1. General comments

1.1 The main points of the manuscript seem to be buried. Some of this is a matter of writing style and structure, but in many ways the key points are not articulated well. My take away after multiple readings is that: (1) Vehicle emissions, even after accounting for SOA production, are an important but not dominant source of OA in Shanghai, and (2) Even after accounting for SOA production, diesel vehicles, which account for less than 20% of VKT, contribute more than 50% of mobile source OA in Shanghai.

Re: Thanks a lot for the reviewer's valuable comment. We also find that the content of this article is messy and the topic is not clear. Based on the comment, we abstract two questions from the article: (1) the contribution of vehicle emission to OA in urban Shanghai? (2) The relative contributions of gasoline and diesel vehicles to vehicular derived OA in urban Shanghai. To focus on these two questions, we rewrite the last part of "Introduction" and "Conclusions". Please see the changes in manuscript.

Changes in manuscript:
(1) Section 1, page 7981, lines 5-12: replace "In this study, we first investigated ...... in the urban atmosphere of Shanghai." with "In this study, we first constructed a vehicular emission inventory of Shanghai for the year of 2012. Then the SOA yields of VOCs emissions from different vehicle types were discussed based on the new measurements of VOCs species from a fleet of vehicles in Shanghai. Finally, we calculated the inventory-based vehicular OA production with the ambient observation data to evaluate the OA contribution of vehicle emission. The main purpose of this study is to discuss: (1) the contribution of vehicle emission to OA in urban Shanghai; (2) the relative contributions of gasoline and diesel vehicles to vehicle derived OA."

(2) Section 4 "Conclustion": based on the changes in the main text, we rewrite Section 4 as follows.
      "To evaluate the OA contribution of vehicle emissions in the urban atmosphere of Shanghai, we developed a vehicular emission inventory and estimated the SOA yields of gasoline, diesel, and motorcycle exhausts and gas evaporation based on measured C2-C12 VOC species and referenced S/IVOC species from Gentner et al. (2012). Higher contents of aromatic were measured in this study and other studies in China compared with the results from the US and European. Loose limit to aromatic contents in the standard of gasoline fuel in China should be responsible for the high aromatic contents, which resulted in larger SOA yield of gasoline exhaust than the results reported by Gentner et al. (2012) based on the same method. However, the estimated yield was still much lower than the results from smog-chamber experiments (Gordon et al., 2014a), which implied the unidentified species were considerable to SOA formation.
      Vehicles dominated the POA emissions and OA productions in the urban atmosphere of Shanghai. Their contributions to OA productions were about 40% and 60% in summer and winter, respectively. The rest of the contributors could be the non-fossil VOC emissions from

solvent use, chemical and petrochemical industrials, etc. and the underestimated SOA productions from unidentified VOC or IVOC species in the exhausts. At present, vehicles are experiencing rapid growth trends in the cities of China. Primary emissions and secondary formation of OA derived from vehicles will lead to further deterioration of fine particle pollution in the urban area. Reduction of primary PM emissions and SOA precursors from vehicle exhausts will be helpful to improve the air quality in the cities of China. The results also indicate diesel exhausts dominate the POA emissions in the urban area. Therefore, strengthening the primary PM emission control of diesel vehicles, especially for the older diesel vehicles with loose emission standards as shown by Fig. 2, plays an important role in OA pollution prevention. Now China is conducting the large-scale elimination of "yellow-labeled" diesel vehicles whose emission standards were lower than Euro 3. It can be expected to effectively reduce the OA pollution caused by diesel vehicles. On the other hand, gasoline exhausts have high potential impacts on SOA formation in the urban area. Tightening the limit of aromatic contents in gasoline fuel will be meaningful to reduce the SOA contributions of gasoline vehicles.

There are still some uncertainties need to be improved in the future. First is the SOA mass yield. More experiments on SOA yields of vehicle exhausts in China will be helpful to the SOA formation potentials of different vehicle types. Especially for gasoline exhausts, the estimated SOA yield was much lower than the experiment results in the US. Vehicular OA contributions will increase about 4%-5% if we replace the estimated SOA yield of gasoline exhaust to the experiment result. It will be meaningful to find out their actual SOA yield and key precursors for urban OA pollution control. Emission inventory is another important source of uncertainty in this study. To reduce the uncertainty of vehicular emission inventory, we localized the vehicle mileage and emission factor data based on the traffic surveys in Shanghai and real-world measurements in some cities of China. However, the CO emission inventories of other sources shown in Fig. S5 still have large uncertainties according to the previous study (Huang et al., 2011). More accurate emission inventory will be helpful to reduce the uncertainty of vehicular OA contribution in this study. However, it can be concluded that vehicle emissions are the most important contributors to OA pollution in the cities of China. Another implication is the potential roles of IVOCs in vehicle exhausts are very important on the SOA formation in the urban area. Therefore, further studies need to pay more attentions to determine the contributions of IVOC emissions to OA pollution in China."

1.2 Part of my trouble in understanding this manuscript is the lack of discussion of the key points. The paper needs some discussion to help readers synthesize all of the results. Right now it reads as a long list of results with limited interpretation. There are many paragraphs where a new observation is followed by 3-4 sentences enumerating results (usually a string of numbers) from previous studies. This is very difficult to follow and takes away from the big picture.

Re: Thanks for the comments. We rewrite the paragraphs in the section of "Results and discussion". Since there are many revisions and most of them are blended with the responses to "Specific comments". Here we don't list the changes in the manuscript. Please see the details in the following responses.

1.3 In addition to the confusion structure, there are several places (outlined below in more detail), where different figures contradict each other. The worst offense seems to be Figure 8, which I cannot reconcile with previous tables and figures, notably Figure 5.

Re: As the reviewer mentioned, the pictures do make readers confuse if there is no clear description. Actually, there are two methods we used to evaluate the OA formation potential of VOC emissions. One is the production of VOC emissions multiplied by SOA yield. This method assumes the maximum SOA formation potential without the consideration of photochemical age and the loss of OA. However, the SOA formation is strongly related with the exposure of photochemical age. In Fig. 8, we calculated the SOA formation in different photochemical ages and considered the loss of organic aerosol according to another method as described in equation (2). However, we agree with the reviewer's comment. To avoid the misunderstanding, we remove the pictures and discussions based on the first method. Please see the changes as follows.

Changes in manuscript:
(1) Section 3.3: to avoid the misunderstanding on different results of SOA formation potentials, we remove the contents of SOA formation potentials in this section and replace the title "Vehicle emission inventory and SOA formation potentials" with "Vehicle emission inventory". The section is revised as follows.

"The emissions of CO, NOx, VOCs, EVA (gas evaporation), EC, and POA (OC*1.2) from vehicles were 343.9, 110.9, 39.4, 8.9, 4.0, and 4.3 k tons in Shanghai for the year of 2012 (See Table 3). Gasoline vehicles (including LDGV, Taxi, HDGV, and Motorcycle) were the major sources of CO, VOCs, and EVA emissions, accounting for 91%, 69%, and 100%, respectively. Diesel vehicles (including LDDV, HDDV, and Bus) were the major source of NOx, EC, and POA emissions, comprising 82%, 99%, and 96%, respectively. CO and VOC (including EVA) emissions decreased by 40% and 38% compared with the results for the year of 2004 from Wang et al. (2008). NOx emission increased by 21%. PM emission were low estimated in that article since the PM emission factors were much lower than real-world measurement data as shown in Fig. 2. Gasoline vehicle emissions have been well controlled even though their VKTs were nearly doubled in the past few years. In comparison, the control effect of diesel vehicle emission was relatively poor. It is clear that diesel exhausts dominate the primary PM (including EC and OA) emissions in Shanghai. However, since VOC emissions are mainly from gasoline vehicles, we will further discuss the contributions of gasoline and diesel exhausts to SOA."

Table 3. Vehicle emission inventory in Shanghai.

Vehicle type	Emission inventory (k ton)					
	CO	NOx	VOCs	EVA	EC	POA (OC*1.2)
in vehicle type						
LDGV	192.03	13.30	15.59	6.15	0.02	0.07
LDDV	1.89	5.72	0.32	0.00	0.17	0.11
Taxi	68.89	3.86	5.56	1.96	0.01	0.03
HDGV	36.79	2.20	2.29	0.29	0.00	0.01
HDDV	24.71	67.56	9.74	0.00	3.16	3.40

Bus	5.53	17.56	2.06	0.00	0.58	0.62
Motorcycle	14.01	0.67	3.85	0.49	0.02	0.06
in fuel type						
Gasoline	311.71	20.04	27.28	8.88	0.05	0.17
Diesel	32.14	90.84	12.12	0.00	3.91	4.13
Total	343.85	110.88	39.40	8.88	3.96	4.30

1.4 The authors may want to consider splitting this work into two manuscripts: one describing the vehicle measurements and another describing the inventory building and ambient data. This might help focus the discussion and reduce reader confusion.

Re: The structures of the article are not established well. According to the reviewer's suggestion, we modified the contents into three parts: (1) the establishment of vehicle emission inventory; (2) the measurements of VOC species and SOA yield estimations; (3) the estimation of vehicular OA contribution based on the ambient data. Most of the paragraphs in the sections of "Materials and methods" and "Results and discussion" were revised into these three parts.

Changes in manuscript:
(1) Section 2.2: replace the title "Vehicular emission inventory" with "Vehicular emission inventory establishment". This section mainly explains how to establish the vehicle emission inventories. It consists of 4 sections, including a new section on "Methodology of emission inventory compilation" at the beginning. Please see the detail changes in the response to No 1.5 general comment. Detail revisions in this section are listed in the responses to Specific Comments.
(2) Section 2.1: replace the title "Vehicular VOC species sampling and analysis" with "VOC species measurements and SOA yield estimation". It consists of 3 sections. The first two sections were separated into 2 sections. Section 2.1.1 is "VOC sampling", including the first two paragraphs in the original section. The third paragraph was separated as Section 2.1.2 "VOC analysis". To describe the methodology of SOA yield estimation discussed in Section 3.2, we add Section 2.1.3 "SOA yield estimation".
(3) Section 2.3: replace the title "Air pollution observation" with "Air pollution observation and vehicular OA contribution determination". It consists of 3 sections. Section 2.3.1 is "Air pollution observation". Section 2.3.2 is "OA production estimation". Section 2.3.3 is "Determination of vehicular OA contribution".
(4) Section 2: move section 2.2 to section 2.1. Title numbers was adjusted accordingly.
(5) Section 3: move section 3.3 to section 3.1. Title numbers was adjusted accordingly.

1.5 General comment on Methods section: This section needs more detail. There were many occasions while reading the manuscript when I was not sure what methods the authors used and felt like the methods were not adequately explained.

Re: Thanks for the comments. We rewrite the section of "Materials and methods" in the manuscript. First, we added a new section of "Methodology of emission inventory compilation" to describe the methodology of vehicle emission inventory compilation. Then each section about the

preparation of required data for emission inventory was revised in the manuscript. Please see the following changes.

Changes in manuscript:
(1) Section 2.2: to better explain the methodology of vehicle emission inventory development, we added a new section at the beginning of the whole section:

"We developed emission inventories for the pollutants including VOCs, CO, EC, and OC with the IVE (International Vehicle Emission) model for Shanghai, China. The methodology of the model has been introduced by Wang et al. (2008). Vehicle kilometers of travel (VKT), vehicle flow distribution, driving pattern, fleet composition and emission factor of each vehicle type were 5 key parameters for the development of vehicle emission inventory. The emissions can be calculated with Eq. (1).

$$E = \sum_t \left\{ VKT_{[t]} \times f_{[t]} \times EF_{[t]} \times \sum_d \left[f_{[dt]} \times K_{[dt]} \right] \right\} \tag{1}$$

Where, E is emission amount of each vehicle type (g). $VKT_{[t]}$ is Vehicle kilometers of travel of each vehicle type (km). $f_{[t]}$ is the fleet composition of each vehicle technology (%), such as fuel type, engine size, and emission standard. $EF_{[t]}$ is the emission factor of each vehicle technology (g·km^{-1}). $f_{[dt]}$ is the fraction of the driving pattern (%). $K_{[dt]}$ is the correction factor of each driving pattern determined by the model (unitless). Evaporative emissions are also calculated with Eq. (1). $EF_{[t]}$ will be evaporative emission factor of each vehicle technology as the evaporative emissions are calculated."

(2) Section 2.2.1: please check the changes in the response to No 2.8 Specific comment.
(3) Section 2.2.3: the contents of the new section "SOA yield estimation" are as follows:

"To investigate the SOA formation potentials of VOC emissions in vehicle exhausts and gas evaporation, we calculated the SOA yields of the exhausts from gasoline, diesel, and motorcycle vehicles and evaporative emissions with the following equation.

$$Y_S = \sum \left(VOC_{i,s} \times Y_i \right) \tag{3}$$

Where, Y_j is the SOA yield of source j (unitless). $C_{i,j}$ is the weight percent (by carbon) of species i in which can be identified by measurements or references from source j (wtC%). VOC_j is the weight percent (by carbon) of total identified SOA precursors and unidentified species. Identified non-SOA precursors were excluded from total VOC emissions. The weight percentages of identified species were determined by the measurements above. The unidentified species accounted for about 25%, 60%, and 50% in gasoline, diesel, and motorcycle exhausts, repectively. Considering IVOCs which had high SOA formation potentials were not measured in this study, 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. Y_i is the yield of species i under high-NOx condition considering the study was focusing on urban area with high NOx concentration (unitless). The yield for each SOA precursor was referenced from Gentner et al. (2012), which listed the yields of known and estimated compounds using a combination of measured SOA yields derived from laboratory-chamber experiments and approximate SOA yields based on box modeling."

