Anonymous Referee #2, 30 July 2015

1. Regarding the IVOCs, the authors have addressed the missing IVOC measurements by inferring the volatility distribution of exhaust based on literature. While this approach is speculative, there is still utility in conducting this analysis as a sensitivity study. I just have two suggestions:
a) These estimations should be referred to as "inferred", not "literature" or "references". For example, in line 13 of the abstract, the "references IVOC species" should be "inferred carbon number distributions".

Re: Thanks for the suggestion. We agree with the comments and make changes in the revised manuscript. Please see the following changes.

Changes in manuscript:
(1) Abstract, line 13: replace "references IVOC species" with "inferred carbon number distributions".
(2) Section 2.2.3, lines 229-232: replace "we combined the amounts of alkanes and aromatics larger than C12 and polycyclic aromatics from Gentner et al. (2012) with the identified species to compare the differences of SOA yields with or without IVOCs." with "we estimated the amounts of IVOCs including alkanes and aromatics larger than C12 and polycyclic aromatics based on Gentner et al. (2012) and varied them by one order of magnitude."
(3) Section 3.3, lines 392-396: replace "For this reason, we combined the amounts of S/IVOCs including alkanes and aromatic larger than C12 and polycyclic aromatics in unburned fuels introduced by Gentner et al. (2012). The SOA yields of each vehicle exhaust and evaporative emission were calculated in two scenarios of with (Y2) or without S/IVOCs (Y1) in Fig. 5." with "For this reason, we introduced the amounts of alkanes and aromatic larger than C12 and polycyclic aromatics in unburned fuels from Gentner et al. (2012) as the inferred S/IVOCs as shown in the light colored bars in Fig. 5(a)."
(4) Section 3.3, line 408: replace "S/IVOCs" with "the inferred S/IVOCs".
(5) Section 3.3, line 421: replace "S/IVOCs" with "the inferred S/IVOCs".
(6) Section 4, line 530: replace "referenced S/IVOC species from Gentner et al. (2012)" with "inferred S/IVOC species based on Gentner et al. (2012)".

b) Readers should be cautioned these are inferred distribution only. I suggest showing the fraction of SOA (or contribution to yield) from these inferred IVOCs in Fig. 5. I also suggest showing the uncertainty in deltaOA/deltaCO as a result of this assumption. (e.g. show deltaOA/deltaCO with and without these inferred IVOCs)

Re: Thanks for the comments. We agree with the comments and revise the corresponding contents and Fig. 5. Please see the following changes.

Changes in manuscript:
(1) Section 3.3, lines 403-404: replace "Fig. 5(b) and (c) show the SOA mass yields and the contributions of different chemical class calculate by measured and combined species,

respectively." with "Fig. 5(b) shows the SOA mass yields of different chemical class. To compare the differences of the SOA yields with or without S/IVOC species, we set two scenarios as "Y1" and "Y2". Y1 indicates the SOA yields of measured C2-C12 VOCs in this study. Y2 includes the extra SOA yields of inferred S/IVOCs."

