings. E. g. Tang et al. (2015) illustrated the differences of gasoline compositions between China and USA and found alkenes and aromatics in China were 4.9% and 9.6% higher than that in USA, respectively. After a while, they also found mortality was correlated with vehicular emissions in Beijing (Tang et al., 2017). Therefore, I suggest the authors discuss these new findings on the chemical compositions of gasoline and the relationship between vehicular emissions and human health, which can emphasize the motivation of this study.

We thank Dr. Tang for providing this information. We have added the following sentence in the discussion. “Recent study found that gasoline aromatic content in China was 9.6% higher than that in USA (Tang et al., 2015).”

Gasoline aromatic: a critical determinant of urban secondary organic aerosol formation

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Abstract

Gasoline vehicle exhaust is an important contributor to secondary organic aerosol (SOA) formation in urban atmosphere. Fuel composition has potentially considerable ~~potential~~ impact on gasoline SOA production, but ~~this impact is still taken little account in the emission regulations due to the poor understanding of~~ the link between fuel components and SOA production~~.~~ is still poorly understood. Here, we present ~~an in-depth study~~chamber experiments to investigate the ~~impact~~impacts of gasoline aromatic content on SOA production through chamber oxidation approach. A significant amplification factor of 3 - 6 for SOA productions from gasoline exhausts ~~was~~is observed as gasoline aromatic content rose from 29% to 37%. Considerably higher ~~emissions of both monocycle and polycyclic~~emission of aromatic volatile organic compounds ~~performed~~(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. Our findings indicate that gasoline aromatics ~~have significant~~significantly influence ~~on~~ ambient $PM_{2.5}$ concentration in ~~megacities~~urban area and highlight that more stringent regulation on gasoline aromatic content will achieve unexpected benefit on urban air quality~~ in urban areas~~.

1 Introduction

Fossil fuel-powered vehicles, an important source of NO_x, volatile organic compounds (VOCs) and atmospheric particulate matter (PM), are always associated with the severe haze events, human health risks and climate forcing, particularly in urban areas (Parrish and Zhu, 2009; Guo et al., 2014; Huang et al., 2014;~~Parrish and Zhu, 2009;~~ Kumar et al., 2014;~~Peng~~ Liu et al., ~~2016b;~~2015a; Kelly and Zhu, 2016;~~Liu~~ Peng et al., ~~2015a~~2016b). Gasoline is the most widely used vehicle fuel and accounts for the largest total transportation energy consumptions in many countries, e.g., U.S. and China (NBSC, 2015; EIA, 2015~~), e.g., U.S. and China.~~). Among all the gasoline related PM components, secondary organic aerosols (SOA) produced via atmospheric oxidation of VOC precursors in the exhaust have been proved by chamber experiments as a large fraction, if not the largest, of gasoline vehicular PM (~~Platt et al., 2014;Liu et al., 2015b;Gordon et al., 2014a;Jathar et al., 2014;~~Zervas et al., 1999; Jimenez et al., 2009; Gordon et al., 2014a; Jathar et al., 2014; Platt et al., 2014; Liu et al., 2015b). Moreover, ambient measurement also demonstrated that gasoline SOA were the largest source of vehicular carbonaceous PM in megacities such as Los Angeles (Bahreini et al., 2012). However, ~~though~~although increasingly stringent gasoline fuel standards, especially on sulfur content, have been ~~implemented~~upgraded in the past decades in many countries to reduce the ~~exhaust~~ emissions, the impacts of fuel compositions on SOA production have not sufficiently been taken into account in the current gasoline fuel standards~~ don't take enough account to the SOA production.~~. This ~~contradiction~~deficiency is mainly ~~attributable~~attributed to the poor understanding of the effects of fuel properties on the related SOA formation, and may ultimately lead to a policy bias on the control of vehicle emission regarding to the reduction of atmospheric pollution.

Aromatic hydrocarbons, unsaturated compounds with at least one benzene ring~~-like structure~~, account for 20% - 40% v/v of gasoline fuel. Aromatic VOCs (i.e., toluene, xylenes and trimethylbenzenes) react exclusively with the OH radical in the atmosphere, leading to the formation of a variety of semi- or low~~-~~-volatile species (e.g., benzoic acid) (Zhang et al., 2015; Schwantes et al., 2017), which will partition onto existing particle and be recognized as anthropogenic SOA. Therefore, the higher emission of aromatic VOCs will likely result in more SOA formation potential. Existing fuel-effect experimental and model studies have ~~exhibited~~shown that high-aromatic fuel in gasoline fuel will lead to more emissions of primary

PM as well as some aromatic VOCs (Zervas et al., 1999; EPA, 2013; Karavalakis et al., 2015;~~Yinhui~~ Wang et al., 2016~~;Zervas et al., 1999;Agency, 2013~~), indicating the considerable potential impact of gasoline aromatic content on SOA production. Furthermore, though aromatic content in diesel fuel may have ~~little~~insignificant impact on SOA formation (Gordon et al., 2014b), SOA production from gasoline vehicle is considered ~~to be~~ more sensitive to aromatic content than that from diesel vehicle (Jathar et al., 2013). However, ~~till~~until now, very few studies have successfully quantified the impact of gasoline aromatic content on SOA production and directly revealed the possible pathway.

In this study, an in-depth comprehensive research was conducted to investigate the link between gasoline fuel compositions, primary gas- and particle- phase emission, and corresponding SOA formation. Gasoline exhaust emissions were examined on two platforms under two different conditions. The first platform was the chassis dynamometer system equipped with a constant volume sampler (CVS). Vehicle exhausts after CVS ~~was~~were introduced into an outdoor environmental chamber and ~~underwent~~subjected to aging under typical polluted urban ~~condition~~conditions to simulate the SOA formation in ambient atmosphere. The second platform was the experimental engine system on which emissions from a port gasoline injection (PFI) engine and a gasoline direct injection (GDI) engine were examined. SOA formation experiments from engine exhausts were carried out ~~under strong oxidizability condition~~with relatively high OH exposure compared to ambient conditions to obtain the ~~highest~~ SOA production potential. Most importantly, different gasoline fuels blended from different refinery streams were utilized in both platforms to probe the critical link among fuel components, VOCs emissions and related SOA production.

2 Materials and methods

2.1 Test fleet, cycle and engine.

~~In order to explore the SOA formation from gasoline vehicles with different standard stage and different working situation, both~~ A commercial PFI vehicle ~~dynamometer PFI and~~, an experimental PFI engine ~~emission~~and a GDI engine were tested in this work.