(4) Section 2.3.1: the whole paragraph is replaced with "To estimate the vehicular OA production

in the atmosphere, we calculated the SOA formation potentials from vehicular VOC emissions based on observation data with a photochemical-age-based parameterization method. The observation data were obtained from a monitoring site on the roof of a 5-floor building (15 m high above the ground) at Shanghai Academy of Environmental Science (31.17ºN, 121.43ºE), which was located southwest of urban area of Shanghai. The site was mostly surrounded by commercial properties and residential dwellings. Vehicle exhaust was a major source of pollutants near this site. Fig. S1 shows the location of monitoring site in this study. Carbon monoxide was continuously measured by an ECOTECH EC9820 CO analyzer. $PM_{2.5}$ concentration was measured by a Thermo Fisher commercial instrument β-ray particulate monitor. Organic carbon (OC) and elemental carbon (EC) were measured by a carbon analyzer (model RT-4, Sunset Laboratory Inc.). Water soluble ions were measured by a commercial instrument for online monitoring of aerosols and gases (MARGA, model ADI 2080, Applikon Analytical B.V.). Individual VOC species were continuously measured every 30 minutes by two on-line gas chromatographs with flame ionization detector (GC-FID) systems (Chromato-sud airmoVOC C2–C6 #5250308 and airmoVOC C6–C12 #2260308, France). Fig. S2 shows the time series data of meteorological parameters and concentrations of major air pollutants observed in urban Shanghai in summer (August in 2013) and winter (January in 2013). We didn't measure the OA concentration due to the lack of observation equipment. The OA concentrations were determined by OC concentrations multiplying the OM/OC ratio. Turpin et al. (2001) suggested a ratio around 1.2-1.6 from fresh emission to aged air mass in remote area. Considering our study was mainly focusing on urban area where emissions were not fully aged, we used the ratio of 1.4 to convert OC concentrations.

New reference:

Turpin, B. J. and Lim, H. J.: Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass, Aerosol Science and Technology, 35, 602-610, 2001."

(5) Section 2.3.2: move the first two paragraphs in Section 3.4 and the 2nd paragraph in Section 3.5 to this section. Then replace the contents with

"The evolution of primary VOC emissions to SOA formation is determined by OH exposure in the atmosphere. The OH exposure can be calculated with Eq. (4) developed by de Gouw et al. (2005, 2008).

$$\Delta t \cdot [OH] = \frac{1}{(k_X - k_E)} \times \left[\ln\left(\frac{[X]}{[E]}\bigg|_{t=0}\right) - \ln\left(\frac{[X]}{[E]}\right) \right] \tag{4}$$

Here, Δt is photochemical age (h). $[OH]$ is the average OH radical concentrations (molecules·cm^{-3}). The ratio of m,p-xylene to ethylbenzene (X/E) was considered as a photochemical clock. k_X and k_E are the OH rate constants of m,p-xylene (18.9×10^{-12} cm^3·molecule^{-1}·s^{-1}) and ethylbenzene (7.0×10^{-12} cm^3·molecule^{-1}·s^{-1}). $[X]/[E]|_{t=0}$ and $[X]/[E]$ are initial emission ratio and the ratio after photochemical reaction of m,p-xylene to ethylbenzene. The concentrations of m,p-xylene and ethylbenzene showed good correlations during the observation (Fig. S3). The different diurnal variations of m,p-xylene and ethylbenzene indicated that they are engaged in different chemical reactions in the daytime

(Fig. S4). Fig. 3 illustrates the diurnal distributions of the ratios of observed m,p-xylene to ethylbenzene in summer and winter of 2013. The initial emission ratios of m,p-xylene to ethylbenzene were determined by the X/E ratio on 97.5 percentiles, which were 2.17 and 1.68 in summer and winter, respectively.
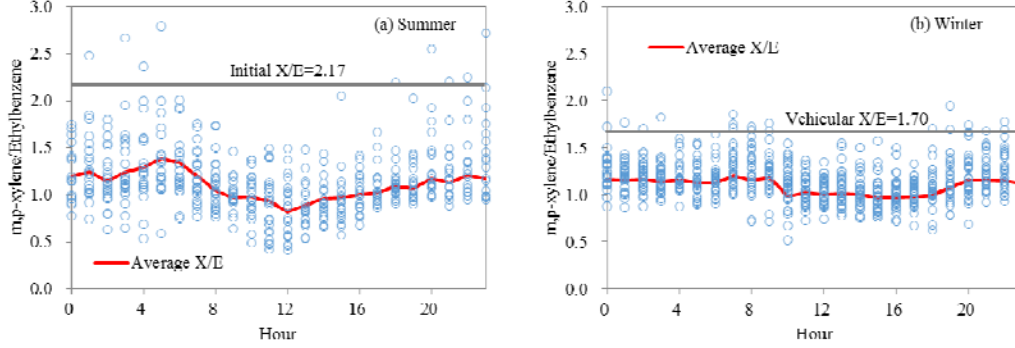

Fig. 3. Diurnal distributions of the ratios of m,p-xylene to ethylbenzene concentrations in summer and winter in the urban atmosphere in 2013."

OA production is determined by the loss terms and formation rates of OA concentration after POA emissions exhaust into the atmosphere. de Gouw et al. (2008) introduced a method to explain the OA evolution during photochemical aging of urban plumes as shown by Eq. (5).

$$\frac{\Delta OA}{\Delta CO} = \frac{\Delta POA}{\Delta CO} + \frac{\Delta SOA}{\Delta CO}$$

$$= ER_{POA} \times \exp(- L_{OA} \cdot \Delta t) + ER_{VOC_j} \times Y_j \times \frac{P_{OA}}{L_{OA} - P_{OA}} \times \left[\exp(- P_{OA} \cdot \Delta t) - \exp(- L_{OA} \cdot \Delta t) \right]$$

(5)

Here, $\Delta OA/\Delta CO$ is the ratio of OA formation versus CO emission after photochemical reaction ($\mu g \cdot m^{-3} \cdot ppmv^{-1}$). ER_{POA} is the primary emission ratio of OA to CO emission ($\mu g \cdot m^{-3} \cdot ppmv^{-1}$). ER_{VOCj} is the primary emission ratios of VOC (including SOA precursors and unidentified species) from source j to CO emission in the unit of $ppbv^{-1} \cdot ppmv^{-1}$. Y_j is the SOA yield of source j, which is determined by Eq. (3). L_{OA} and P_{OA} are the loss and formation rate of organic aerosol, respectively. We used the empirical parameters derived by de Gouw et al. (2008), which were 0.00677 h^{-1} and 0.0384 h^{-1}, respectively. Δt is the photochemical age calculated by equation (4). Because there is no OH measurement in Shanghai, we reference the 24-h average OH concentration (3×10^6 molecules$\cdot cm^{-3}$) from de Gouw et al. (2008)."

(6) Section 2.3.3: we add a new section to explain how to determine vehicular OA production contributions in the atmosphere.

"The observed $\Delta OA/\Delta CO$ in the atmosphere represents the ratio of total POA emissions and their SOA formation to total CO emissions from all sources, which can be explained by Eq. (6) as follows.

$$\left(\frac{\Delta OA}{\Delta CO} \right)_{obs} = \frac{POA_{total} + SOA_{total}}{CO_{total}} = \frac{(POA_{veh} + SOA_{veh})}{CO_{total}} + \frac{(POA_{oth} + SOA_{oth})}{CO_{total}} = \frac{OA_{veh}}{CO_{total}} + \frac{OA_{oth}}{CO_{total}} \quad (6)$$

The contribution of vehicular OA to total OA production in the atmosphere can be determined by the ratio of OA_{veh}/CO_{total} to $(\Delta OA/\Delta CO)_{obs}$. Here, $(\Delta OA/\Delta CO)_{obs}$ is the ratio of observed ΔOA (Obs, OA-OA$_{background}$) to observed ΔCO (Obs, CO-CO$_{background}$) in the unit of

$\mu g \cdot m^{-3} \cdot ppmv^{-1}$. OA_{veh}/CO_{total} is the ratio of vehicular POA emission and SOA formation to total CO emissions, which can be calculated by Eq. (5). ER_{POA} and ER_{VOCj} in Eq. (5) should be substituted by the ratios of vehicular POA and VOC emissions to total CO emissions from vehicle and other sources. The total amount of CO emission was 1.2×10^6 tons according to the annually updated emission inventory in Shanghai for the year of 2012. Iron & steel manufacturing was the major source of CO emission, which accounted for 54% of the total. The sector produced 19.7×10^6 and 18×10^6 tons of pig irons and crude steels, and consumed more than 10×10^6 tons of coal in 2012. Vehicles were the second largest source, accounting for 27.8% of the total. Detailed information is shown in Fig. S5. However, considering the observation site was located in the urban area and most of the large CO emission sources were located at the surrounding areas (about 30-50 km from city center), 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."

2. Specific comments

2.1 Abstract Line 13: The OA emission rate of 15.6 ug/m3/ppm-CO is for primary emissions. I think readers would understand this sentence better if the term "primary emissions" was used instead of "initial emissions."

Re: We agree with the comment. All the sentences with "initial emissions" have been replaced. Please see the following changes.

Changes in manuscript:
(1) Abstract, page 7978, line 12: replace "initial emission" with "primary emission".
(2) Section 3.4, page 7989, line 23: replace "initial emission" with "primary emission".
(3) Section 3.4, page 7991, line 8: replace "initial emission" with "primary emission".
(4) Section 3.5, page 7992, line 17: replace "initial emission" with "primary emission".
(5) Section 3.5, page 7992, line 18: replace "initial emission" with "primary emission".

2.2 Abstract Line 13: It is not clear if the secondary OA production rates are maximum production or SOA production after a set amount of oxidation time.

Re: This is the maximum SOA production. To better understand, we revise it in the manuscript. Please see the following changes.

Changes in manuscript:
(1) Abstract, page 7978, line 13: add "maximum" before "OA production".

2.3 Abstract Line 24: "a large number of OA mass" is grammatically incorrect.

Re: Thanks. Please see the following changes.

Changes in manuscript:
(1) Abstract, page 7978, line 24: replace "a large number" with "a large amount".

2.4 Page 7979, Line 14: Semi-volatile, not semi-volatility. Also, while IVOCs seem to be good SOA precursors, SVOCs do not necessarily generate much new OA mass upon oxidation. Under most atmospheric conditions at least some SVOCs will be in the particle phase. Thus oxidizing the SVOC vapors causes SVOC POA to evaporate, creating a "pumping" mechanism that leads to relatively little mass generation but overall oxidation of the OA.

Re: Thanks for the comments. "Volatility" has been revised in the manuscript. We also agree with the reviewer's comment that IVOCs are more important than SVOCs in SOA production. However, here we directly quote the sentence from Robinson et al.'s article. So we suggest to keep this sentence. In the following sentence, we further point out that IVOCs are more important to SOA.

Changes in manuscript:
(1) Section 1, page 7979, line 14: replace "intermediate-volatility" and "semi-volatility" with "intermediate-volatile" and "semi-volatile".

2.5 Page 7980 Line 13: "The number of vehicles in Shanghai increased to 1.9 times of the number in the last decade" Does this mean that the number of vehicles doubled in the last decade?

Re: Yes. We have revised it in the manuscript. Please see the following changes.

Changes in manuscript:
(1) Section 1, page 7980, lines 13-14: replace "The number of vehicles in Shanghai increased to 1.9 times of the number in the last decade" with "The number of vehicles in Shanghai was doubled in the last decade".

2.6 Page 7982 Line 1: What is the ECE urban cycle? Is the ECE urban cycle a 1-bag test, or were VOC samples only collected from 1 bag of a multi-bag test?

Re: It is a 1-bag test of the ECE urban cycle. We have revised it in the manuscript. Please see the following changes.

Changes in manuscript:
(1) Section 2.1, page 7982, line 1: replace "VOC sample was collected from a 1-bag test of the ECE urban cycle" with "The driving cycle of VMAS contains only 1 bag from ECE urban cycle".

2.7 Page 7982, Line 21: What is the IVE model? The acronym needs to be defined.

Re: IVE is a vehicle emission model developed by University of California, Riverside. It's full name is "International Vehicle Emission" model. The model is widely used to compile vehicle emission inventories in developing countries. We have added the acronym in the manuscript. Please see the following changes.

Changes in manuscript:
(1) Section 2.2.1, page 7982, line 21: add "(International Vehicle Emission)" after "IVE".

2.8 Section 2.1: What range of VOCs were analyzed in the GC system? My general experience with GCs equipped with cryotrap pre-concentrators and sampling from SUMMA canisters is that species in the C2-C12 range can be quantified. However the figures later in the manuscript (Figs 3 and 4) seem to indicate that this method was used to dentify species up to C20. More detail on the pre-concentrator and GC method is required to convince me that C20 species were quantitatively measured with this method.