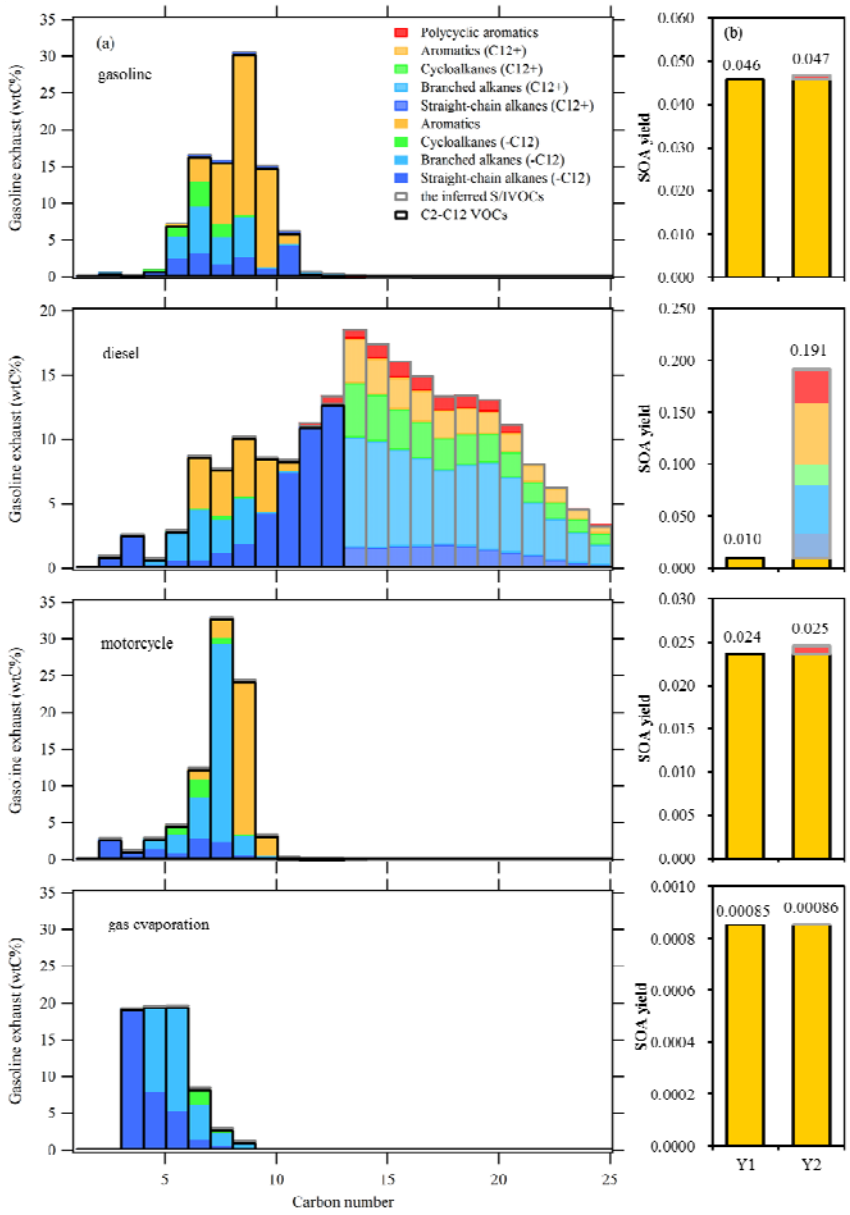

Fig. 5. (a) Distributions of mass by chemical class in carbon number of different vehicle exhausts and evaporative emissions; (b) Calculated SOA yields based on C2-C12 VOCs measured in this study (Y1) and C2-C12 VOCs plus the inferred S/IVOC species (Y2). The inferred S/IVOC species are shown in light colored bars.

(2) Please see the changes in the following changes.

2. Line 316-323: the authors used the urban vehicular fraction of CO emissions instead of the fraction for the whole of Shanghai. They did so because their measurements were conducted in urban Shanghai. This might not be a correct assumption. The authors need to show that the

observed deltaCO is indeed coming from urban Shanghai only, and that CO from neighboring industrial areas will only be observed as background in the current set of measurements and are subsequently subtracted out. Based on what is shown in the manuscript, I do not agree with this assumption, since CO is a long-lived species can easily be transported between different areas of Shanghai.

Re: Thanks for the comments. It was difficult to distinguish the source of CO at receptor only based on the emission inventory. On this account, we decided to use CMAQ model to simulate the contribution of CO concentration from vehicle exhausts and other sources to the receptor. Two scenarios (with or without vehicle emission inventory) were simulated by using brute force method. Please see the detail in the revised supplement materials. The results showed that vehicular CO emission contributed 66% and 70% to total CO concentrations at the observation site in summer and winter, respectively. Therefore, the vehicular fraction of CO emissions was determined to 68%. The inventory-based vehicular OA to total CO emission was also revised based on the new fraction. Please check the following changes.