The chosen PFI vehicle belonged to a commonly used vehicle model in China, which certified to China IV emission standard (equivalent to Euro 4). The mileage of the test fleet was about 3000 km. The fleet was driven on a chassis dynamometer system (Burke E. Porter Machinery Company) using cold-start Beijing cycle in order to better simulate the actual driving situation in Beijing. Beijing cycle was about 17 min long, with highest speed about 50 km h^{-1} (Fig. S1). The temperature and the absolute humidity in the dynamometer room were kept at 23.0 ± 1.0°C and 8.4 ± 0.9 g m^{-3}, respectively, for all vehicle experiments (Table S1).

Vehicle exhaust underwent the first stage of dilution with filtered ambient air using a constant volume sampler (CVS) operated at 5.5 m^3 min^{-1} for all experiments. Approximately 5.3 L min^{-1} of diluted exhaust from the CVS was introduced into the 1.2 m^3 chamber to be further diluted with the clean air in the chamber (Fig. 1). The average dilution factor was approximately 20 in the CVS and was approximately 15 in the chamber. During the entire cycle, a light-duty gasoline vehicle emissions testing system (HORIBA, Ltd.) was used to measure the average and real-time concentration of THC, CO_2, CO~~, CO2 and NO_x~~ and NO_x. Besides, a filter based sampler (AVL SPC 472) was used to sample primary particles from gasoline vehicles for chemical composition analysis.

The PFI and GDI engines were manufactured by a domestic Chinese automaker and equipped with turbocharger together with downsized displacement. 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 IV emission standard. The operation mode of the PFI and GDI engine for chamber experiments was 2000 round per minute with 50% ~~loading~~load. After the engine became stable at this operating mode, the exhaust were introduced into the chamber passing through a heater (150°C) and a filter, with a flowrate of 5 L/min~~ for 1 min~~. During the injection, the ~~emission was transferred from the~~ engine exhaust ~~system~~steam was continuously introduced from the exhaust pipe into the chamber~~, successively.~~ through a 1-meter-long tubing for 1 min. Particle number, mass and chemical composition, as well as VOCs in the exhaust were characterized at the same operating mode. 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. Detail description of the engine experiments can be found in our previous study (Du et al., 2017) and all engine experiments used in this study are illustrated in Table S2.

2.2 Fuels

Three fuels (F1, F2 and F3) were utilized in this study to investigate the impacts of the gasoline fuel on SOA formation. A commercial Phase V gasoline (F1 fuel) with equivalent octane number of 93 was used as the base fuel. F1 fuel contains ~~30~~29.8% aromatics and 4.1% olefin content (Table S3).

F2 fuel was blended from 80% of F6 fuel and 20% of refinery catalytic stream. Octane ~~level~~(18.8%) and aromatic content (28.5%) in F2 fuel are very similar with that in F1 fuel, with the only difference to be the olefin content.

F3 fuel was blended from 80% of F2 fuel, 15–20% of refinery reformate stream with high aromatic content and very small amount of o-octane and n-heptane to keep the same octane level. Compared with F2 fuel, F3 fuel ~~contains~~contained similar olefin content (15.4%) but higher aromatic content (~~37~~36.7%) (Table S3), but both F2 and F3 fuels meet the Phase V gasoline standard. ~~Detail information about the fuels can be found in our previous paper (Yinhui et al., 2016).~~

On the basis of the aromatic contents, the F2 and F3 fuel can be well representative of the fuel normally used in the year around 2010 and after 2013, respectively, in Chinese market such as Beijing and Shanghai~~, respectively~~. The mass fraction of molecular components in all three fuels used in this study can be found in Table S4.

2.3 Chamber Simulation

The quasi-atmospheric aerosol evolution study (QUALITY) chamber was utilized ~~were conducted~~ to quantify SOA formation from both gasoline engine exhaust and gasoline vehicle exhaust. The 1.2 m^3 two-layer chamber ~~was comprised~~composed of an inner layer of 0.13 mm PFA Teflon and an outer rigid 5.6 mm thick acrylic shell (Cyro Industries Acrylite, OP-4). Both ~~of them~~layers allowed for efficient transmission of sunlight in UV ranges (Peng et al., 2016b). Pre-experiments ~~have shown~~showed that wall loss decreased the particle number concentration by about 50% in about ~~2~~ 3.5 hours~~,~~. SO_2 and NO_x decreased to about 50% after 20 hours, while toluene and isoprene did not show obvious wall loss during a two-day experiment (Peng et al., ~~2016b~~2017).

Prior to each experiment, the QUALITY chamber was covered with two layers of anti-UV cloth to shield the chamber from sunlight and flushed by zero air with a flowrate of 10 L min^{-1} for more than 15 hours to ensure a clean condition. In both vehicle and engine experiments, excess (1 ml, 30~~%)~~% v/v) H_2O_2 was also injected into the chamber via the makeup zero air~~ flow~~ as an extra hydroxyl radical (OH) source after adding the exhaust~~ to perform~~. Chamber experiments were ~~meanly~~normally conducted from ~~moon~~noon to later afternoon, with inside temperature of 30 - 35 °C and~~ of~~ relative humidity (RH) of 40 - 60%. A suite of high time resolution state-of-the-art aerosol instruments were utilized to ~~simultaneously~~ measure the gas concentration and a comprehensive set of particle properties throughout the experiments, including concentrations of HONO, SO_2, NO_x, O_3, CO, CO_2 and several VOCs, the particle diameter, mass, chemical composition (Fig. ~~1).~~1 and Table S5).

~~During each chamber experiment, a suite of state-of-art instruments was utilized to characterize the evolution of gas- and particulate- phase pollutants intermittently (Table S4).~~ Particle number distributions were measured with a scanning mobility particle sizer (SMPS) system, which was composed by one differential mobility analyzer (DMA, TSI, Inc., model 3081) and one condensation particle counter (CPC, TSI, Inc., model 3772). The mass concentration and size distribution of ~~secondary species~~particle chemical compositions, including organic aerosol (OA), sulfate, nitrate, ammonium and chloride, were measured by a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.). The evolution of several ~~volatile organic (~~VOCs~~) species were~~ was measured continually ~~tracked~~ by a proton transfer reaction mass spectrometer (PTR-MS, Ionicon HSL experiments). ~~Meanwhile, VOCs in the chamber were also sampled by canisters every 1 hour during each experiment and analyzed by GC-MS/FID system (Wang et al., 2015). Hydroxyl radical (OH) levels in the chamber were inferred from the measured concentration ratios of toluene to benzene in this study (Yuan et al., 2013).~~ Dedicated gas monitors, including the SO2, NOx, CO, CO_2 and O3 monitors (Thermo~~)~~ Inc.), were utilized, and calibrated each experiment day. ~~Zero airflow was connected to the chamber during experiment to make up the sampling airflow.~~VOCs in the chamber were also sampled by canisters every 1 hour during vehicle experiments and analyzed by GC-MS/FID system (Wang et al., 2015).

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.