Re: Sorry. We didn't explain this section clear. As mentioned by the reviewer, only C2-C12 VOCs were analyzed by the GC system in this study. In Fig. 3, VOC compounds only covered C2-C12 in this study. However, in order to evaluate the SOA yields from all known VOC species in vehicle exhausts, we quoted the data of alkanes larger than C12 and polycyclic aromatics from the Schauer et al. (1999, 2002). We rewrite the section 2.1 in the manuscript. Please see the following changes.

Changes in manuscript:
(1) Section 2.1, page 7982, line 11: replace "Concentration of individual VOC in samples was determined by a GC–MS system" with "Concentration of C2-C12 VOCs in samples were determined by a GC–MS system".
(2) Section 2.1: we add Section 2.1.3 "SOA yield estimation". The contents of this section has been describe in the response to No 1.4 General Comment.

2.9 Section 2.2.1: It is not clear how the data from the video camera surveys was merged with the GPS data collected for individual vehicles. Also, Table 1 shows aggregated VKT data for the full Shanghai fleet. Was this determined from the camera survey, the GPS data, or a combination of both?

Re: Vehicle kilometers of travel (VKT), vehicle flow distribution, driving pattern, fleet composition and base emission factor of each vehicle type were 5 key parameters for the development of vehicle emission inventory. VKTs and their weights on 3 road types (including highway, arterial road, and residential road) were surveyed from transportation for the year of 2012. VKTs on each road type were further separated into 7 vehicle types by the use of video camera surveys. The distributions of each vehicle type were surveyed on various road types with video cameras from March to May. About 4000 valid hours were obtained on 15 roads covering 3 road types. Survey days include weekdays and weekends and each day covers 24 h. GPS data were used to determine the driving patterns of various vehicle types. The driving patterns included

the average speeds and VSP (Vehicle Specific Power) distributions used to adjust the emission factors. We installed GPS units on light-duty cars, taxis, buses, and heavy-duty trucks to record the driving speeds and altitudes second by second. VSP of each vehicle and road type can be calculated with Eq. (1) introduced by Jimenez (1999).

$$VSP(kW \cdot t^{-1}) = v \times [1.1a + 9.81 \times (a \cdot \tan(\sin(grade))) + 0.132] + 0.000302 \times v^3 \quad (1)$$

Where, v is vehicle speed (m·s⁻¹). a is vehicle acceleration (m·s⁻²). *grade* is vertical rise/slope length.

For a better explanation of Section 2.2.1, we rewrite it as follows.

Changes in manuscript:

(1) Section 2.2.1 is revised to:

"VKTs and their weights on 3 road types (including highway, arterial road, and residential road) were surveyed from transportation for the year of 2012. VKTs on each road type were further separated into 7 vehicle types by the use of video camera surveys. The distributions of each vehicle type were surveyed on various road types with video cameras from March to May. About 4000 valid hours were obtained on 15 roads covering 3 road types. Survey days included weekdays and weekends and each day covered 24 h. The results show that light-duty vehicles (including light-duty cars, light-duty trucks, and taxis) are the major vehicle types on the road, accounting for 56% of the total flows. Heavy-duty vehicles (including heavy-duty bus, heavy-duty truck, and city bus) comprise 19% of the whole VKTs in Shanghai. GPS data were used to determine the driving patterns of various vehicle types. The driving patterns were determined by the average speeds and VSP (Vehicle Specific Power) distributions. We installed GPS units on light-duty cars, taxis, buses, and heavy-duty trucks to record the driving speeds and altitudes second by second. About 150 hours of valid GPS data were collected in this study. The data covered 2831 km of roads and were composed of 3 road types and 4 vehicle types. VSP of each vehicle and road type can be calculated with Eq. (2) introduced by Jimenez (1999).

$$VSP(kW \cdot t^{-1}) = v \times [1.1a + 9.81 \times (a \cdot \tan(\sin(grade))) + 0.132] + 0.000302 \times v^3 \quad (2)$$

Where, v is vehicle speed (m·s⁻¹). a is vehicle acceleration (m·s⁻²). *grade* is vertical rise/slope length. Table 1 shows the daily VKT and average speeds of various vehicle and road types in 2012.

New reference:

Jimenez, J. L.: Ph. D thesis of Understanding and quantifying motor vehicle emissions with vehicle specific power and TILDAS remote sensing, Massachusetts: Massachusetts Institute of Technology, 1999."

2.10 Section 2.2.2: How were the fleet composition data from the vehicle database used in the inventory? E.g., are they combined with the data from Section 2.2.2?

Re: The fleet composition data were used to separate the VKT of each vehicle type (as shown in Table 1 in Section 2.2.1) into the factions of specific technologies, such as fuel type, engine size,

and emission standard. To better explain the use of fleet composition data, we revise the section as follows.

Changes in manuscript:

(1) Section 2.2.2, page 7983, lines 13-15: replace "Fleet composition data were collected from the vehicle information database of the Vehicle Management Department of Public Security Bureau of Shanghai. Each vehicle type was classified by fuel type, engine size, and emission standard." with "Fleet composition data were used to separate the VKT of each vehicle type (as shown in Table 1) into the fractions of specific technologies, such as fuel type, engine size, and emission standard.".

2.11 Bottom of page 7983 and Fig 1: What are the meanings of the "static" and "adjusted" fleet? How were these determined?

Re: The "static" fleet refers to the fleet compositions directly summarized from the vehicle information database. In the "static" fleet, the fraction of each specific technology was determined by the ratio of its population in the database. However, the fraction of each specific technology should be changed with its occurrence frequency in the real-world. Generally, older vehicles show less occurrence frequency than newer vehicles, which means the annual mileage of older vehicle should be less than the newer one. For this reason, we considered to adjust the fleet compositions according to their real-world annual average mileages. About 30,000 vehicles were surveyed at 4 inspection stations in this study. Vehicle age and odometer reading were recorded for each vehicle. The survey data showed that the annual average mileages of light-duty truck, heavy-duty bus, and heavy-duty truck tended to decrease with the increase of their vehicle ages. The "adjusted" fleet compositions were determined by the multiplication of vehicle populations and their surveyed annual mileages. To better explain the meanings of the "static" and "adjusted" fleet, we revise the section as follows.

Changes in manuscript:

(1) Section 2.2.2, page 7983, lines 15-28: replace "Given that …… adjusted fraction by the vehicle fleet in Shanghai." with "The data were determined by the ratios of the populations of specific technologies in the vehicle information database from the Vehicle Management Department of Public Security Bureau of Shanghai. We call this "static" fleet. Light-duty cars and taxis were mainly composed of gasoline vehicles, which occupied 98% and 97%, respectively. Diesel vehicles dominated in light-duty truck, heavy-duty bus, heavy-duty truck, and city bus, comprising 56%, 91%, 89%, and 98%, respectively. Euro 2 vehicles were the majority of light-duty cars and light-duty trucks, accounting for 51% and 68%, respectively. Heavy-duty buses and trucks were mainly composed of Euro 2 and Euro 3 diesel vehicles, which comprised 40% and 45% of each vehicle type. However, the fraction of each specific technology should be changed with its occurrence frequency in the real-world. Generally, older vehicles show less occurrence frequency than newer vehicles, which means the annual mileage of older vehicle should be less than the newer one. For this reason, we considered to adjust the fleet compositions according to their real-world annual average mileages. About 30 thousand vehicles were surveyed at 4 inspection stations in this study. Vehicle age and

odometer reading were recorded for each vehicle. The survey data showed that the annual average mileages of light-duty truck, heavy-duty bus, and heavy-duty truck tended to decrease with the increase of their vehicle ages. The "adjusted" fleet compositions were determined by the multiplication of vehicle populations and their surveyed annual mileages. Fig. 1 shows the static and adjusted fraction by each vehicle type in Shanghai. It is indicated that the adjusted fractions of the older vehicles with pre-Euro and Euro 1 emission standard for light-duty truck, heavy-duty bus, heavy-duty truck, and city bus were much smaller than those of the static ones. Correspondingly, the adjusted fractions of the newer vehicles with Euro 3 emission standard increased a lot compare with the static ones".

2.12 Page 7984, Lines 1-2: "Vehicle emission factors were calculated with the IVE model and adjusted by the results of real-world emission measurements in major cities of China." What emissions measurements, and in what cities, are the authors referring to? I thought the purpose of testing the vehicles in Table 1 was to build the emissions inventory.

Re: The emission measurements were conducted by different people in different cities of China. The cities included Shanghai, Beijing, Guangzhou, Xi'an, Shenzhen, Jinan, and Yichang. We have listed the references in Page 7984, line 7. All of the measurements were conducted with PEMS (Portable Emission Measurement System) in the real-world. The vehicles were installed with PEMS equipment and tested under a designed route in each city. We quoted the results of the measurements in these studies to adjust the base emission factors in the model. Fig. 2 shows the comparisons of calculated by the model after adjustment and the measurement results. The purpose of testing the vehicles listed in Table 1 was to measure the VOC species but not emission factor. To avoid the misunderstanding, we revised the Section 2.2.3 in the manuscript. Please see the following changes.

Changes in manuscript:

(1) Section 2.2.3 is revised to:

"The emission factors of each vehicle technology were modeled with the IVE model. However, most of the default emission factors in the model are based on the measurements in the US. To localize the emission factors in this study, we collected the published emission factors based on the real-world measurements in the previous studies to adjust the modeled emission factors. The measurements were all conducted with Portable Emission Measurement Systems (PEMS) under designed driving routes in the cities of China. The cities included Shanghai, Beijing, Guangzhou, Xi'an, Shenzhen, Jinan, and Yichang (Chen et al., 2007; Huo et al., 2012a; Huo et al., 2012b; Wu et al., 2012; Huang et al., 2013). Fig. 2 shows the comparisons of the adjusted emission factors with the measured ones. The evaporative emission factors were not adjusted due to the lack of measurement data. Default factors in the model were used to calculate evaporative emissions in this study. It is indicated that the adjusted emission factors of each vehicle type generally fit well with the measured results. The emission factors are reliable to be used to establish the emission inventory. "

2.13 Figure 2: Were the same vehicles tested in this study and the previous studies? The organization of the bars (current study) and data points from previous studies give the

impression that the same vehicles were tested multiple times.

Re: Thanks for the comment. We didn't measure the emission factors in this study. We just used the measured emission factors in the previous studies (the data points in Fig. 2) to adjust the default emission factors in the model. The bars indicate the calculated emission factors with the IVE model. The points are measured emission factors in the previous studies. The purpose of this figure is to prove that the calculated emission factors are reliable. To avoid the misunderstanding, we revised the legends of the figure as follows.

Changes in manuscript:
(1) Section 2.2.3, Fig. 2: the legends in the figure are revised as follows.
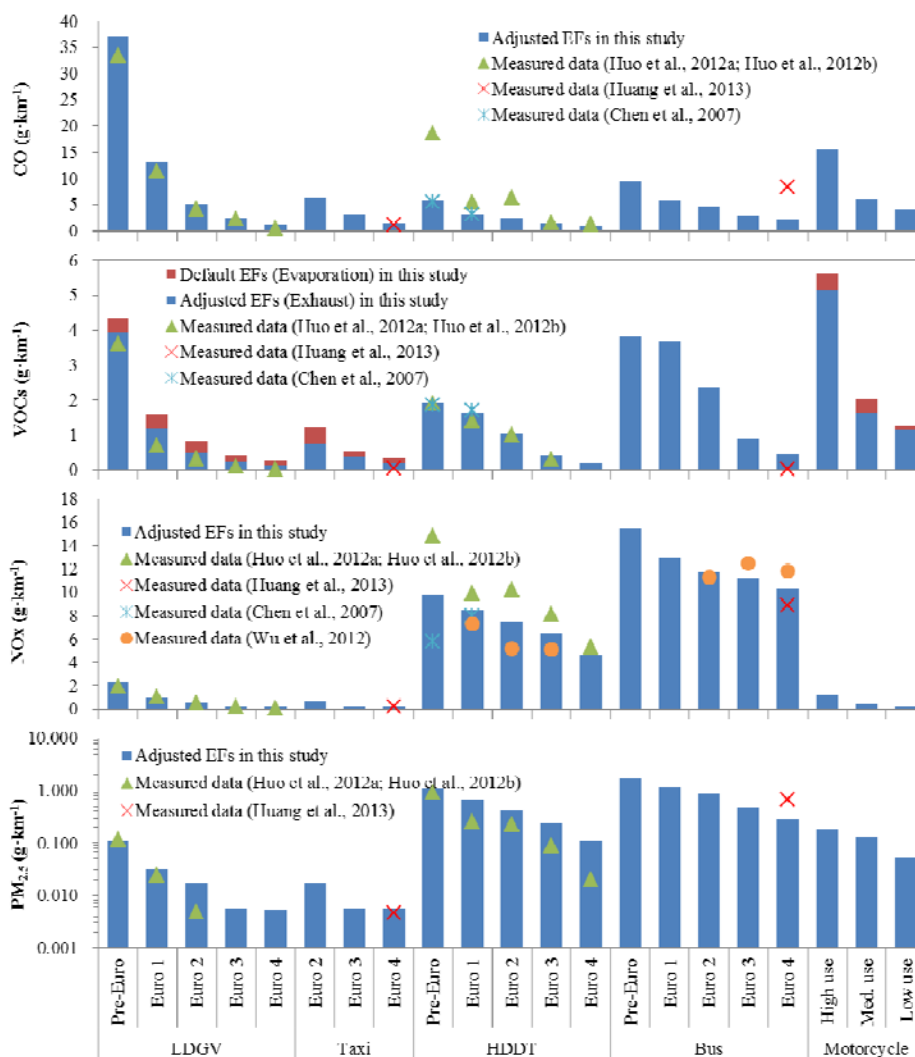
Fig. 2. Adjusted emission factors of various vehicle types (blue bars) and their comparisons with measured emission factors in the previous studies (dots).