Changes in manuscript:

(1) Section 2.3.3, lines 318-323: replace "it would be more reasonable to exclude the emissions out of the urban area. The emissions of various sources in the urban area were extracted based on their spatial distributions. Vehicle POA, VOC (including evaporative emissions), and CO emissions in urban area were 1.8, 13.4, and 170.7 k tons, respectively. Vehicles dominated CO emission in urban Shanghai, accounting for 85% of total CO emission in the urban area." with "it would be more reasonable to simulate the contribution of CO concentration from vehicle exhausts and other sources to the receptor by using numerical model. Here we used CMAQ model and brute force method to simulate the CO concentrations during January and August in 2013 under two scenarios of with or without vehicular CO emission. The meteorological data was from the results of the Weather Research and Forecasting Model (WRF). Detailed information is shown in the supplement materials. The results showed that vehicles dominated CO emission in urban Shanghai, accounting for 66% and 70% of total CO concentrations in summer and winter, respectively. On this account, the vehicular fraction of total CO emissions used in this study was determined to 68%."

(2) Section 3.4, line 442: replace "11.6μg·m^{-3}·ppmv^{-1}" with "10.6μg·m^{-3}·ppmv^{-1}".

(3) Section 3.4, line 444: replace "almost the same with primary emission ratio" with "close to the primary emission ratio".

(4) Section 3.4, lines 445-449: replace "The dotted orange line in Fig. 6 represents the maximum OA production ratio (assuming SOA precursors were 100% reacted) calculated with the SOA yields in Y2 scenario. The maximum OA production ratio reached 18.7 μg·m^{-3}·ppmv^{-1}. It was considerable underestimated compared with the observation data." with "The dotted pink and orange lines in Fig. 6 represent the maximum OA production ratios (assuming SOA precursors were 100% reacted) calculated with the SOA yields in Y1 (only detected VOCs in this study) and Y2 scenarios (detected VOCs plus the inferred S/IVOCs). The maximum OA production ratios were 13.8 and 18.7 μg·m^{-3}·ppmv^{-1}, respectively. It was indicated that S/IVOCs played much more important roles to SOA productions of vehicle exhaust. However, the max. OA production ratio for Y2 scenario was still considerable underestimated compared with the

observation data".