3 Results

3.1 Simulation of SOA formation from gasoline exhausts. The temporal evolution of gas- and particle- phase species during the chamber experiment ~~was examined and~~ is illustrated in Figure 2~~. The vehicle exhaust was diluted for about 20 times in CVS and additional 15 times in the chamber~~. The initial concentration of NO_x, benzene and toluene in the chamber were 163 ppb, 5.6 ppb and 16.8 ppb, respectively, corresponding to the severe urban haze condition in the megacities (Guo et al., 2014). After the chamber was exposed to the sunlight, 99% of NO was converted to NO_2 within the first 10 min~~ due to~~. This is because the fast photolysis of H_2O_2 produced large amount of OH radical and further HO_2/RO_2 radicals inside the chamber~~.~~, which reacted with NO to form NO_2 (Seinfeld and Pandis, 2006). Then, the concentration of O_3 increased rapidly to ~~approximate~~approximately 400 ppb after 1 h exposure, and gradually decreased later in this experiment (Fig.2a).

Over the entire experiment, benzene and toluene experienced gentle decay in the concentrations, but with different decay coefficients (Fig. 2b). 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 ~~production~~productions in different experiments (in which solar flux were different~~ from each other~~), OH exposures ~~are~~were calculated based on the ratios of benzene and toluene concentrations, which ~~react~~reacted at different rates with OH radical (de Gouw et al., 2005). Besides, ~~assuming that the OH concentration is 1.6 × 10^6 cm^{-3}, photochemical age is estimated to compare our results~~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 × 10^6 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.

New particle formation occurred inside the chamber within 10 min of exposure to the sunlight (Fig. 2c). These newly formed particles performed as seeds for the further formation of secondary species. A large quantity of secondary aerosols was then formed in the chamber, leading to the fast growth in the diameter of these particles to approximately 70 nm after 3h aging. The measurement of the particle compositions by ~~a High time resolution ToF Aerosol Mass Spectrometer (AMS)~~the AMS reveals that the largest mass fraction of secondary aerosols in the chamber was SOA (approximately ~~96~~95%, Fig. S2), indicating the critical role of the SOA for the secondary aerosol formation from gasoline exhausts. Because of the low aerosol loading (initially lower than 2 μg m^{-3}) and low relative humidity (40 - 50%) inside the chamber, heterogeneous reactions and aqueous phase processing were not important for the formation of SOA in this study (Zhang et al., 2015). Furthermore, the O:C ratio of SOA formed in the chamber stayed stable around 0.4 over the entire experiment, indicating that condensed phase reactions, i.e., aqueous or heterogeneous reactions, which produce ~~high~~highly oxidized oligomers, was not significant in the chamber experiments in this study. These SOA, therefore, were likely formed via condensation of less volatile products oxidized through gas phase reactions of VOCs precursors with limited multigenerational chemistry (Robinson et al., 2007; Jimenez et al., 2009; Jathar et al., 2014). The AMS spectrum profile of gasoline SOA obtained in this study ~~is~~was highly correlated with the ambient ~~SV~~low oxidized secondary organic aerosols (LO-OOA) in Beijing (R^2=0.99, Fig. S3), further confirming the important contribution of gasoline emission on ambient $PM_{2.5}$.

SOA ~~production~~productions per fuel consumption~~/~~ or mileage ~~is~~were calculated on the basis of SOA ~~formation~~mass concentration inside the chamber, dilution factors both in the CVS and inside the chamber, and fuel consumption/mileage ~~for~~of our working cycle. SOA mass concentration inside the chamber ~~is~~was corrected according to the particle wall loss curve (Fig. S4) as well as the dilution effect ~~for~~of both particles and gas precursors duo to the make-up zero air (Fig. S5). SOA production at the end of this experiment ~~is~~was calculated to be 80 mg kg-fuel^{-1}, or 6.7 mg km^{-1} after 3.5-hour aging (Fig. 2d). These values ~~are 5~~were 6.8 times higher than the emission factors (EFs) of primary particles (including both primary organic ~~aerosols (POA) for the same vehicle~~matters and elemental carbon) at the same cycle.

3.2 Fuel impacts on SOA production. ~~High~~The average fuel consumption per unit distance using F1, F2 and F3 fuels were 0.113, 0.112 and 0.113 L km^{-1}, respectively, indicating no difference in fuel economy among the three fuels. On the other hand, high-aromatic content gasoline ~~leads~~led to ~~appreciably~~noticeably large enhancement on SOA production from both vehicle and engine experiments. As illustrated in Figure 3a, the final SOA production from gasoline vehicle exhaust ranged from 30 mg kg-fuel^{-1} to 98 mg kg-fuel^{-1} at the end of each experiment, comparable to the results from cold start experiments in previous studies (Gordon et al., 2014a; Jathar et al., 2014). Experiments using F3 fuel (with 36.7 % v/v aromatic content) exhibit the highest SOA production factors, followed by F1 fuel (with 29.8 % v/v aromatics content) and F2 fuel (with 28.5 % v/v aromatics content), successively. The average SOA production at ~~after~~ 12 equivalent photochemical-hours using F3 fuel was 76 mg kg-fuel^{-1}~~,~~ (6.3 mg km^{-1}), equivalent to 3 times of that using F2 fuel~~, which has similar parameters with F3 fuel except the aromatic content. In addition~~ (25 mg kg-fuel^{-1}, 2.1 mg km^{-1}). Additionally, we ~~observe noticeably large~~observed much larger amount of the SOA formation in the first few photochemical hours in all experiments. The average production ~~rate~~rates of SOA ~~can be~~were as high as 5 - 13 mg kg^{-1} h^{-1}~~, indicating~~ over each experiment, suggesting that the first-generation oxidation of some precursors inside the chamber produced large amount of SOA. This indicated the existence of some semi-volatile ~~species that could partition to particle phase after first generation oxidation (Keyte et al., 2013;~~organic compounds (SVOCs) (Robinson et al., 2007; Keyte et al., 2013). 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 experiment conclusion that higher fuel aromatics led to higher SOA production.

SOA formation experiments from ~~an experimental~~the PFI engine exhaust were conducted under high oxidizing condition to obtain the SOA formation potential. As illustrated in Figure 3b, most of the SOA were formed within the first half an hour of each engine experiment and very little increase was observed over the following hours. The SOA formation potential from the engine exhaust using F3 fuel ~~is~~was 3.3 g kg-fuel^{-1} at this condition, equivalent to 5.~~6 folders~~8 times of that using F2 fuel, which ~~is~~was 0.~~59~~57 g kg-fuel^{-1} on average. The high emission of the experimental PFI engine suggests that ~~our~~ the results of engine ~~exhaust experiment can~~experiments could represent the SOA production from gasoline vehicles with ~~low treatment technics.~~higher emission factor. Therefore, our results with two different experimental sets (vehicle and engine experiments) demonstrate the applicability of the ~~enhancement of~~ SOA formation enhancement using high-aromatic fuel~~, using~~ for gasoline vehicle with either high or low ~~after treatment technology~~emission factor, at either representative cycle condition or steady-state operating condition.