2.14 Page 7984, Lines 12-13: "Limited number of measurements made it difficult to verify the accuracies of the emission factors." Which accuracies are the authors referring to? The previous data or their own? They should have a good idea of the accuracy of the measurements and methods used in each test. Perhaps if every vehicle was tested only once there would be

uncertainty about test-to-test variability (precision), but this is a separate issue than accuracy.

Re: Thanks for the comment. We delete the sentence in the revised manuscript.

2.15 Figure 3: Why do so many bars go above 100%?

Re: The VOC species measured in different studies are not the same. For example, we only measured C2-C12 PAMS species in this study, but carbonyls or semi-volatile organic compounds were also measured in other studies (Schauer et al., 1999; Schauer et al., 2002; May et al., 2014). The ratios cannot be compared if we consider all measured species as 100%. However, all studies have measured C2-C12 alkanes, alkenes, alkynes, and single-ring aromatics. So we normalized the concentrations of these compounds in each study as 100%. The ratios of other compounds were determined by their relative concentrations to the C2-C12 compounds. To avoid the misunderstanding, we remove the other compounds from Fig. 3. Please check the following changes.

Changes in manuscript:
(1) Section 3.1, page 7985, lines 6-9: replace "To compare the VOC compositions of the exhausts from different types of vehicles, we selected their common species such as C2–C12 alkanes, alkenes, alkynes, and single-ring aromatics, and normalized the concentrations of carbon." With "Since the VOC species measured in different studies are not the same, we normalized the concentrations of the common species including C2-C12 alkanes, alkenes, alkynes, and single-ring aromatics in each study as 100%. Other compounds and unidentified VOCs were excluded in the comparison. "
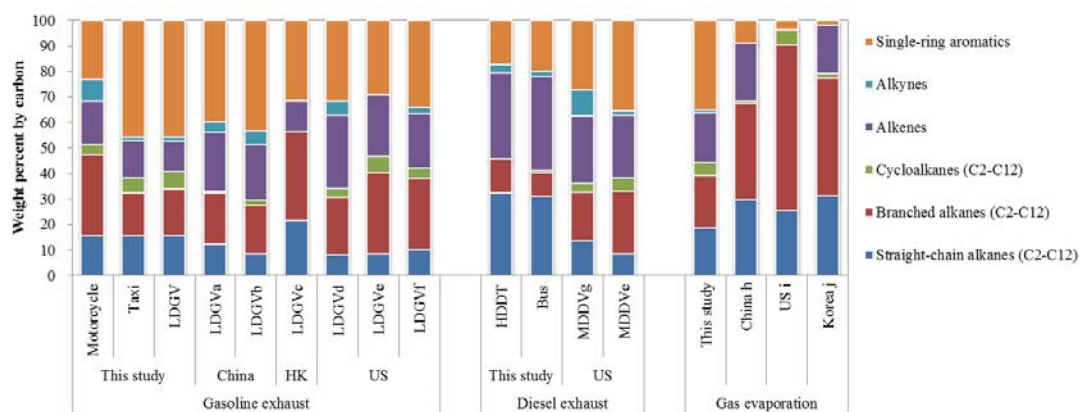

Fig. 4. Comparisons of measured VOC compositions of the exhausts from different vehicle types and gas evaporation to the results in other studies (a. Liu et al., 2008; b. Wang et al., 2013; c. Guo et al., 2011; d. Schauer et al., 2002; e. May et al., 2014; f. Gentner et al., 2013; g. Schauer et al., 1999; h. Zhang et al., 2013; i. Harley et al., 2000; j. Na et al., 2004).

2.16 Page 7986, Lines 5-10: Make sure this is an apples-to-apples comparison for the diesel vehicles. Were the same methods used? In both May and Schauer there was a significant amount of unidentified VOC mass - e.g., the sum of spectated VOCs did not match the total carbon from an FID. How was that handled here?

15

Re: Thanks for the comments. As mentioned in 2.14, we compared the identified species of C2–C12 alkanes, alkenes, alkynes, and single-ring aromatics in Fig. 3. Unidentified VOC mass were excluded in the comparison. The ratio of VOC species in Fig. 3 were determined by the relative concentration of one species to the total identified C2-C12 species. In the revised manuscript, we have added some description to this point. The unidentified species accounted for 25%, 60%, and 50% in gasoline, diesel, and motorcycle exhausts, repectively. We have stated in the new section of 2.2.3. Please check it in the response to General comment of No. 1.5. In the original text, we combined the amounts of alkanes larger than C12 and polycyclic aromatics from Schauer et al. (1999, 2002) into the unidentified species. However, the amounts were still not enough to represent for the IVOCs. The weight percent of VOC species larger than C12 showed steep fall in diesel exhaust. So we replace the data with IVOCs in unburned fuels from Gentner et al. (2012) according to the suggestion by another reviewer. The SOA yields of measured and combined VOC species were both calculated to compare the differences with or without IVOCs. Please check the following changes.

Changes in manuscript:

(1) Section 3.1, page 7985, line 11: add "Unidentified VOC mass were excluded in the comparison." at the end of the paragraph.

(2) We add a new section of 2.2.3 to explain the method of calculating the SOA yield. There we mentioned how we handled the unidentified VOC mass in SOA yield estimation. Please check the response to the general comment of No. 1.5.

(3) Section 3.2, the 1st paragraph: replace with

"VOC species of vehicle emissions and gas evaporation were classified into 5 categories by their chemical classes, and their distributions of carbon numbers were shown in Fig. 5(a). Previous studies have confirmed that IVOCs, which were not detected in this study, played important roles to SOA production (Jathar et al., 2013; Zhao et al., 2014). 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. The carbon numbers of VOCs in gasoline and motorcycle exhausts mainly concentrated in the intervals between C6 to C9 whether the IVOCs were merged or not. Comparatively, exhausts from diesel vehicles had a wider distribution of carbon number, ranging from C2 to C25. More than half of the species were S/IVOCs and most of them were alkanes. The carbon numbers of VOCs in gas evaporation were mainly distributed within the range of C3-C7, which were much smaller than those in vehicle exhausts."
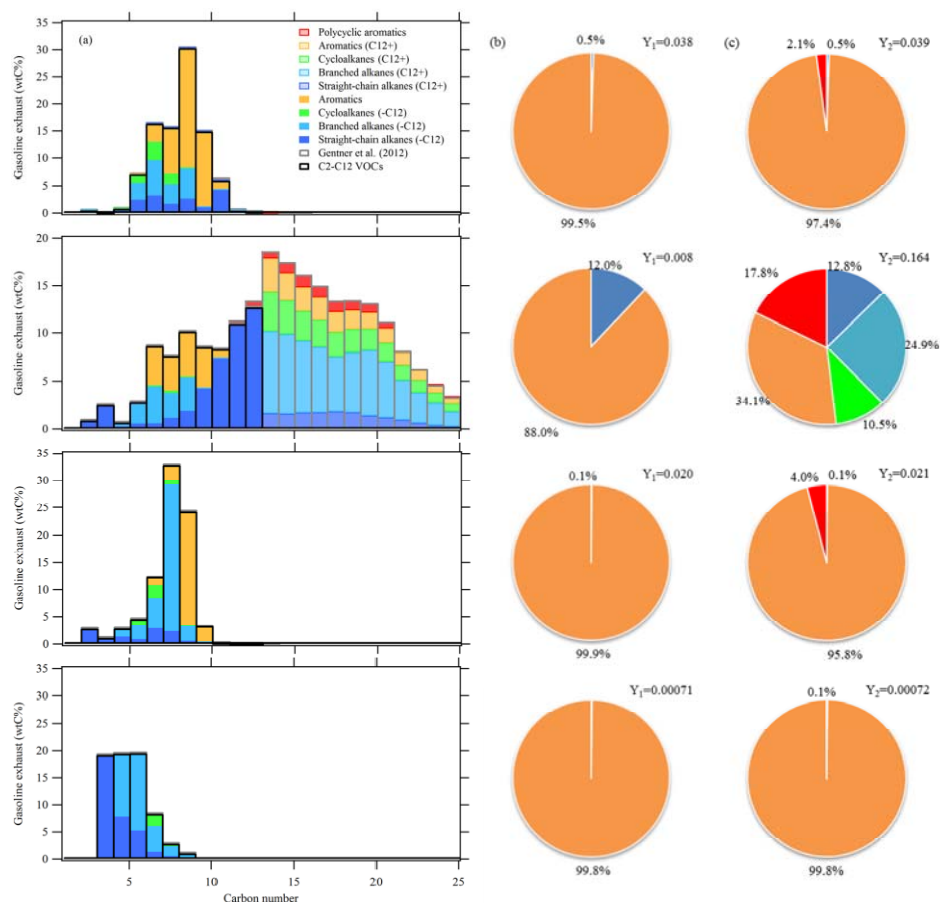
(4) Fig. 4: replace to

Fig. 5. (a) Distribution 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 and their contributors; (c) Calculated SOA yields based on C2-C25 VOCs combined with S/IVOC species in unburned fuel referenced from Gentner et al. (2012) and their contributors."

(5) Section 3.2, the 2nd paragraph: replace with

"Fig. 5(b) and (c) show the SOA mass yields and the contributions of different chemical class calculate by measured and combined species, respectively. S/IVOC species had no effect on the SOA yields of gasoline exhausts and evaporative emissions. Aromatics dominated the yields which accounted for almost 100% of the total. However, the SOA yield of diesel exhaust was significantly affected by S/IVOCs. The yield increased from 0.008 to 0.164 as S/IVOCs were considered. Aromatics were still the largest contributors (34.1%) to but not dominating the yield. Next were branched alkanes, polycyclic aromatics, and straight-chain alkanes, which accounted for 24.9%, 17.8%, and 12.8%."

2.17 Page 7987, comparison to Gordon et al - the best comparison would be to map the Euro standards to the closest LEV standard, since SOA yields were higher for newer vehicles in Gordon et al. Line 1 page 7988 - Gordon's off-road engines had no catalytic converter. Do the motorcycles tested here have one or similar pollution control?

Re: Thanks for the comments. LEV-1 standard was closest to Euro 1-3 standards which were tested in this study. So we compared the SOA yield of gasoline exhaust with the experiment

results from LEV-1 vehicles. The motorcycles have no catalytic converter either. We have added a statement on that in the revised manuscript. To clearly describe the technologies of tested vehicles, we added some descriptions in "Materials and methods" section. Please check the following changes.

Changes in manuscript:

(1) Section 2.1, page 7981, lines 19-20: replace "All MTs were 4-stroke with 125 cc 20 displacement." With "All MTs were 4-stroke with 125 cc displacement and without catalytic converter or any other pollution control device. All gasoline vehicles were equipped with catalytic converters. Diesel vehicles didn't install any aftertreatment device like DPF (Diesel Particle Filter)."

(2) Section 3.2, the 3rd paragraph: replace with

   "The SOA yield of gasoline exhaust was larger than the yield of liquid gasoline reported by Gentner et al. (2012). We found the aromatic contents in gasoline exhausts of this study which dominated the SOA yield were much higher than those in the reference. This may be due to the loose limit of aromatics for the gasoline fuel in China. However, the estimated yield of gasoline exhaust was much smaller than the effective yields (3-30%) of LEV-1 (tier 1 of low emission vehicle standard in California, US) gasoline vehicles (similar to Euro 1-3 LDGVs tested in this study) investigated using a smog-chamber experiment by Gordon et al. (2014a). The reason for the underestimate was still unclear. In contrast, the estimated SOA yield of diesel exhaust which combined S/IVOCs (Y2) was higher than the average effective yields (9±6%) for HDDVs without DPF based on smog-chamber experiments by Gordon et al. (2014b). Since there were few experiments on motorcycle exhaust, we compared the SOA yield of motorcycle exhaust with the experiment results from the exhausts of 2- and 4-stroke gasoline off-road engines (Gordon et al., 2013). Neither motorcycles nor off-road engines had catalytic converter. The estimated yield was close to the experiment results of off-road engine exhausts (2-4%)."

2.18 Section 3.3: The emissions inventory is developed from which data, specifically? Emission rates presented in this manuscript and the vehicle survey? Or were previous vehicle measurements also included?

Re: The data of vehicle kilometers of travel (VKT), vehicle flow distribution, driving pattern, fleet composition and emission factor of each vehicle type were all needed to develop the vehicle emission inventory. Previous vehicle measurements were used to adjust the default emission factors in the model. To more clearly illustrate the methodologies of vehicle emission inventory compilation in this study, we have revised Section 2.2 and made a supplement of Section 2.2.1 "Methodology of emission inventory compilation" at the beginning of Section 2.2.

Changes in manuscript:

(1) Please see the response to No. 1.5 general comment.

2.19 Section 3.3: How were evaporative emissions calculated? And how are the evaporative emissions assigned to specific vehicle classes?