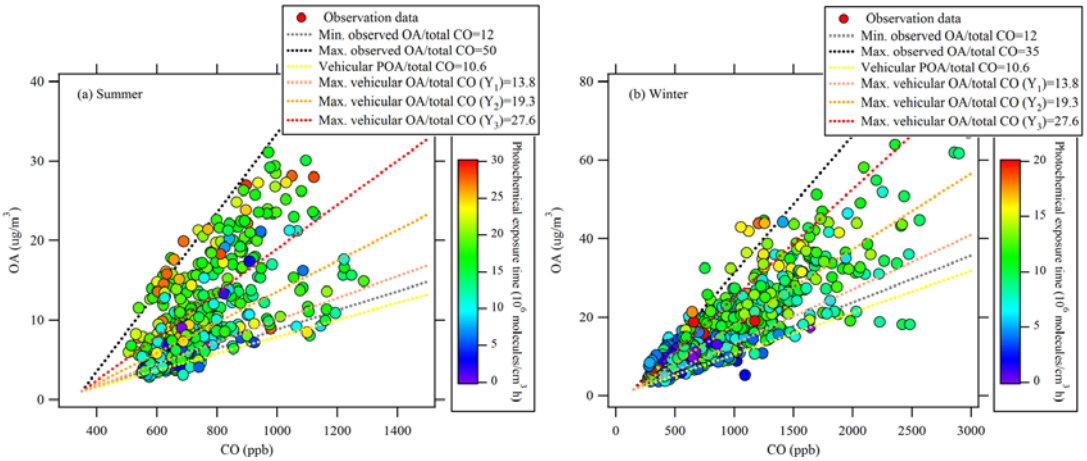

Fig. 6. Relationship of measured OA and CO concentrations color-coded by the photochemical exposure in the summer (a) and winter (b) of 2013 in urban Shanghai according to equation (4). Minimum and maximum ratios of observed OA to CO concentrations are shown by dotted grey and black lines. Vehicular POA/Total CO is shown by dotted yellow line. The minimum and maximum OA formation ratios of vehicle emissions calculated with three different SOA yields of Y1, Y2 and Y3 are shown by the dotted pink, orange and red lines, respectively.

(5) Section 3.4, line 455: replace "almost the same with primary emission ratio" with "close to the primary emission ratio".

(6) Section 3.4, line 455: replace "27.3 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$" with "27.6$\mu g \cdot m^{-3} \cdot ppmv^{-1}$".

(7) Section 3.5, lines 470-500: replace the whole paragraph with

"To evaluate the contribution of vehicle emission to OA production in urban atmosphere, we estimated the vehicular OA formation ratio to total CO emissions with Eq. (5) in three scenarios. Fig. 7(a) and (b) showed the results of vehicular OA formation ratios to total CO emissions in Y1 scenario. The SOA yields of gasoline, diesel, and motorcycle exhausts and gas evaporation were 0.046, 0.010, 0.024, and 0.0009, respectively. Fig. 7(c) and (d) showed the results in Y2 scenario where the inferred S/IVOCs were merged. The SOA yields of gasoline, diesel, and motorcycle exhausts and gas evaporation were 0.047, 0.191, 0.025, and 0.0009, respectively. Fig. 7(e) and (f) showed the results in Y3 scenario. The SOA yield of gasoline exhaust was replaced to 0.190 based on the experiment by Gordon et al. (2014a). The photochemical age (Δt) in each hour was calculated with Eq. (4). Due to the lack of OH measurement in Shanghai, we referenced the 24-h average OH concentration (3×10^6 molecules$\cdot cm^{-3}$) from de Gouw et al. (2008). The grey and yellow lines were the ratio of vehicular POA and OA production to total CO emissions. The average vehicular OA production ratios to total CO emission in the urban area were 10.6 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ and 10.8 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in summer and winter in Y1 scenario, 11.8 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ and 11.4 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in Y2 scenario, and 13.3 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ and 12.4 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in Y3 scenario. The vehicular OA mass accounted for 34% and 52% of the average observed OA in summer and winter in the urban atmosphere of Shanghai in Y1 scenario. The contributions would increase to 37% and 55% in Y2 scenario, and 41% and 59% in Y3 scenario. It was indicated that vehicle emission was the major source of OA mass in the urban atmosphere of

Shanghai. For Y2 scenario where the inferred S/IVOC species were merged to SOA yield estimation, the vehicular OA production ratios increased about 3%. For Y3 scenario where the SOA yield of gasoline exhausts was enhanced to the smog chamber experiment result (0.190), the vehicular OA production ratios further increased about 4%. Vehicular SOA formation ratios accounted for 4% of the total vehicular OA in Y1 scenario, 9%-13% in Y2 scenario and 16%-23% in Y3 scenario. The SOA formation ratios in both scenarios were lower than expected. There were two possible reasons for the underestimation. One reason was that other emission sources with high SOA formation potentials in addition to vehicles were not considered in this study. The non-fossil VOC emissions from solvent use, chemical and petrochemical industrials, etc. reported by the previous studies could be the rest of contributors (Cai et al., 2010; Wang et al., 2013). Another possible reason was the SOA yields were still underestimated in this study. There were about 30%, 50% and 15% of VOC species still unidentified in gasoline, diesel, and motorcycle exhausts even after we combined the inferred S/IVOC species reported in Gentner et al. (2012). The SOA formation potentials of the identified VOC species may contribute more SOA than expected."