Though good ~~reproducible is~~reproducibility was found for SOA production using either F2 or F3 fuels, there ~~are~~were inevitably several biases in the chamber simulation approach. For example, the SOA production in both vehicle and engine experiments might be underestimated due to loss of ~~semi-volatile~~SVOC vapors to the chamber wall as well as the condensation of low organic vapor onto the particles that already lost on the chamber wall (Zhang et al., 2014). Also, the SOA production in engine experiments could be overestimated because the high concentration in the chamber might drive the gas-particle partitioning of the ~~semi-volatile components~~SVOCs into particle phase (Robinson et al., 2007). Nevertheless, the relative enhancement factor of SOA for different fuels ~~is~~was not largely influenced by these biases.

3.3 Aromatic emission and SOA production. To reveal the reason of this large amplification on SOA production owing to fuel constitution, gasoline PM and VOC emissions using F2 and F3 fuels were investigated ~~and their emission factors (EFs) are illustrated in Figure~~(Fig. 4~~. Huge~~). Significant differences in the EFs among different gas- and particle-phase species were observed. For example, the EFs of primary PM in both number and mass concentration using F3 fuel were only 20% larger than those using F2 fuel, consistent with previous studies~~(Administration.).~~ (EPA, 2013; Karavalakis et al., 2015). Similar results ~~are~~were also obtained for most of the alkane VOCs as well as NO. On the contrary, the EFs for ~~three types of species exhibit marked enhancement using high-aromatic gasoline fuel, i.e.,~~ SOA, aromatic VOCs and particle-phase Polycyclic Aromatic Hydrocarbons (PAHs~~).~~) exhibited marked enhancement using high-aromatic gasoline fuel. The EFs of each aromatic VOCs from the exhaust ~~experimented an increase~~experiment increased by a factor of 0.2 ~~to~~- 9.5 using high-aromatic gasoline fuel, with ~~an~~ enhancement ~~factor~~ factors of 3.3 and 2.7 for total aromatic VOCs ~~of 3.3 and 2.7~~ in vehicle and engine experiments, respectively (Fig. 4). Coincidentally, the total particle-phase PAHs emission was amplified for 1.8 times using high-aromatic gasoline fuel~~,~~ (F3 vs F2), with the amplification factor of each PAH species varied from 1.1 to 2.2. ~~This reveals that the~~ Since both gas-phase aromatic VOCs (one ring) and particle-phase PAHs (mostly 3-7 rings) exhibited much higher EFs using high-aromatic ~~content~~gasoline fuel~~ will favour the emission of all aromatic species from one cycle~~, it is reasonable to ~~seven cycles, including some aromatic ~~speculate higher EFs of the semi-volatile ~~organic components (SVOC).~~ PAHs (2-3 rings) in our experiments.

~~There are two main routes of aromatic~~Aromatic components ~~into~~in the exhaust mainly come from two routes, which are the survival of fuel aromatic ~~survival~~contents and the combustion-derived ~~aromatics~~formation in the engine. Ethylene and acetylene are the key species for the combustion-derived aromatics. High ~~concentration~~concentrations of ethylene and acetylene ~~will~~ accelerate the acetylene addition reaction, which ~~will generate~~generates light aromatic VOC as well as PAHs in the engine~~(Frenklach, 2002;~~ (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 ~~before the three-way catalyst met an enhancement~~were enhanced by a factor of 3.3 and 2.7, respectively~~ (Fig. 4), suggesting~~, indicating that more aromatics were formed through the addition reaction of acetylene and ethylene ~~were formed from~~in the ~~dissociation of fuel aromatic contents~~engine.

SOA production (Δ~~OA*prediction*~~$OA_{predicted}$) from ~~aromatic VOCs~~VOC precursors in the exhaust was roughly estimated by multiplying the mass loss of each ~~aromatic ~~VOC ~~precursor~~precursors (Δi) by its SOA yield, Yi (Donahue et al., 2006):

$$\Delta \mathrm{OA}_{predicted} = \sum_i (\Delta_i \times Y_i)$$

(1)

The SOA precursors here ~~include~~included benzene, toluene, C8-aromatics, C9-aromatics and styrene~~. SOA formation from C10-aromatics, ~~, which were all measured by PTR-MS during each experiment. The contributions of the alkenes and alkanes ~~is found~~(7-11 carbons) to ~~be neglectable~~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 ~~are not taken account in ~~alkanes (7-11 carbons) only accounted for approximately 4% of the total predicted SOA ~~prediction in this study.~~concentration (Fig. S6) duo to the low emission factors as well as the small reacted proportion of these species inside the chamber. The yields of VOCi under high NOx condition are used (Ng et al., 2007; Platt et al., 2013~~;Ng et al., 2007~~), due to the low initial

VOCs/NOx ratios which ranged from 0.5 to 1.0.

Figure 5 exhibits the two typical vehicle experiments with observed and predicted SOA concentration as a function of photochemical age using F2 and F3 fuels, respectively. The predicted SOA in the end of the two experiments ~~accounts~~accounted for 46% and 30% of the observed SOA formation with toluene and C9-aromatics to be the largest contributors, consistent with the previous results (Nordin et al., 2013; Platt et al., 2013; Gordon et al., 2014a~~;Platt et al., 2013;Nordin et al., 2013).~~). Predicted SOA concentration using F3 fuel ~~is~~was about 90% higher than that using F2 fuel, suggesting the import role of single-ring aromatic VOCs on the enhancement of SOA formation using high-aromatic fuel. However, more than 50 % of the SOA concentration cannot be explained by gas-phase oxidation of these single-ring aromatic VOCs. This value ~~is~~was even ~~large~~higher (up to 80%) in the first few photochemical hours in both experiments. ~~In addition~~Additionally, much larger percentage of SOA using F3 fuel cannot be explained by the single-ring aromatic VOCs. This suggests the existence of some unspeicated organic vapors, most likely ~~semi-volatile species~~SVOCs, which are considered to have ~~both large emission factor from vehicles and~~ high SOA yield and might partition to particle phase after the first~~-~~-generation oxidation (~~Chan et al., 2009;Liu et al., 2015b;~~Robinson et al., 2007; Chan et al., 2009; Jathar et al., 2014~~).~~; Liu et al., 2015b). Two-ring and three-ring ~~gas-phase~~ PAHs, e.g., naphthalene and phenanthrene, which ~~have been~~were proved to have higher EFs using high-aromatic fuel (Chan et al., 2009), ~~are a majority of these unspeicated organic~~likely contributed importantly to the SVOC vapors and ~~may~~might play a crucial role for the enhancement of SOA production using high-aromatic fuel.