Re: Evaporative emissions are calculated with the same method of exhaust emissions, which is multiplying VKT of each vehicle technology with its emission factor in simple terms. Each specific vehicle technology has an evaporative emission factor as shown in Fig. 2. However, we didn't adjust the default factors of evaporative emissions due to the lack of measurement data. A description of evaporative emission calculation was added in the response to No. 1.5 general comment. In the response to No. 2.12 specific comment, we made a supplement about how we got the evaporative emission factors of different vehicle types

2.20 I do not understand what the audience is supposed to learn from Fig 6. First, the red line is undefined (I assume it is the mean diurnal profile). Second, what is the difference between "Initial" and "Vehicular" X/E? It seems that the "Initial" X/E is supposed to account for all sources, and therefore varies seasonally. It is not clear whether initial or vehicular X/E is used to determine the photochemical clock from equation 1.

Re: Thanks for the comment. We used Fig. 6 to introduce the potential of photochemical reaction in summer and winter of Shanghai. The red line is the mean diurnal profile. We have added the legends in Fig. 6. We used "Initial" X/E to characterize the primary emission ratio of m,p-xylene to ethylbenzene before photooxidation. The "Initial" X/E considered all emission sources in the atmosphere. Taking the statistical significance of the observation data into account, we used the X/E ratio on 97.5 percentiles in this study. Vehicular X/E was the calculated value based on the emission inventory. Our original thought was to evaluate whether vehicle emissions dominated the primary emission ratios in the atmosphere. We used initial X/E to determine the photochemical clock. To avoid the misunderstanding, we removed the vehicular X/E in Fig. 6 in the revised manuscript. Since the major purpose of these contents is to introduce the method of calculating photochemical age, we moved them into Section 2 "Materials and methods".

Changes in manuscript:
(1) Please check the changes in the response to No. 1.6 General comment.

2.21 Figure 7: (1) The color bar should have units on it. (2) The text states that the inventory POA/CO line is pink. It is orange.
2.22 Page 7991, Lines 8-9: What is meant by the "initial" POA/CO ratio (4.84 ug/m3/ppm-CO)? How is this determined? In Figure 7 this seems to be labeled as Vehicular POA, but it is not clear that this is Vehicular POA. Also the slope in Fig 7 is 4.3, not 4.84.
2.23 Page 7991, Line 10: Vehicles only account for 25% of CO emissions? This seems very low. What are the other sources?

Re: Thanks for the comment. We think these 3 comments above are talking about the same problems in Section 3.4. First is how we determine the "initial" vehicular POA/CO ratio. The vehicular POA/CO is the ratio of POA emission from vehicles to total CO emission in Shanghai. Vehicular POA emission is 4.3 k tons and total CO emission in Shanghai is 1263 k tons. Vehicular POA/CO should be 4.3 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ based on the emission inventory (Sorry, 4.84 is a mistake). Vehicles account for 27.8% of CO emissions. The major source of CO emission is the industrial

process of iron & steel production, accounting for 54% of the total. The iron & steel industry produced 19.7×10^6 and 18×10^6 tons of pig irons and crude steels, and consumed more than 10×10^6 tons of coal in 2012. Vehicles were the second largest source, accounting for 27.8% of the total. Detailed information is shown in Fig. S5. Considering the observation site was located in the urban area, it would be more reasonable to use the emissions of the urban area to evaluate the OA production. For this reason, we extracted the emissions based on their spatial distributions. CO and POA emissions from vehicles in the urban area were 170 k tons and 1.85 k tons, respectively. Vehicles dominated CO emission in the urban area of Shanghai, which accounted for 85% of the total. According to the emissions in the urban area, the vehicular POA/total CO was 11.6 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$. So we changed the lines in Fig. 7. Maximum vehicular OA/total CO (Vehicular POA/total CO * yield) were calculated based on two yields. One yield was calculated based on the VOC species combined S/IVOCs as shown in the response of 2.16. For the other, we changed the yield of gasoline exhaust based on the results published by Gordon et al. (2014a). We replaced these two lines with the others. Data of observed OA concentrations were also changed in Fig. 7 because the ration of OA/OC (1.6) what we used in original manuscript was not very reasonable in the urban area. We changed it to 1.4. In addition, we removed about 10 highest points seem like outliers from the summer data in Fig. 7(a) as suggested by another reviewer. All observed OA concentrations were changed in Fig. 7. Then we added two lines in the figure. One is the minimum ratio of observed OA to CO concentrations, which were 12 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ both in summer and winter. The other is the maximum ratio of observed OA to CO concentrations, about 50 and 35 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in summer and winter, respectively. We also added the units on the color bar and modified the wrong description in the text. Please see the following changes.

Changes in manuscript:

(1) To better explain the methodologies of OA production estimation, we added Section 2.3.3 in "Materials and methods" section. The comments on 2.23 have been replied in the response to General comment No. 1.5 (6). Please see the detail responses in that section.

(2) Section 3.4, the last paragraph: replace the whole contents with "Fig. 7 is a scatterplot of OA versus CO concentrations measured in urban Shanghai in the summer and the winter of 2013. The observation data were color-coded by OH exposure ($\Delta t \cdot [OH]$) determined by equation (4). It was indicated from the figure that the ratios of OA to CO concentrations generally showed growing trends with the increase of OH exposure both in summer and winter. The results were similar to the previous studies in the United States, Japan, and Mexico (Bahreini et al., 2012; de Gouw et al., 2008; Takegawa et al., 2006; DeCarlo et al., 2008). The primary emission ratios of POA to CO were determined by the minimum slopes of the observed OA to CO concentrations, about 12 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in both summer and winter (as shown by the dotted grey lines). The maximum slopes of OA to CO were 50 and 35 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ (as shown by the dotted black lines) in summer and winter, respectively. The SOA formation ratio in summer was much higher than in winter. The inventory-based vehicular POA emission to total CO emission was 11.6 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in the urban area of Shanghai (shown by the dotted yellow lines), almost the same with primary emission ratio observed in the atmosphere, which indicated that vehicles dominated the POA emissions in urban Shanghai. 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 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$. It was considerable underestimated compared with the observation data, which implied that the SOA yields derived by known and estimated species were still far from explaining the actual SOA formation rate in the atmosphere. For this reason, we introduced the measured SOA yield of gasoline exhaust (~0.190) from Gordon et al. (2014a) to substitute the yield for gasoline vehicles (0,039) in Y2 scenario and defined the new group as Y3 scenario. The maximum OA production ratio (shown by the dotted red lines) increased to 27.3 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$, but still failed to reach the max. observed $\Delta OA/\Delta CO$. There must be other emission sources of SOA precursors in the atmosphere of Shanghai. Previous studies have revealed that VOC emissions from solvent usage, chemical and petrochemical industrial, and coal burning, etc. comprised more than 70% of the observed VOCs in the atmosphere of urban Shanghai (Cai et al., 2010; Wang et al., 2013). The SOA productions of VOC emissions from these sources also cannot be ignored.
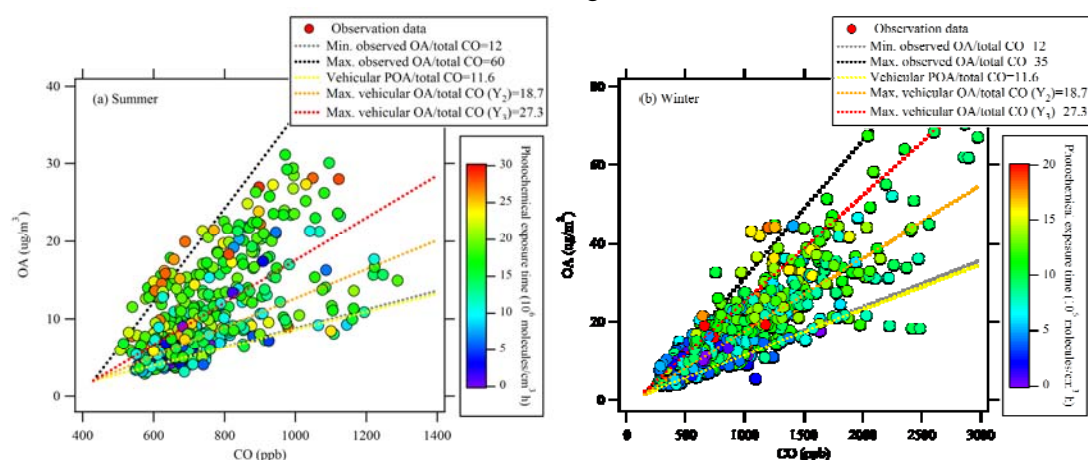

Fig. 6. Relationship of measured OA and CO concentrations color-coded by the photochemical exposure in the summer (a) and winter (b) of 2013 in urban Shanghai according to equation (4). Minimum and maximum ratios of observed OA to CO concentrations are shown by dotted grey and black lines. Vehicular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

2.24 Fig 8: Why are OA/CO from vehicles so low? Other tables/figs (e.g., Figure 5) show that SOA/CO is between 15.6 and 42.7 ug/m3/ppm-CO, but in this figure it is below 10. I don't understand how this figure relates to previous figures.

Re: In Fig. 8, we used the total CO emissions (including the emissions from vehicles, power plants, boilers, industrial processes, etc.) in the whole city of Shanghai to calculate the vehicular OA/CO. The total CO emission was so large that the vehicular OA/CO seemed low. In Fig. 5, CO emission only from vehicles (27.8% of the total CO emission) was used to calculate the OA/CO. In addition, complete photochemical reaction and no loss term were not considered. That's why the vehicular OA/CO was much higher in Fig. 5 than in Fig. 8. However, to avoid the misunderstanding, we remove Fig. 5 and switch the total emissions in Shanghai to the emissions in urban area to estimate the vehicular OA/total CO. In addition, to compare the difference between two different SOA yields in Y2 and Y3 scenario, we added two figures in Y3 scenario.

The vehicular OA/total CO increased a lot after the switch. Besides of the figure, we also revised the contents in Section 3.5. Please check the following changes.

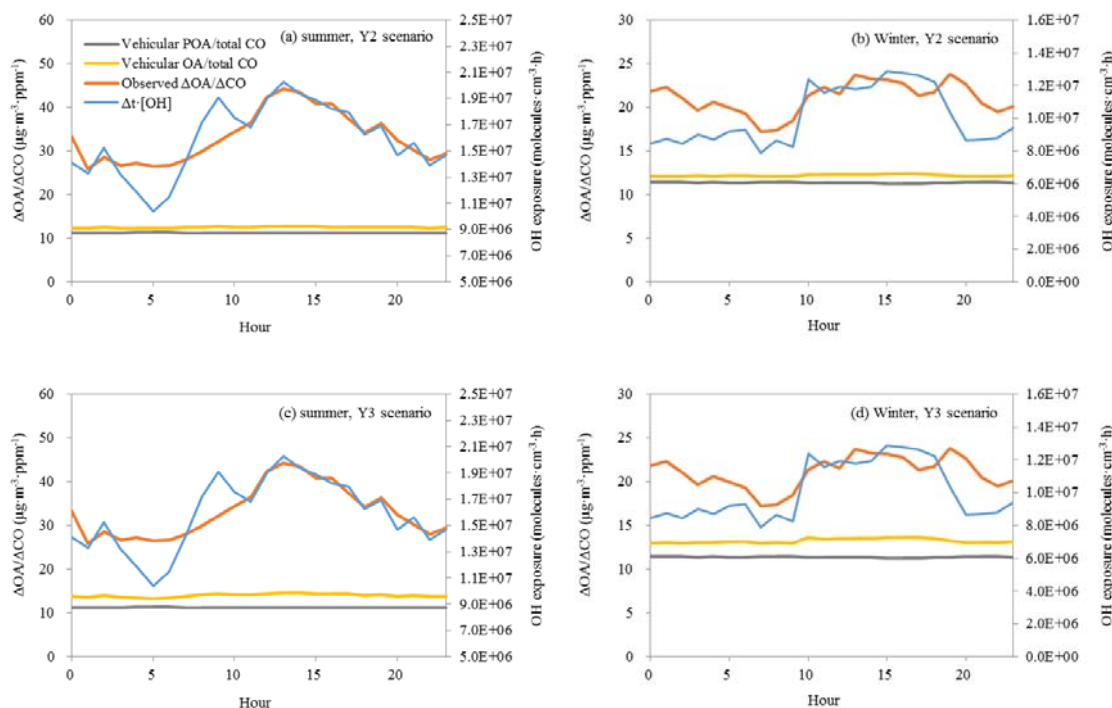**Changes in manuscript:**

(1) Fig. 8: replace with "

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 two scenarios (Y2 and Y3) in summer and winter in the urban area of Shanghai for the year of 2013."

(2) Section 3.5, the 1st paragraph: replace the whole paragraph with

"Fig. 7 shows the diurnal variations of average observed ΔOA/ΔCO and OH exposure in summer and winter. There was a strong correlation between the observed ΔOA/ΔCO and OH exposure, which indicated the photooxidation dominated the SOA formation in the atmosphere. In the role of photochemical reaction, the observed ΔOA/ΔCO showed rapid growth trend in the afternoon in summer and reached a peak around 13:00~14:00. The average observed ΔOA/ΔCO in urban atmosphere of Shanghai were 33.2 and 21.1µg·m^{-3}·ppmv^{-1} in summer and winter, respectively."