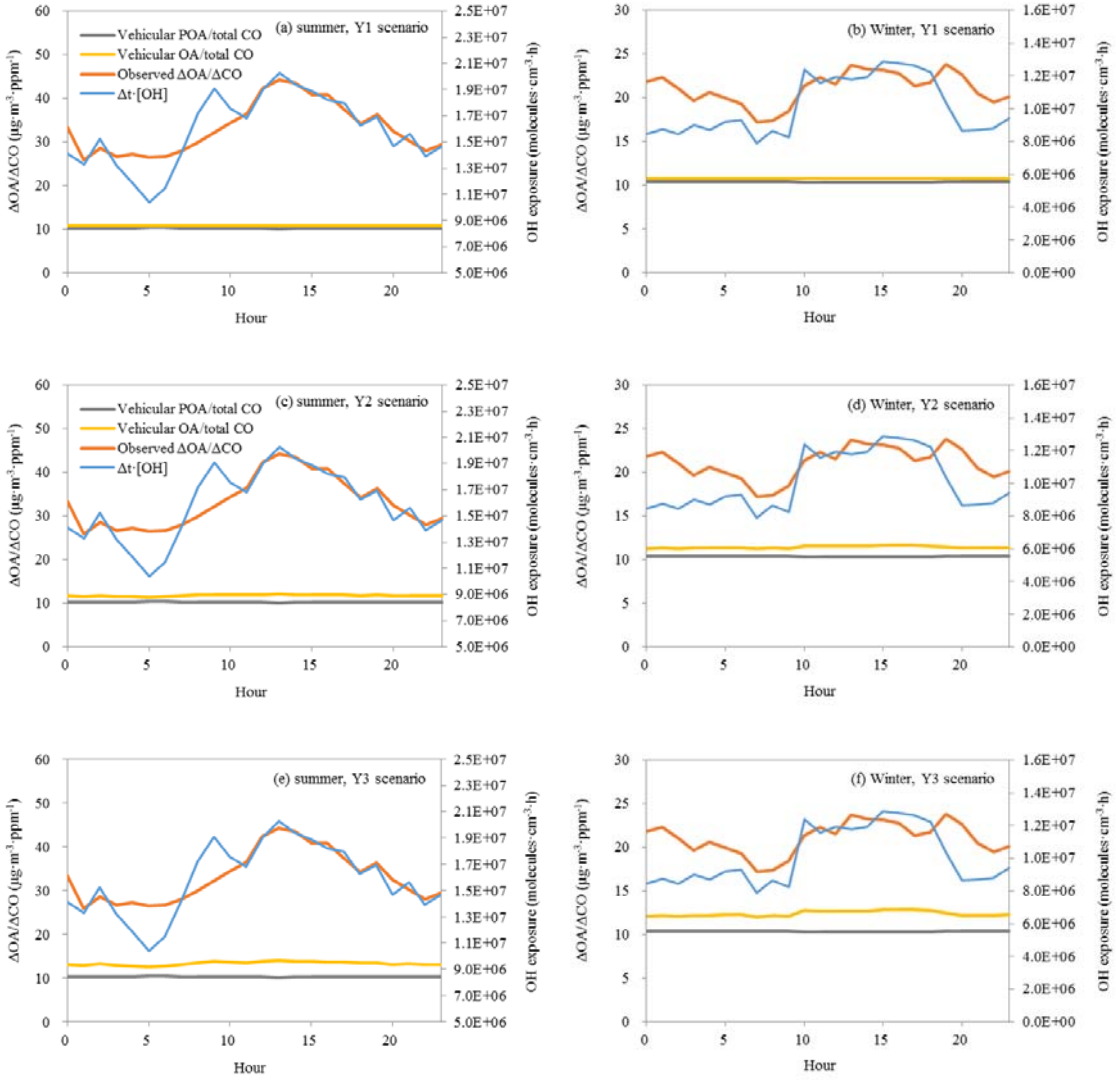

Fig. 7. Diurnal variations of observed ΔOA/ΔCO in the atmosphere (red line), OH exposures (blue line), and the ratios of vehicular POA emission (grey line) and OA formation (orange line) to total

CO emissionswith the SOA yields in three scenarios (Y1, Y2 and Y3) in summer and winter in the urban area of Shanghai for the year of 2013.