4 Discussion

Our results exhibit the critical impact of gasoline aromatics on urban SOA formation. We observed an amplification factor of 3-6 on SOA formation using high-aromatic gasoline, which ~~is~~was mainly caused by the high emission of one-ring aromatic ~~VOC~~VOCs as well as SVOC such ~~low-molecular~~as gas-phase PAHs. This enhancement of SOA formation, meanwhile, ~~is~~was found using not only ~~using~~ a new vehicle ~~with new after-treatment technology~~meeting China IV emission standard, operated at a representative cycle condition in Beijing, but also ~~using~~an experimental engine ~~with not well-performed after-treatment~~which emitted more gaseous pollutants and was operated at steady~~-~~ state~~ operating condition~~, suggesting the extensive applicability of our results.

Moreover, photo-oxidation of aromatics leads to significant production of small dicarbonyls, i.e., glyoxal and methylglyoxal, which have high SOA yield via aqueous reactions (Zhang et al., 2015). If this aqueous SOA pathway is taken account, the influence of fuel on SOA formation will be much more remarkable. More work is needed to evaluate the aqueous pathway of SOA formation from gasoline exhaust.

Currently, aromatic content in gasoline fuel is increasing ~~continuous~~continuously in China, where more stringent standard on gasoline sulfur content ~~are undertaking~~has been upgraded and the oil refining procedure are changing to meet the new standard. For example, we found the average aromatic content for gasoline fuel in the market meeting Beijing Ⅲ, Ⅳ and Ⅴ standards were 23.4%, 28.5% and 36.3%, respectively. Recent study found that gasoline aromatic content in China was 9.6% higher than that in USA (Tang et al., 2015). Hence, the enhancement in SOA formation exerted by the increase of aromatic content in gasoline fuel from 29% to 37 % in this study can well represent the extra SOA formation due to the gasoline standard change in Beijing. Neglect of this side effect of fuel standard change may ~~partially~~potentially offset the tremendous endeavors on vehicle emission control by the local government. From another perspective, our findings provide a new direction in controlling air pollution from vehicles, which is to decrease the aromatic content in the gasoline fuel. This may ~~request~~require more hydrogenation catalysis ~~instead of catalytic reforming~~ process in the petroleum refining procedure instead of catalytic reforming process, in which large amount of aromatic contents might be produced. Compared with the vehicle restriction regulation that met the shrill opposition voice from the society and the elimination of polluted vehicles that brought large amount of expenses, this direction might be more acceptable, efficient and economical. Additionally, current vehicle emission evaluation system, which mainly measures the emissions of PM, THC, NOx and CO, will fail to tell the consequences of using the high-aromatic gasoline fuel, as these species do not increase much when high-aromatic fuel is using (Fig. 4). Aromatic VOCs, especially the SVOC, should be considered in future vehicle emission evaluation.

Furthermore, this influence of gasoline aromatic content on air quality is not only adoptable in China. Strikingly, the current standard on gasoline aromatic content are not stringent enough in most of the countries and regions in the world, where fuel standards with very high maximum gasoline aromatic content (ranging from 35 % to 42% in different countries, Table S7) are implemented, even including some developed countries and regions, i.e., Europe, Japan, Australia. Our findings highlight the necessity of a more stringent regulation on gasoline aromatic content in the next renewal of the gasoline standard.

Acknowledgement

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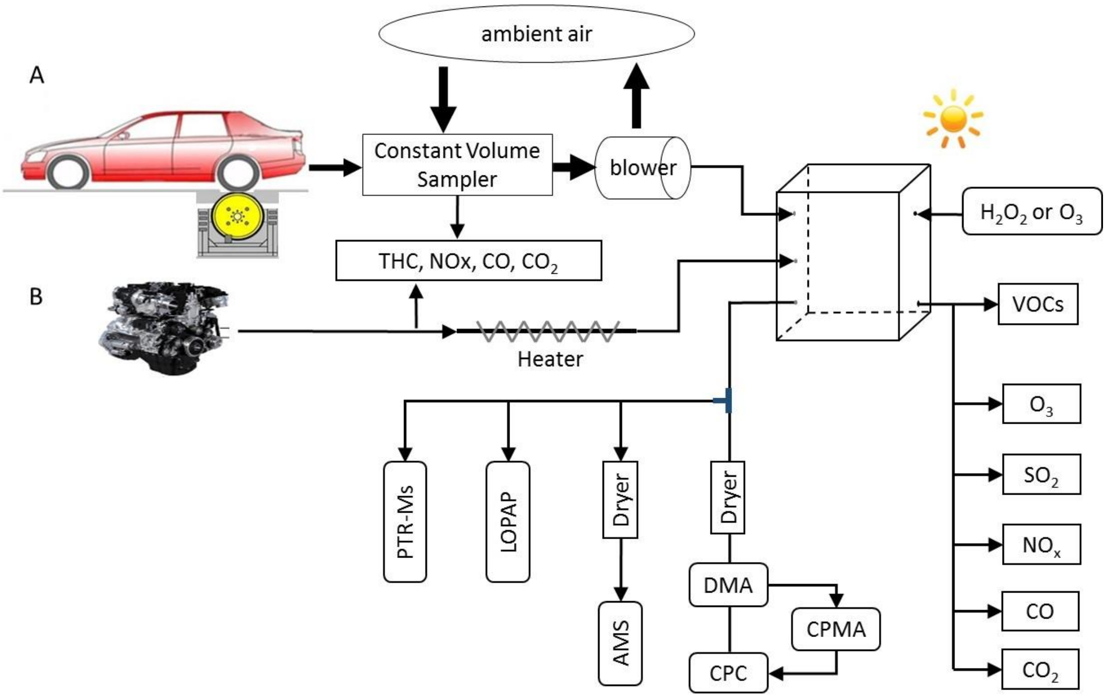
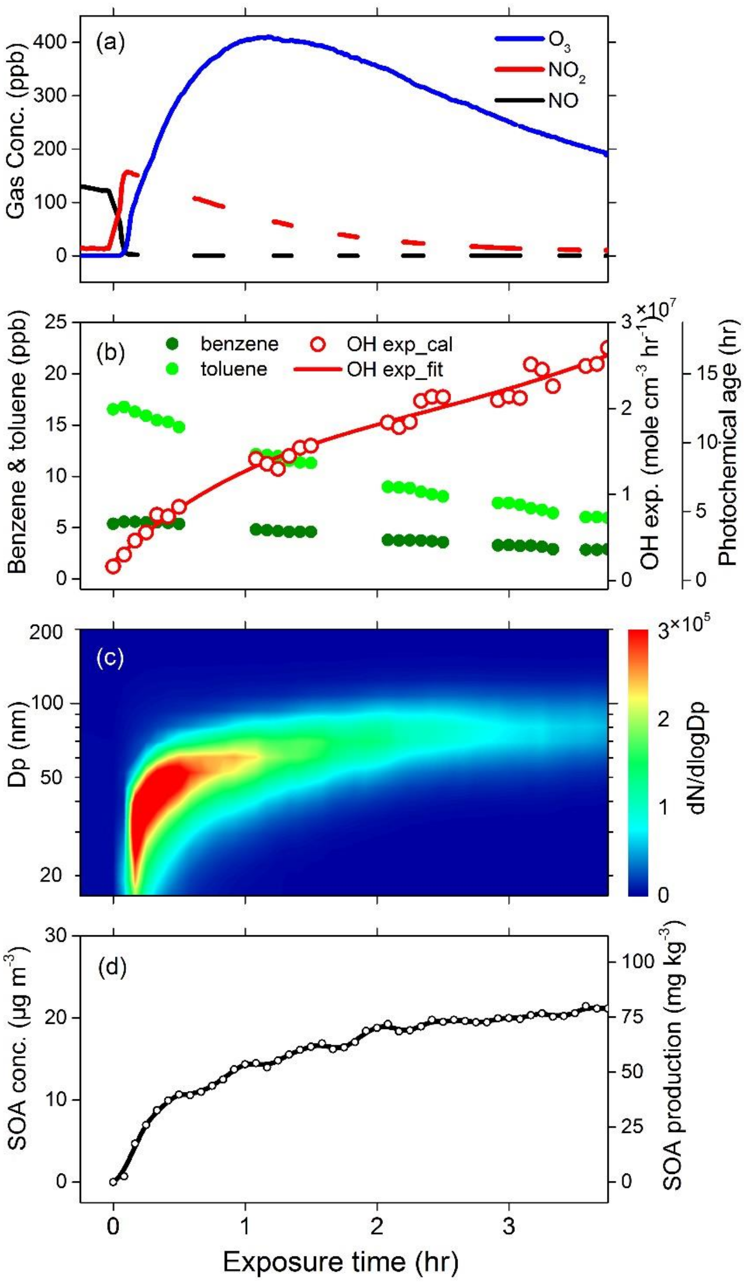