(3) Section 3.5, the last two paragraphs: replace the whole contents 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 two scenarios. Fig. 7(a) and (b) show the results in Y2 scenario. The SOA yields of gasoline, diesel, and motorcycle exhausts and gas evaporation were 0.039, 0.164, 0.021, and 0.0007, respectively. Fig. 7(c) and (d) show the results in Y3 scenario. The SOA yield of gasoline exhaust was replaced to 0.190 based on the experiment results (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·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 12.5 µg·m^{-3}·ppmv^{-1} and 12.2 µg·m^{-3}·ppmv^{-1} in summer and winter in Y2 scenario, and 14.0 µg·m^{-3}·ppmv^{-1} and 13.2 µg·m^{-3}·ppmv^{-1} in Y3 scenario. The vehicular OA mass accounted for 39% and 58% of the average observed OA in summer and winter in the urban atmosphere of Shanghai in Y2 scenario. The contributions would increase to 43% and 63% in Y3 scenario. It was indicated that vehicle emission was the major source of OA mass in the urban atmosphere of Shanghai. Enhancing the SOA yield of gasoline exhaust increased about 4%-5% of their contributions to OA, which implied gasoline exhaust didn't dominate the OA mass in the urban atmosphere. Vehicular SOA formation ratios accounted for 7%-10% of the total vehicular OA in Y2 scenario and 14%-20% in Y3 scenario. The SOA formation ratios in both scenarios were lower than expected. There must be other emission sources with high SOA formation potentials in addition to vehicles in the urban atmosphere. 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 S/IVOC species reported in Gentner et al. (2012). The SOA formation potentials of the identified VOC species may contribute more SOA than expected.

At present, few SOA observations in the cities of China can be referenced to verify the results in this study. Huang et al. (2014) has reported the fossil OA dominated the OA mass (~40%) in Shanghai based on the observation data in the first quarter of 2013, which was slightly lower than our result. The possible reason for the difference could be the location of observation site (close to urban or suburban). However, the studies both indicated that vehicle emission was the major source of OA mass in large cities of China."

2.25 Figure 9: Does this figure only include tailpipe emissions or are evaporative emissions also included?

Re: Yes. The evaporative emissions are included in emissions of the corresponding vehicle types in Fig. 9. Since the SOA yields and Primary emission ratio of vehicular POA to CO have been changed, we make some revisions in Fig. 9 and the contents in Section 3.6. Please check the following changes.

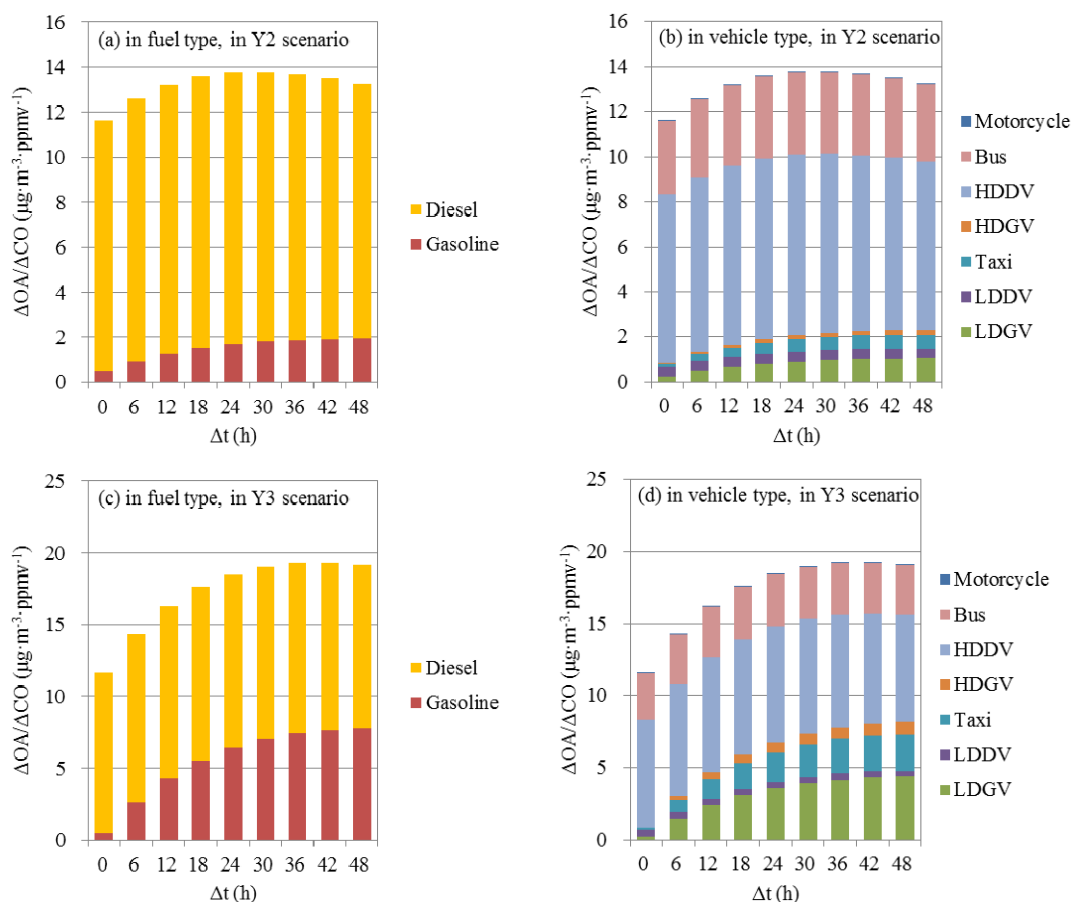**Changes in manuscript:**
(1) Fig. 9: replace with "

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

(2) Section 3.6, page 7993, line 14: replace "contribution" with "contributions".

(3) Section 3.6: replace the whole paragraph to

"Fig. 9 shows the changes of OA formation ratios of vehicle emissions in different vehicle types (see Fig. 9(a)) and fuel types (see Fig. 9(b)) with the increase of the photochemical age. The OA formation ratios were calculated under low NOx condition for each vehicle types with Eq. (6). The OA produced from evaporative emissions were combined in the corresponding vehicle types. The vehicular $\Delta OA/\Delta CO$ ratio shows a rapid growth trend with the photochemical ages in the first 30 hours and then stabilized, which implies that there will be more SOA contributions in downwind area of urban. Gasoline vehicles (including LDGV, taxi, HDGV, and motorcycle) showed a much higher growth rate of $\Delta OA/\Delta CO$ ratios than diesel vehicles (including LDDV, HDDV, and bus). The POA emission of gasoline vehicles only accounted for 4%. Their contributions increased to 21% after 6 hours and 39% after 24 hours of photochemical aging. HDDV, LDGV, and bus were major contributors of vehicular OA formation, accounting for 40%, 21% and 19% of the total in the scenario of 24-hour photochemical aging. The results indicate that diesel vehicles, which account for less than 20% of VKT, contribute more than 60% of vehicular OA in Shanghai. In addition, even though gasoline vehicles contribute less POA emissions, their SOA contributions are also considerable. At present, primary PM emission control of diesel vehicles is the key point of vehicle pollution control in China. What we suggest via this study is to pay more attention on

the SOA precursors from gasoline and diesel vehicles."

Other changes in manuscript:

(1) Abstract: based on the changes in the main text, we rewrite this section as follows.

"VOC species from vehicle exhaust and gas evaporation were investigated by chassis dynamometer and on-road measurements of 9 gasoline vehicles, 7 diesel vehicles, 5 motorcycles, and 4 gas evaporation samples. The SOA mass yields of gasoline, diesel, motorcycle exhausts, and gas evaporation were estimated based on the mixing ratio of measured C2-C12 VOC species and references IVOC species. High aromatic contents were measured in gasoline exhaust and contributed more SOA yield comparatively. A vehicular emission inventory was compiled based on a local survey of on-road traffic in Shanghai and real-world measurements of vehicle emission factors from previous studies in the cities of China. The inventory-based vehicular OA productions to total CO emissions were compared with the observed $\Delta OA/\Delta CO$ in the urban atmosphere. The results indicate that vehicles dominate the POA emissions and OA productions, which contributed about 40% and 60% of OA mass in the urban atmosphere of Shanghai. Diesel vehicles, which accounted for less than 20% of VKT, contribute more than 90% of vehicular POA emissions and 80%-90% of OA mass derived by vehicles in urban Shanghai. Gasoline exhaust could be an important source of SOA formation. Tightening the limit of aromatic content in gasoline fuel will be helpful to reduce its SOA contribution. IVOCs in vehicle exhausts have great contributions to SOA formation in the urban atmosphere of China. However, more experiments need to be conducted to determine the contributions of IVOCs to OA pollution in China."

C1772: 'Reviewer's comments', Anonymous Referee #2, 21 April 2015

1. Major comments

1.1 It is not clear what is the carbon number range considered by the authors for SOA formation calculation. In Figs. 3 and 4, there appears to VOC species measured at C13-C20 for diesel exhaust. However, the authors stated repeatedly in the manuscript that IVOCs are not considered. Does that mean that the alkanes above C12 were measured but not considered quantitative enough for SOA calculation? If so, I suggest removing them from Fig. 3 and 4 because they are misleading and gives the wrong impression.

1.2 If IVOCs were not considered, I suggest that the authors do a sensitivity analysis: make a best estimate of amounts of different IVOCs based on literature (e.g. can refer to Gentner et al., 2013 for approximate ratios of IVOCs to total VOCs < C12), and vary that by one order of magnitude, and see how that affects the final SOA contribution. That would allow readers to assess whether missing S/IVOCs is more important or other non-vehicular sources are more important, and would guide future research.

1.3 If the authors did indeed include IVOCs in their calculations, I would raise serious doubts about how quantitative the measurements are, because there seems to be a sharp drop off after C12 (Fig. 4) and the Entech system is likely designed for VOCs < C12. In general, the lack of discussion regarding IVOCs (comments 1 through 3) is a major weakness in the manuscript and it is important that the authors address this issue.

Re: Thanks for the comments. Since the comments 1.1-1.3 mentioned the same problems on the determination of VOC and IVOC species. We would like to give the response together. We only detected the C2-C12 alkanes, alkenes, alkynes, and single-ring aromatics. S/IVOCs were not detected in this study. Considering S/IVOCs play important roles to SOA yields, we merged the measurement data of alkanes larger than C12 and polycyclic aromatics from Schauer et al. (1999, 2002) into our measurement results. However, IVOCs were not included yet. That's why the weight percent of VOCs larger than C12 from diesel exhaust show a sharp drop off. In Fig. 3, we compared C2-C12 VOCs from various studies in the same scale. To avoid the misunderstanding, we have removed the species other than C2-C12 alkanes, alkenes, alkynes, and single-ring aromatics. As suggested by the reviewer, we combine the amounts of S/IVOCs from Gentner et al. (2012) in Fig. 4 to compare the SOA yields with or without S/IVOCs. The SOA yield of diesel exhaust increased significantly. In the revised manuscript, we replace Fig. 4 (which was Fig. 5 in the revised manuscript) and related contents in Section 3.2 (Section 3.3 in the revised manuscript). In the revised figure, we excluded the contents of alkenes since they were not SOA-precursors. Please check the following changes.

Changes in manuscript:

(3) Section 3.1, page 7985, lines 6-9: replace "To compare the VOC compositions of the exhausts from different types of vehicles, we selected their common species such as C2–C12 alkanes, alkenes, alkynes, and single-ring aromatics, and normalized the concentrations of carbon." With "Since the VOC species measured in different studies are not the same, we normalized the concentrations of the common species including C2-C12 alkanes, alkenes, alkynes, and

single-ring aromatics in each study as 100%. Other compounds and unidentified VOCs were excluded in the comparison. "
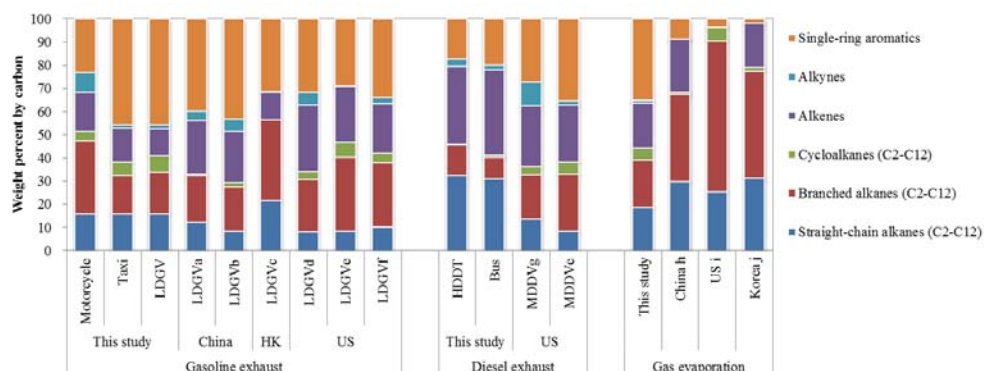