Other comments:

- The abstract is full of abbreviations that are not defined (IVOCs, VKT, SOA, deltaOA/deltaCO etc.) They should be fully defined, or not used in the abstract.

Changes in manuscript:

(1) Abstract, line 9: replace "VOC" with "Volatile organic compound (VOC)".
(2) Abstract, line 11: replace "SOA" with "secondary organic aerosol (SOA)".
(3) Abstract, line 18: replace "OA" with "organic aerosol (OA)".
(4) Abstract, line 19: replace "ΔOA/ΔCO" with "OA to CO concentrations (ΔOA/ΔCO)".
(5) Abstract, line 20: replace "POA" with "primary organic aerosol (POA)".
(6) Abstract, line 22: replace "VKT" with "vehicle kilometers of travel (VKT)".
(7) Abstract, line 25: replace "IVOCs" with "Intermediate-volatile organic compounds (IVOCs)".
(8) Section 1, line 32: replace "Secondary organic aerosol (SOA)" with "SOA".
(9) Section 1, line 36: replace "volatile organic compounds (VOCs)" with "VOCs".
(10) Section 1, line 39: replace "organic aerosol (OA)" with "OA".
(11) Section 1, line 44: replace "intermediate-volatile organic compounds (IVOCs)" with "IVOCs".
(12) Section 2.1.1, lines 102-103: replace "Vehicle kilometers of travel (VKT)" with "VKT".

- Line 68: "The number of vehicles in Shanghai was doubled..." should be "The number of vehicles in Shanghai has doubled..."

Changes in manuscript:

(1) Section 1, line 68: replace "The number of vehicles in Shanghai was doubled..." with "The number of vehicles in Shanghai has doubled..."

- Line 235-237: SOA yields are defined for a specific organic loading, based on semivolatile partitioning theory. Using Gentner's yields may not be appropriate since total OA is likely higher in Shanghai than it is in LA.

Re: Thanks for the comments. The SOA yields for all compounds from Gentner et al. (2012) were calculated or modeled assuming an average organic loading of 10 $\mu g \cdot m^{-3}$. However, the average organic concentration in winter and summer in Shanghai urban was about 15.5 $\mu g \cdot m^{-3}$ based on the observation data. To evaluate the influence of higher organic concentration to SOA yields, we recalculated the SOA yields of the compounds using a semi-empirical model based on absorptive gas-particle partitioning of two semi-volatile products introduced by Odum et al. The results show that if the organic loading is increased from 10 to 15$\mu g \cdot m^{-3}$ under high-NOx conditions, the SOA yields of straight alkanes will increase by an average of 16% in the range of 12-17 carbon atoms, C6-8 aromatics will increase by ~19%, and naphthalene will increase by ~12%. Therefore, we corrected the yield of each chemical compound based on the increments above. The correction factors for other compounds were assumed to be the same with those in similar chemical class.

The results of SOA yields of each vehicle exhaust and evaporative emission were also revised based on the new yields. Please check the following changes.

Changes in manuscript:

(1) Section 2.2.3, line 237: add "However, considering the average organic loading in Shanghai (15.5μg·m^{-3}) was relatively higher than that in the reference (10μg·m^{-3}), we recalculated the SOA yields of the compounds using a semi-empirical model based on absorptive gas-particle partitioning of two semi-volatile products introduced by Odum et al. (1997). The SOA yields of straight alkanes increased by an average of 16% in the range of 12-17 carbon atoms, C6-8 aromatics increased by ~19%, and naphthalene increased by ~12%. The yields of the compounds in similar chemical class were corrected based on the increments above." at the end of the paragraph.