Figure 1. Schematic diagram of chamber experiments.


(a)
Gas Conc. (ppb)
400
300
200
100
0
O_3
NO_2
NO
(b)
Benzene & toluene (ppb)
25
20
15
10
5
0
benzene
toluene
OH exp_cal
OH exp_fit
3×10^7
2
1
0
OH exp. (mole cm^{-3} hr^{-1})
Photochemical age (hr)
15
10
5
0
(c)
Dp (nm)
200
100
50
20
3×10^5
2
1
0
dN/dlogDp
(d)
SOA conc. (μg m^{-3})
30
20
10
0
SOA production (mg kg^{-3})
100
75
50
25
0
0
1
2
3
Exposure time (hr)

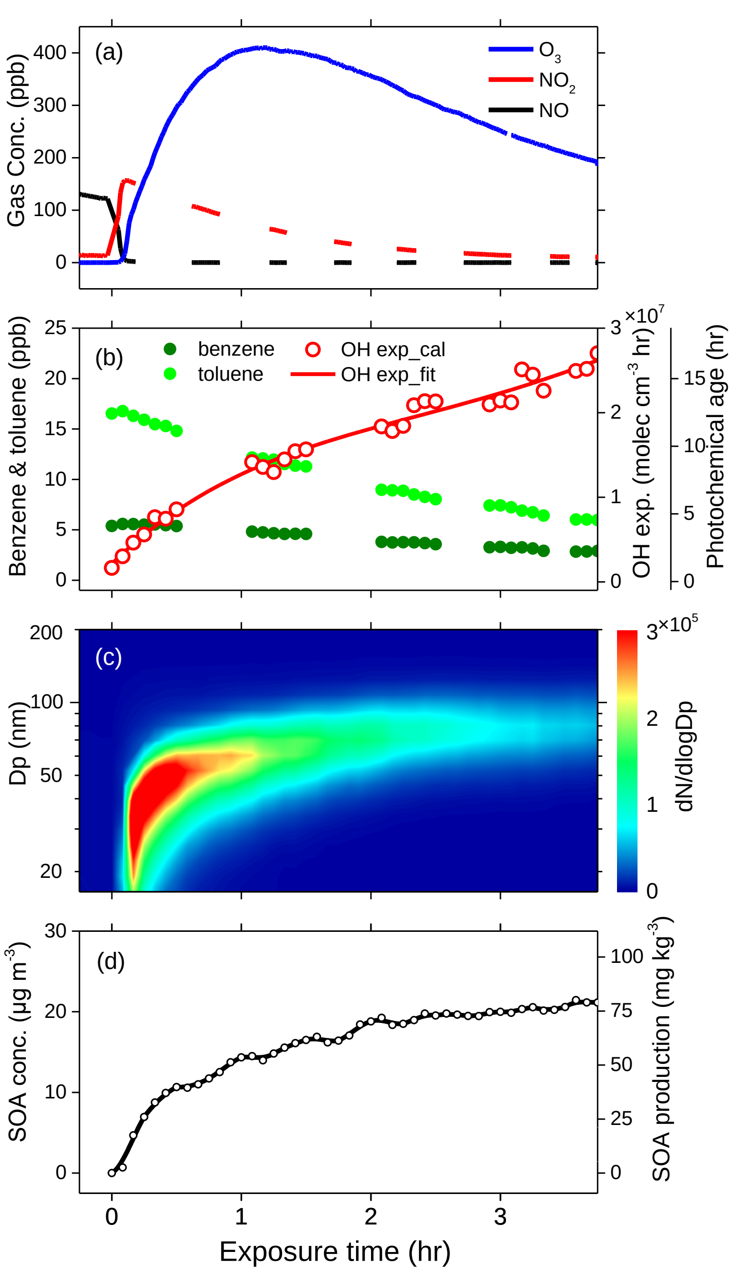
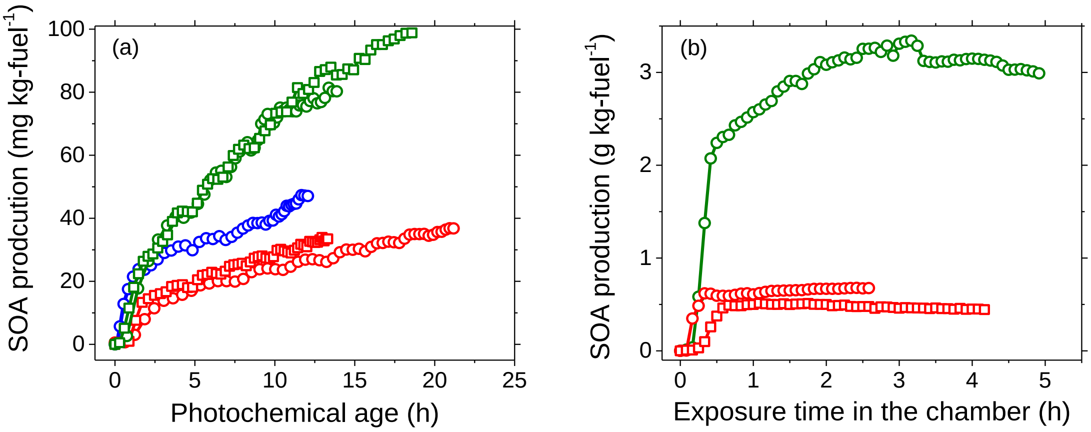