Fig. 4. Comparisons of measured VOC compositions of the exhausts from different vehicle types and gas evaporation to the results in other studies (a. Liu et al., 2008; b. Wang et al., 2013; c. Guo et al., 2011; d. Schauer et al., 2002; e. May et al., 2014; f. Gentner et al., 2013; g. Schauer et al., 1999; h. Zhang et al., 2013; i. Harley et al., 2000; j. Na et al., 2004).
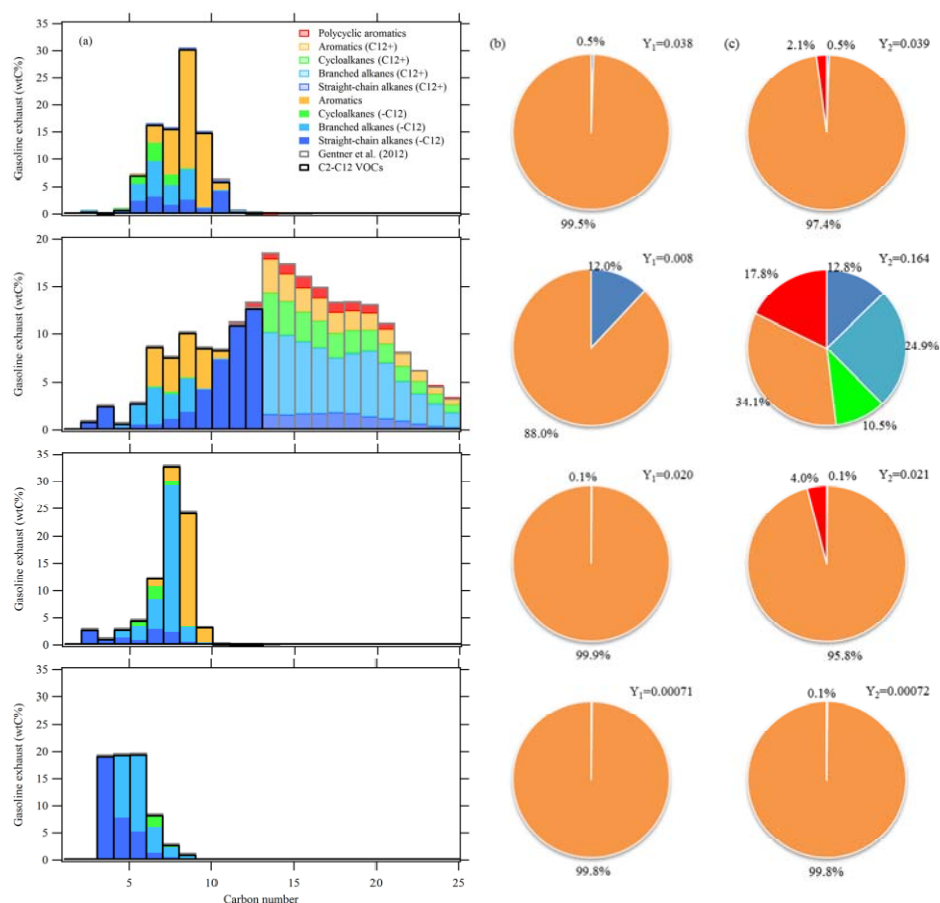
(4) Fig. 4: replace to

Fig. 5. (a) Distribution 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 and their contributors; (c) Calculated SOA yields based on C2-C25 VOCs combined with S/IVOC species in unburned fuel referenced from Gentner et al. (2012)

and their contributors."

(5) Section 3.2, the 1st paragraph: replace with

"VOC species of vehicle emissions and gas evaporation were classified into 5 categories by their chemical classes, and their distributions of carbon numbers were shown in Fig. 5(a). Previous studies have confirmed that IVOCs, which were not detected in this study, played important roles to SOA production (Jathar et al., 2013; Zhao et al., 2014). 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 (Y1) or without S/IVOCs (Y2) in Fig. 5. The carbon numbers of VOCs in gasoline and motorcycle exhausts mainly concentrated in the intervals between C6 to C9 whether the IVOCs were merged or not. Comparatively, exhausts from diesel vehicles had a wider distribution of carbon number, ranging from C2 to C25. More than half of the species were S/IVOCs and most of them were alkanes. The carbon numbers of VOCs in gas evaporation were mainly distributed within the range of C3-C7, which were much smaller than those in vehicle exhausts."

(6) Section 3.2, the 2nd paragraph: replace with

"Fig. 5(b) and (c) show the SOA mass yields and the contributions of different chemical class calculate by measured and combined species, respectively. S/IVOC species had no effect on the SOA yields of gasoline exhausts and evaporative emissions. Aromatics dominated the yields which accounted for almost 100% of the total. However, the SOA yield of diesel exhaust was significantly affected by S/IVOCs. The yield increased from 0.008 to 0.164 as S/IVOCs were considered. Aromatics were still the largest contributors (34.1%) to but not dominating the yield. Next were branched alkanes, polycyclic aromatics, and straight-chain alkanes, which accounted for 24.9%, 17.8%, and 12.8%."

(7) Section 3.2, the 3rd paragraph: replace with

"The SOA yield of gasoline exhaust was larger than the yield of liquid gasoline reported by Gentner et al. (2012). We found the aromatic contents in gasoline exhausts of this study which dominated the SOA yield were much higher than those in the reference. This may be due to the loose limit of aromatics for the gasoline fuel in China. However, the estimated yield of gasoline exhaust was much smaller than the effective yields (3-30%) of LEV-1 gasoline vehicles (similar to Euro 1-3 LDGVs tested in this study) investigated using a smog-chamber experiment by Gordon et al. (2014a). The reason for the underestimate was still unclear. In contrast, the estimated SOA yield of diesel exhaust which combined S/IVOCs (Y2) was higher than the average effective yields (9±6%) for HDDVs without DPF based on smog-chamber experiments by Gordon et al. (2014b). Since there were few experiments on motorcycle exhaust, we compared the SOA yield of motorcycle exhaust with the experiment results from the exhausts of 2- and 4-stroke gasoline off-road engines (Gordon et al., 2013). Neither motorcycles nor off-road engines had catalytic converter. The estimated yield was close to the experiment results of off-road engine exhausts (2-4%)."

1.4 Also, it is not clear how the CO-based emission factor is used. The authors noted that vehicles accounted for 27.8% of the total CO emissions. Did the authors take this into account when looking at OA/CO in Fig. 7? The OA production rate of 22.3 ug m-3 ppmv-1 (high NOx,

see below about high/low NOx) is OA production per unit of *vehicular* CO, not total CO. In the analysis summarized by Fig. 7, one should use a production rate of 22.3 ug m-3 / 0.278ppmv CO, i.e. 80 ug m-3 ppmv-1. If so, the conclusions may change significantly because it would seem like vehicles are responsible almost all of the OA. If the authors did indeed take the 27.8% into account, that should be stately very clearly in the manuscript.

Re: Sorry for the confusion. We do take 27.8% of the total CO emissions into account. The OA production rate of 22.3 ug m^{-3} ppmv^{-1} only represents the OA formation potential of vehicle exhaust. However, there are other sources whose OA production rates were unknown. Vehicular OA only takes a part of the total. It can be expressed as "Vehicular OA/vehicular CO=vehicular OA/(0.278*total CO)=22.3 ug m^{-3} ppmv^{-1}". Thus, vehicular OA/total CO (high NOx) should be 22.3*0.278=6.2 ug m^{-3} ppmv^{-1}. This value represented the actual vehicular OA production in the urban plume of Shanghai. To avoid the misunderstanding, we removed Fig. 5 and the related contents. Fig. 7 was also revised based on the ratios of vehicular OA to total CO. To clearly explain the methodology how we determined the contribution of vehicular OA production, we added a new section in "Materials and methods". In addition, we found total CO emissions needed to be reconsidered as the results of vehicular OA production versus total CO were unreasonably low. The monitoring site in this study was located in the urban area. While most of the large CO emission sources like steel manufacturing companies and power plants were located at the surrounding areas, which were 30-50 km from city center. It would be more reasonable to constrain the total CO emissions into urban area. So we extracted the emissions from urban area based on their geographic information. 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. Vehicular POA/total CO would be 11.6 ug m^{-3} ppmv^{-1}. In addition, based on your other comments, we reconsidered the OA/OC and changed it from 1.6 to 1.4 (more suitable in urban area). We have also removed about 10 highest points seem like outliers from the summer data in Fig. 7(a). In the revised figures, we replaced the lines with maximum vehicular OA/total CO (Vehicular POA/total CO * yield) calculated based on two scenarios. Please see the details in the last response. We also added two lines in the figure. One is the minimum ratio of observed OA to CO concentrations, which were 12 μg·m^{-3}·ppmv^{-1} both in summer and winter. The other is the maximum ratio of observed OA to CO concentrations, about 50 and 35 μg·m^{-3}·ppmv^{-1} in summer and winter, respectively. Please check the following changes.

Changes in manuscript:
(6) Section 3.3, 2nd paragraph: remove all the contents and Fig. 5.
(7) Section 3.3, 1st paragraph: move all the contents and Table. 3 to the beginning of Section 3 "Results and discussion". Only emission inventory was discussed in this section. The contents are as follows.
   "The emissions of CO, NOx, VOCs, EVA (gas evaporation), EC, and POA (OC*1.2) from vehicles were 343.9, 110.9, 39.4, 8.9, 4.0, and 4.3 k tons in Shanghai for the year of 2012 (See Table 3). Gasoline vehicles (including LDGV, Taxi, HDGV, and Motorcycle) were the major sources of CO, VOCs, and EVA emissions, accounting for 91%, 69%, and 100%, respectively. Diesel vehicles (including LDDV, HDDV, and Bus) were the major source of NOx, EC, and

POA emissions, comprising 82%, 99%, and 96%, respectively. CO and VOC (including EVA) emissions decreased by 40% and 38% compared with the results for the year of 2004 from Wang et al. (2008). NOx emission increased by 21%. PM emission were low estimated in that article since the PM emission factors were much lower than real-world measurement data as shown in Fig. 2. Gasoline vehicle emissions have been well controlled even though their VKTs were nearly doubled in the past few years. In comparison, the control effect of diesel vehicle emission was relatively poor. It is clear that diesel exhausts dominate the primary PM (including EC and OA) emissions in Shanghai. However, since VOC emissions are mainly from gasoline vehicles, we will further discuss the contributions of gasoline and diesel exhausts to SOA."

Table 3. Vehicle emission inventory in Shanghai.

Vehicle type	Emission inventory (k ton)					
	CO	NOx	VOCs	EVA	EC	POA (OC*1.2)
in vehicle type						
LDGV	192.03	13.30	15.59	6.15	0.02	0.07
LDDV	1.89	5.72	0.32	0.00	0.17	0.11
Taxi	68.89	3.86	5.56	1.96	0.01	0.03
HDGV	36.79	2.20	2.29	0.29	0.00	0.01
HDDV	24.71	67.56	9.74	0.00	3.16	3.40
Bus	5.53	17.56	2.06	0.00	0.58	0.62
Motorcycle	14.01	0.67	3.85	0.49	0.02	0.06
in fuel type						
Gasoline	311.71	20.04	27.28	8.88	0.05	0.17
Diesel	32.14	90.84	12.12	0.00	3.91	4.13
Total	343.85	110.88	39.40	8.88	3.96	4.30

(8) In Section 2.3, we add a new section to explain how to determine vehicular OA production contributions in the atmosphere. The contents are:

"The observed $\Delta OA/\Delta CO$ in the atmosphere represents the ratio of total POA emissions and their SOA formation to total CO emissions from all sources, which can be explained by Eq. (6) as follows.

$$\left(\frac{\Delta OA}{\Delta CO}\right)_{obs} = \frac{POA_{total} + SOA_{total}}{CO_{total}} = \frac{(POA_{veh} + SOA_{veh})}{CO_{total}} + \frac{(POA_{oth} + SOA_{oth})}{CO_{total}} = \frac{OA_{veh}}{CO_{total}} + \frac{OA_{oth}}{CO_{total}} \quad (6)$$

The contribution of vehicular OA to total OA production in the atmosphere can be determined by the ratio of OA_{veh}/CO_{total} to $(\Delta OA/\Delta CO)_{obs}$. Here, $(\Delta OA/\Delta CO)_{obs}$ is the ratio of observed ΔOA (Obs, OA-OA$_{background}$) to observed ΔCO (Obs, CO-CO$_{background}$) in the unit of $\mu g \cdot m^{-3} \cdot ppmv^{-1}$. OA_{veh}/CO_{total} is the ratio of vehicular POA emission and SOA formation to total CO emissions, which can be calculated by Eq. (5). ER_{POA} and ER_{VOCj} in Eq. (5) should be substituted by the ratios of vehicular POA and VOC emissions to total CO emissions from vehicle and other sources. The total amount of CO emission was 1.2×10^6 tons according to the annually updated emission inventory in Shanghai for the year of 2012. Iron & steel sector was the major source of CO emission, which accounted for 54% of the total. The sector produced 19.7×10^6 and 18×10^6 tons of pig irons and crude steels, and consumed more than 10×10^6 tons

of coal in 2012. Vehicles were the second largest source, accounting for 27.8% of the total. Detailed information is shown in Fig. S5. However, considering the observation site was located in the urban area and most of the large CO emission sources were located at the surrounding areas (about 30-50 km from city center), 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."