(2) Section 3.3, line 408: replace "0.008 to 0.164" with "0.010 to 0.191".

(3) Section 3.3, line 409: replace "Aromatics were still the largest contributors (34.1%) to but not dominating the yield." with "In Y2 scenario, Aromatics were still the largest contributors (34.9%) to but not dominating the yield."

(4) Section 3.3, line 411: replace "accounted for 24.9%, 17.8%, and 12.8%" with "accounted for 24.8%, 17.1%, and 12.7%"

(5) Section 3.6, lines 509-518: replace "Fig. 9(a) and (b) show the changes of OA formation ratios in different fuel and vehicle types in Y2 scenario with the increase of the photochemical age. The OA produced from evaporative emissions were combined in gasoline vehicles and corresponding vehicle types. Diesel exhausts dominated the OA productions, which accounted for 96%, 93% and 88% after 0, 6, and 24 hours of photochemical reaction. HDDV and bus were major sources of OA productions. Fig. 9(c) and (d) show the changes of OA formation ratios in Y3 scenario. The contribution of gasoline vehicles in this scenario increased a lot. Although gasoline vehicles only accounted for 4% of POA emission, their contributions to vehicular OA formation increased to 19% and 35% after 6 and 24 hours of photochemical reaction, respectively." with "Fig. 8(a) and (b) show the changes of OA formation ratios in different fuel and vehicle types in Y1 scenario with the increase of the photochemical age. The OA produced from evaporative emissions were combined in gasoline vehicles and corresponding vehicle types. The inventory-based ΔOA/ΔCO show downward trends in Y1 scenario. Diesel exhausts dominated the OA productions, which accounted for 96%, 91% and 84% after 0, 6, and 24 hours of photochemical reaction. HDDV and bus were major sources of OA productions. Fig. 9(c) and (d) show the changes of OA formation ratios in Y2 scenario. The ΔOA/ΔCO show upward trends in Y2 scenario. The contributions of diesel exhausts in this scenario increased to 92% and 87% after 6 and 24 hours of photochemical reaction. Fig. 9(e) and (f) show the changes of OA formation ratios in Y3 scenario. The contribution of gasoline vehicles in this scenario increased a lot. Although gasoline vehicles only accounted for 4% of POA emission, their contributions to vehicular OA formation increased to 18% and 34% after 6 and 24 hours of photochemical reaction, respectively."