Figure 2. Evolution of gas-phase species (a, b), particle size distribution (c), and SOA concentration and production (d) during a typical chamber experiment (V2). OH exposure and photochemical age are calculated based on the ratios of benzene and toluene concentrations, assuming that OH concentration is 1.6 ×10^6 ~~mole~~molec cm^{-3}. The SOA mass concentration is obtained by intergrading size distribution of particles inside the chamber on the basis of measured particle density. The measured SOA mass concentration is corrected according to the particle wall loss curve as well as the dilution effect for both particles and gas precursors.



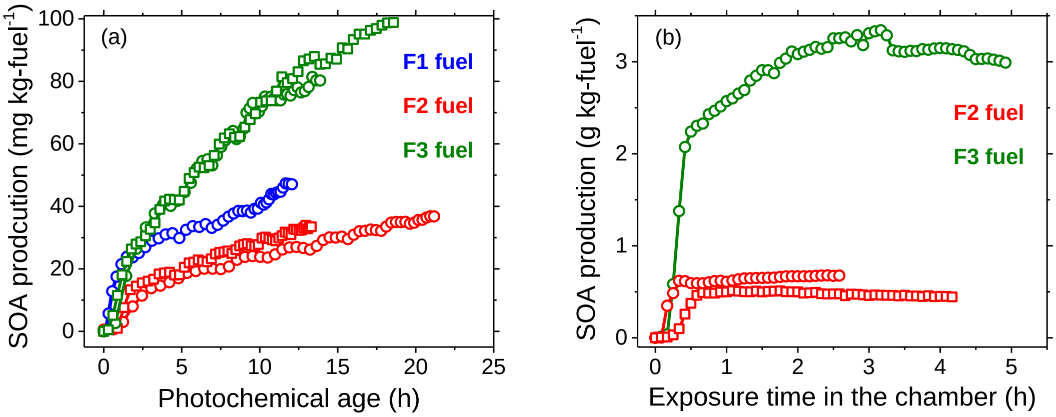
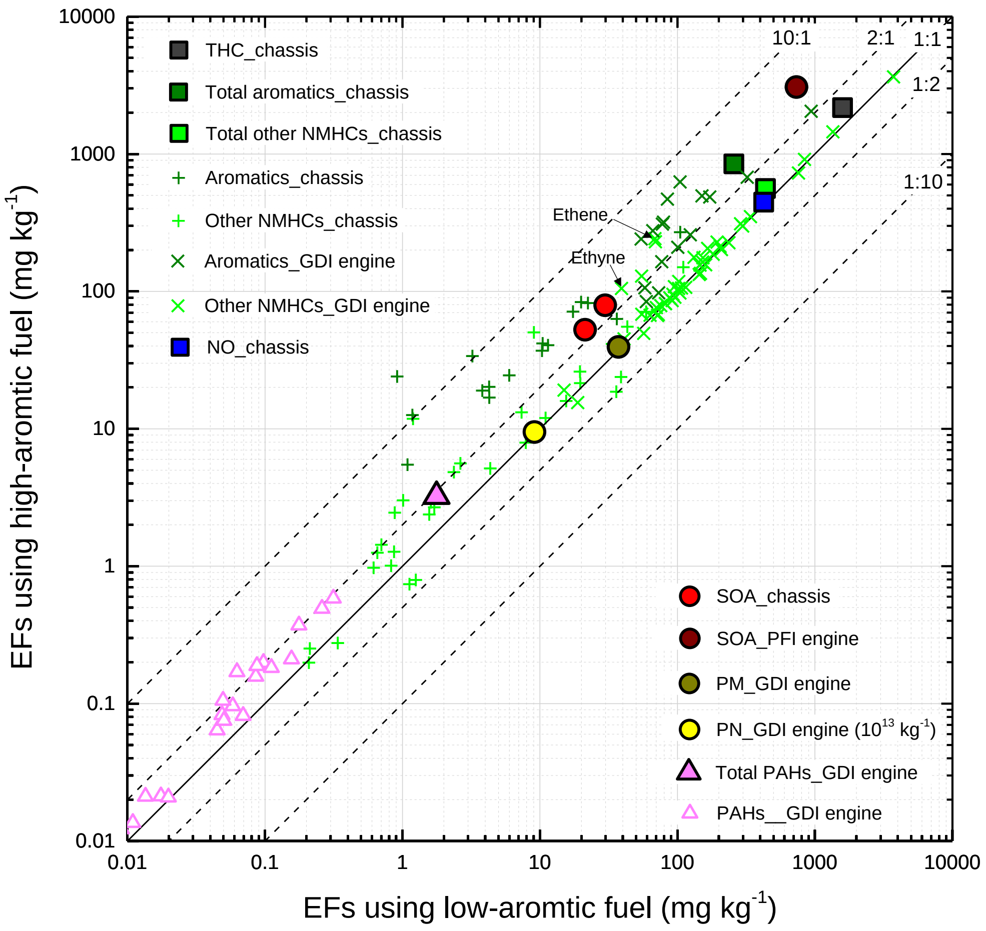


Figure 3. SOA production in the vehicle experiments as a function of photochemical age (a) and in the engine exhaust experiments as a function of exposure time (b). ~~The blue, red and green symbols represent experiments using the F1, F2 and F3 fuels, respectively.~~ The green squares, green circles, red squares, red circles and blue circles (a) represent the ~~experiments~~experiment V1, V2, V3, V4 and V5 shown in Table S1, respectively. The green circles, red squares and red circles (b) represent the experiments E1, E2 and E3 shown in Table S2, respectively.


THC_chassis
Total aromatics_chassis
Total other NMHCs_chassis
Aromatics_chassis
Other NMHCs_chassis
Aromatics_GDI engine
Other NMHCs_GDI engine
NO_chassis
SOA_chassis
SOA_PFI engine
PM_GDI engine
PN_GDI engine (10^{13} kg^{-1})
Total PAHs_GDI engine
PAHs__GDI engine
Ethene
Ethyne
10:1
2:1
1:1
1:2
1:10
EFs using high-aromtic fuel (mg kg^{-1})
EFs using low-aromtic fuel (mg kg^{-1})
10000
1000
100
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
10000

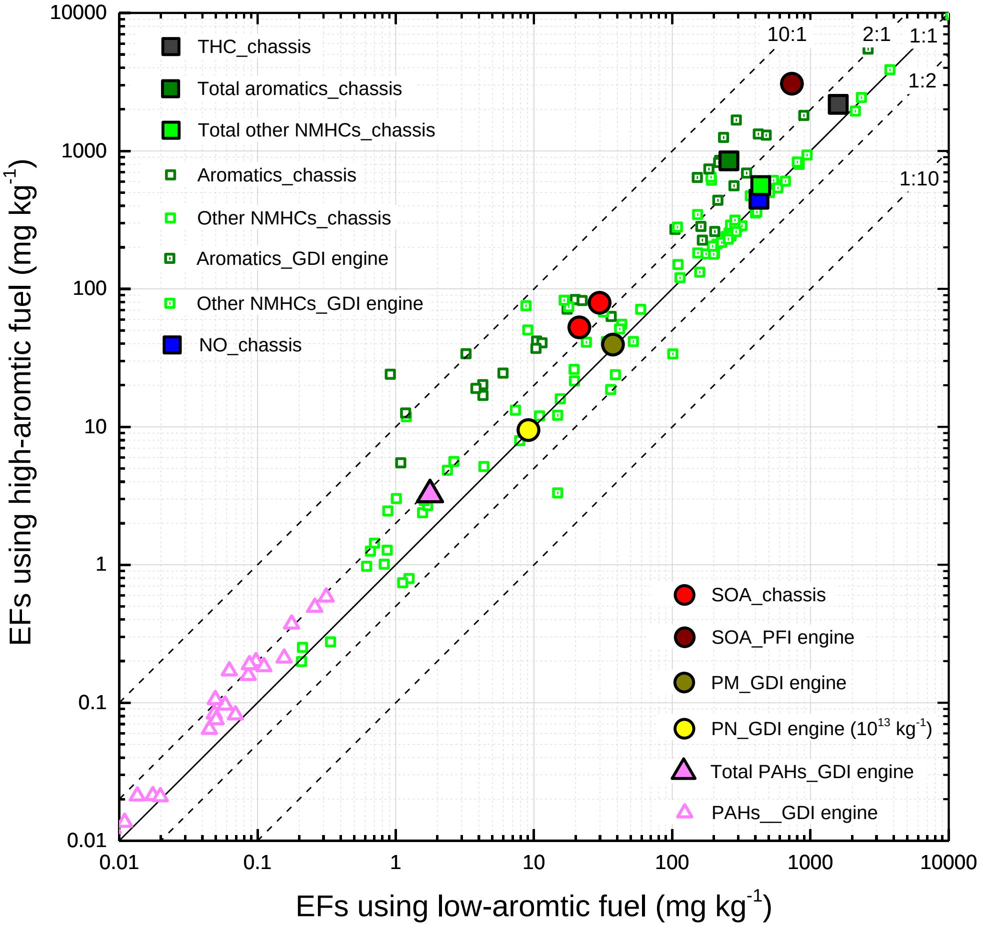


Figure 4. Comparison of emission factors (EFs) of gas- and particle species using high-aromatic fuel (F3 fuel) to those using low-aromatic fuel (F2 fuel). ~~The symbols in the figure represent as following: the red circles: SOA productions after 6 and 12 photochemical hours; the wine circle: SOA production potential in PFI engine experiments; the light and dark yellow circle: total particle number and mass EFs for GDI engine; the hollow and solid purple triangle: EFs of each Polycyclic Aromatic Hydrocarbons (PAH) and total PAHs EFs for GDI engine; the dark gray, dark green and light green solid square: EFs of total hydrocarbons (THC), total aromatics and total other non-methane hydrocarbons (NMHCs) in the vehicle experiments, respectively; dark green and light green crosses: EFs of aromatics and other NMHCs species, respectively; blue solid square: EF of NO.~~The total hydrocarbons (THC) were measured by vehicle emissions testing system, HORIBA, Ltd.), and the total aromatics and non-methane hydrocarbons (NMHCs) were measured by offline GC-MS. The black line denotes that the ratio of EFs using aromatic-rich fuel over aromatic-poor

fuel is 1:1, and dashed lines stand for the ratios of 10:1, 2:1, 1:2, and 1:10, respectively. Note that the PAHs and VOCs data for the GDI engine were measured before the three-way Catalyst (TWC).

Value in the figure can be found in Table S6.

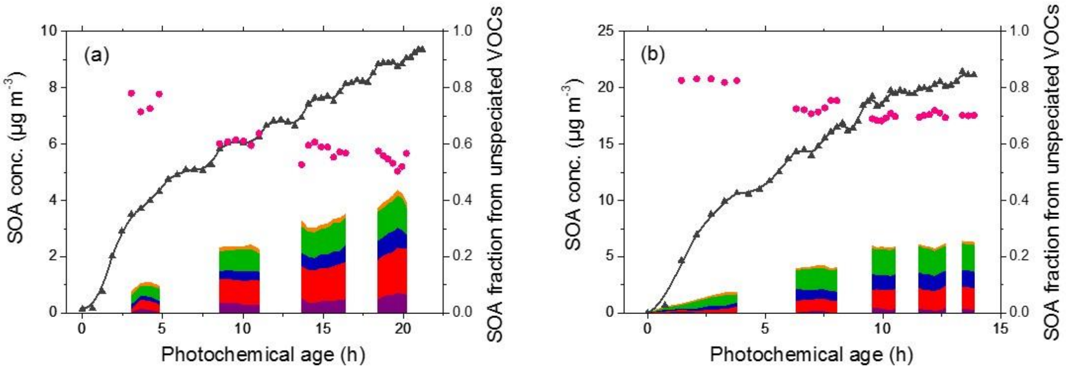


Figure 5. Observed and predicted SOA concentration, and SOA fraction from unspeciated VOCs as a function of photochemical age in typical chamber experiments using (a) F2 (~~a~~experiment V4) and (b) F3 (~~b~~experiment V2) fuels. Black line and triangles represent the corrected SOA concentrations in the chamber experiments. The purple, red, blue, green and yellow areas represent the predicted SOA from the oxidation of benzene, toluene, C8-aromatics, C9-aromatics and styrene, respectively. The pink circles represent the SOA fractions that cannot predicted by the one-ring aromatic VOC precursors.