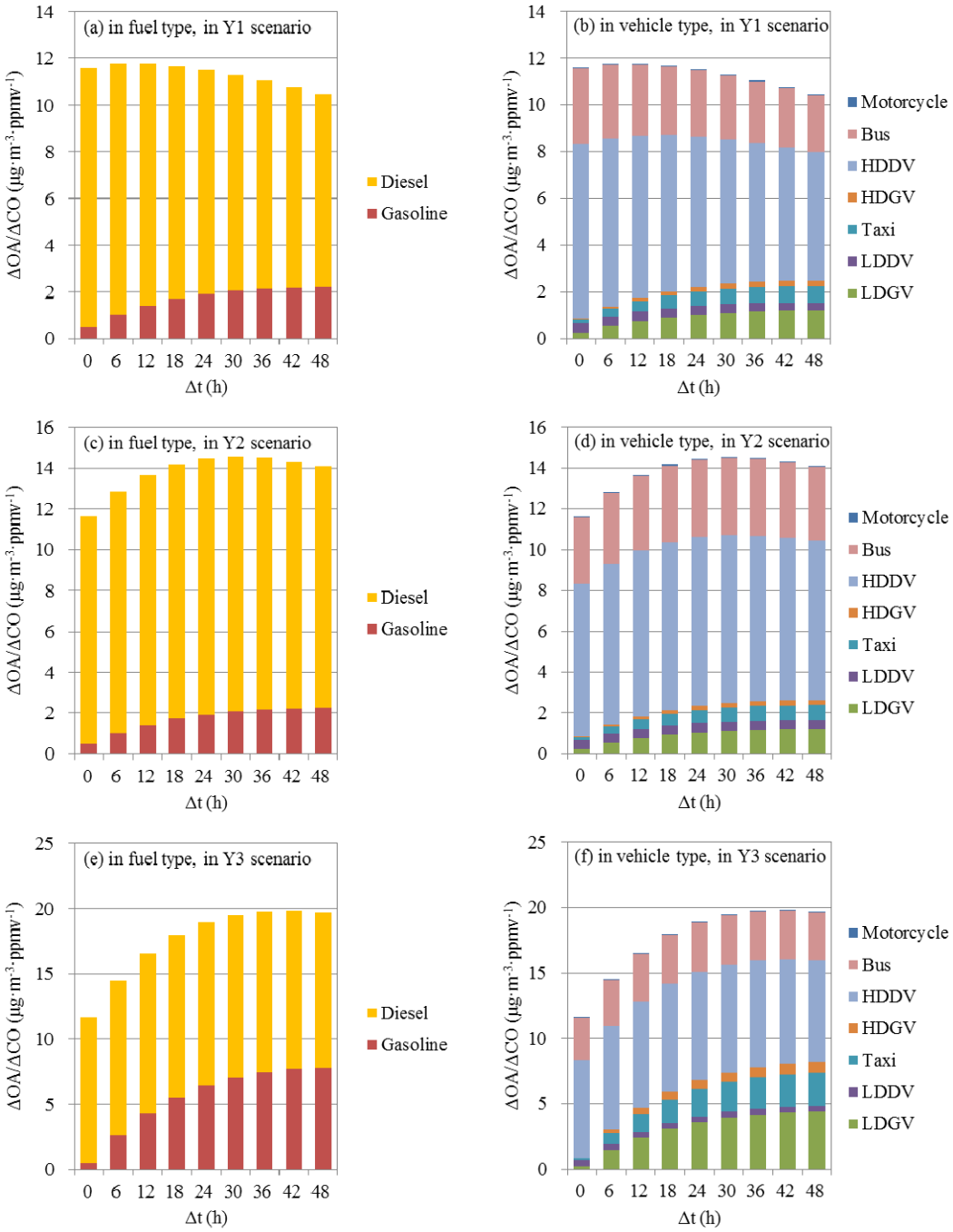

Fig. 8. Contributions of vehicle emissions to OA formation ratios in different vehicle and fuel types in Y1, Y2 and Y3 scenarios with the changes of photochemical ages.

- Line 278: Stating that xylene and ethylbenzene are "engaged in different chemical reactions in the day time" is misleading. They are oxidized by the same radical to form the same type peroxy radicals that lead to their decay. To be more precise, xylene and ethylbenzene are oxidized *at different rates* from each other.

Re: Thanks for the comments. Please check the following change.

Changes in manuscript:

(1) Section 2.3.2, line 278: replace “they are engaged in different chemical reactions in the daytime” with “they are oxidized at different rates from each other”.

- Line 430: Fig. 7 should be Fig. 6

Changes in manuscript:

(1) Section 3.4, line 430: replace “Fig. 7” with “Fig. 6”.

Other changes in manuscript:

(1) Section 2.2.3, line 223: remove “in” before “which”.
(2) Section 2.3.3, line 308: replace “should be substituted by” with “represented for”.
(3) Section 3.4, line 461: remove “also”.
(4) Section “Acknowledgement”, lines 579-580: replace “the National Natural Science Foundation of China (NSFC) via grant No. 41205122,” with “Chinese Academy of Sciences Strategic Priority Research Program via grant No. XDB05020302,”.