(9) Section 3.4, the last paragraph: replace the whole contents with "Fig. 7 is a scatterplot of OA versus CO concentrations measured in urban Shanghai in the summer and the winter of 2013. The observation data were color-coded by OH exposure ($\Delta t \cdot [OH]$) determined by equation (4). It was indicated from the figure that the ratios of OA to CO concentrations generally showed growing trends with the increase of OH exposure both in summer and winter. The results were similar to the previous studies in the United States, Japan, and Mexico (Bahreini et al., 2012; de Gouw et al., 2008; Takegawa et al., 2006; DeCarlo et al., 2008). The primary emission ratios of POA to CO were determined by the minimum slopes of the observed OA to CO concentrations, about 12 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in both summer and winter (as shown by the dotted grey lines). The maximum slopes of OA to CO were 50 and 35 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ (as shown by the dotted black lines) in summer and winter, respectively. The SOA formation ratio in summer was much higher than in winter. The inventory-based vehicular POA emission to total CO emission was 11.6 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$ in the urban area of Shanghai (shown by the dotted yellow lines), almost the same with primary emission ratio observed in the atmosphere, which indicated that vehicles dominated the POA emissions in urban Shanghai. 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 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$. It was considerable underestimated compared with the observation data, which implied that the SOA yields derived by known and estimated species were still far from explaining the actual SOA formation rate in the atmosphere. For this reason, we introduced the measured SOA yield of gasoline exhaust (~0.190) from Gordon et al. (2014a) to substitute the yield for gasoline vehicles (0,039) in Y2 scenario and defined the new group as Y3 scenario. The maximum OA production ratio (shown by the dotted red lines) increased to 27.3 $\mu g \cdot m^{-3} \cdot ppmv^{-1}$, but still failed to reach the max. observed $\Delta OA/\Delta CO$. There must be other emission sources of SOA precursors in the atmosphere of Shanghai. Previous studies have revealed that VOC emissions from solvent usage, chemical and petrochemical industrial, and coal burning, etc. comprised more than 70% of the observed VOCs in the atmosphere of urban Shanghai (Cai et al., 2010; Wang et al., 2013). The SOA productions of VOC emissions from these sources also cannot be ignored.
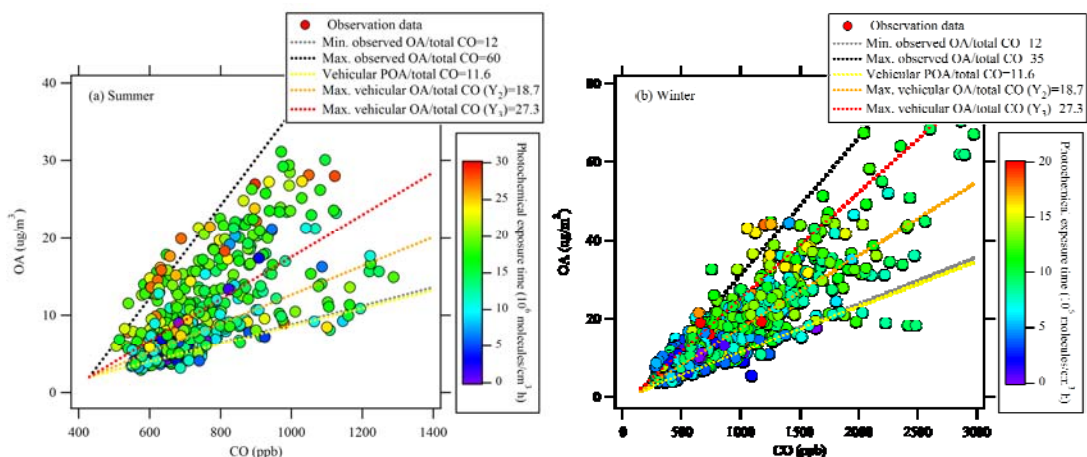
Fig. 6. Relationship of measured OA and CO concentrations color-coded by the photochemical exposure in the summer (a) and winter (b) of 2013 in urban Shanghai according to equation (4). Minimum and maximum ratios of observed OA to CO concentrations are shown by dotted grey and black lines. Vehicular POA/Total CO is shown by dotted yellow line. The minimum and maximum OA formation ratios of vehicle emissions calculated with two different SOA yields of Y2 and Y3 are shown by the dotted orange and red lines, respectively.

1.5 I have a hard time reconciling Figs. 7 and 8. Looking at the summer data in Fig. 7, it seems that other than the 10 highest points, there does not seem to be a dependence on photochemical age. The 10 highest points seem like outliers. Are those points associated with one particular day? In Fig. 8, there seems to a very strong correlation between deltaOA/deltaCO vs photochemical age, when viewed as diurnal variations. Can the authors should plot all deltaOA/deltaCO vs photochemical age to see if there truly is a trend, following de Gouw et al., (2008), or redo the diurnal averages Fig. 8 but remove the 10 outliers.

Re: Thanks for the comments. We have removed the outliers of highest points from summer data in Fig. 6 (the original Fig. 7). The maximum and diurnal profiles of the observed ΔOA/ΔCO changed in Fig. 6 and Fig. 7 (the original Fig. 8). Please check the changes in the last response. The diurnal average observed OA/CO will change to be smoother than the original figure in summer. To compare the difference between two different SOA yields in Y2 and Y3 scenario, we added two figures in Y3 scenario. The vehicular OA/total CO increased a lot after the switch. Besides of the figure, we also revised the contents in Section 3.5. Please check the following changes.
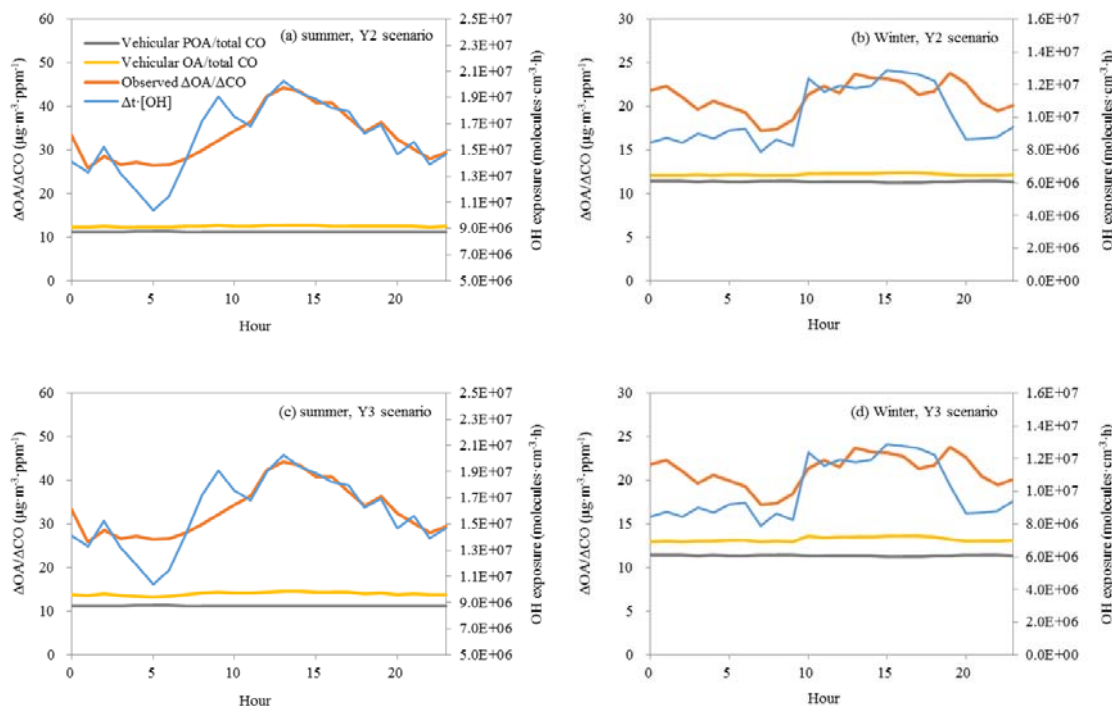
Changes in manuscript:
(4) Fig. 8: replace with "

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 two scenarios (Y2 and Y3) in summer and winter in the urban area of Shanghai for the year of 2013."

(5) Section 3.5, the 1st paragraph: replace the whole paragraph with

"Fig. 7 shows the diurnal variations of average observed ΔOA/ΔCO and OH exposure in summer and winter. There was a strong correlation between the observed ΔOA/ΔCO and OH exposure, which indicated the photooxidation dominated the SOA formation in the atmosphere. In the role of photochemical reaction, the observed ΔOA/ΔCO showed rapid growth trend in the afternoon in summer and reached a peak around 13:00~14:00. The average observed ΔOA/ΔCO in urban atmosphere of Shanghai were 33.2 and 21.1μg·m^{-3}·ppmv^{-1} in summer and winter, respectively."

(6) Section 3.5, the last two paragraphs: replace the whole contents 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 two scenarios. Fig. 7(a) and (b) show the results in Y2 scenario. The SOA yields of gasoline, diesel, and motorcycle exhausts and gas evaporation were 0.039, 0.164, 0.021, and 0.0007, respectively. Fig. 7(c) and (d) show the results in Y3 scenario. The SOA yield of gasoline exhaust was replaced to 0.190 based on the experiment results (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·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 12.5 μg·m^{-3}·ppmv^{-1} and 12.2 μg·m^{-3}·ppmv^{-1} in summer and winter in Y2 scenario, and 14.0 μg·m^{-3}·ppmv^{-1} and 13.2 μg·m^{-3}·ppmv^{-1} in Y3 scenario. The vehicular OA mass accounted for 39% and 58% of the

average observed OA in summer and winter in the urban atmosphere of Shanghai in Y2 scenario. The contributions would increase to 43% and 63% in Y3 scenario. It was indicated that vehicle emission was the major source of OA mass in the urban atmosphere of Shanghai. Enhancing the SOA yield of gasoline exhaust increased about 4%-5% of their contributions to OA, which implied gasoline exhaust didn't dominate the OA mass in the urban atmosphere. Vehicular SOA formation ratios accounted for 7%-10% of the total vehicular OA in Y2 scenario and 14%-20% in Y3 scenario. The SOA formation ratios in both scenarios were lower than expected. There must be other emission sources with high SOA formation potentials in addition to vehicles in the urban atmosphere. 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 S/IVOC species reported in Gentner et al. (2012). The SOA formation potentials of the identified VOC species may contribute more SOA than expected.

At present, few SOA observations in the cities of China can be referenced to verify the results in this study. Huang et al. (2014) has reported the fossil OA dominated the OA mass (~40%) in Shanghai based on the observation data in the first quarter of 2013, which was slightly lower than our result. The possible reason for the difference could be the location of observation site (close to urban or suburban). However, the studies both indicated that vehicle emission was the major source of OA mass in large cities of China."

1.6 The authors should describe how OA is calculated in the ambient data. Is this done by converting OC to OA? If so, what is the OM/OC ratio used? From Section 3.3, it seemed like 1.2 was used for POA, but for SOA it should be higher (likely around 1.3 to 1.6). That would increase the apparent slope of OA vs CO plot and likely decrease the vehicular contribution to OA even further.

Re: Thanks for the comments. Turpin et al. (2001) has suggested a ratio around 1.2-1.6 from fresh emission to aged air mass in remote area. So we used 1.2 to calculate POA from OC emissions and 1.6 to determine the observed OA concentrations. However, we reconsidered the ratio during the revision. Our observation was conducted in the urban area. The air mass what we measured was not fully aged. The photochemical ages we calculated based on the observation data were relatively short. So we changed the ratio to 1.4 in the revised manuscript. We have added the explanation about the OM/OC ratio in "Materials and methods" section. Please see the following changes. The figures and contents in Section 3.4 and 3.5 were also adjusted since the change. Please check them in the responses above.

Changes in manuscript:
(1) Section 2.3, page 7985, line 2: add the following contents at the end of the paragraph. "Fig. S2 shows the time series data of meteorological parameters and concentrations of major air pollutants observed in urban Shanghai in summer (August in 2013) and winter (January in 2013). We didn't measure the OA concentration due to the lack of observation equipment. The OA concentrations were determined by OC concentrations multiplying the OM/OC ratio.

Turpin et al. (2001) suggested a ratio around 1.2-1.6 from fresh emission to aged air mass in remote area. Considering our study was mainly focusing on urban area where emissions were not fully aged, we used the ratio of 1.4 to convert OC concentrations."

1.7 The treatment of low vs high NOx is too simplistic. In general, high-NOx would be more relevant for urban areas, and the statement that "low-NOx conditions were more realistic in the atmosphere" is not applicable here. At short atmospheric ages (i.e. hours), emissions will not have travelled to areas where NOx is low. Also, measurements are made within the city of Shanghai, where NOx is likely dominating peroxy radical chemistry. Therefore, discussion of low-NOx does not apply here.

Re: Thanks. We agree with the comments and remove the contents about low-NOx. Only the SOA yields under high-NOx yield were discussed. Please see the following changes.

Changes in manuscript:
(1) Section 3.2, page 7988, lines 10-21: remove the paragraph all.
(2) Section 3.3: based on the comments from another reviewer, the OA/CO ratio in Fig. 5 was easy to be confused with the results in Fig. 7 and Fig. 8. The main reason was the methodologies of these two results were different. To avoid the misunderstanding, we removed Fig. 5 and related contents in Section 3.3.
(3) Section 3.4: please check the changes in the response to the comment No. 1.4(5).
(4) Section 3.5: please check the changes in the response to the comment No. 1.5.
(5) Section 3.6: the contents and figures in this section were replaced with

"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. LDGV would be the second large contributor after HDDV. It can be indicated that diesel vehicles were the largest contributors to vehicle derived OA in both scenarios although they only accounted for less than 20% of VKTs in Shanghai. Control of the POA emissions and SOA precursors from diesel vehicles are equally important. Gasoline vehicle could be another important contributor to vehicular OA formation. However, there still exist some debates on the SOA yield of gasoline exhaust. It will be meaningful to find out their actual SOA yield and key precursors for urban OA pollution control.
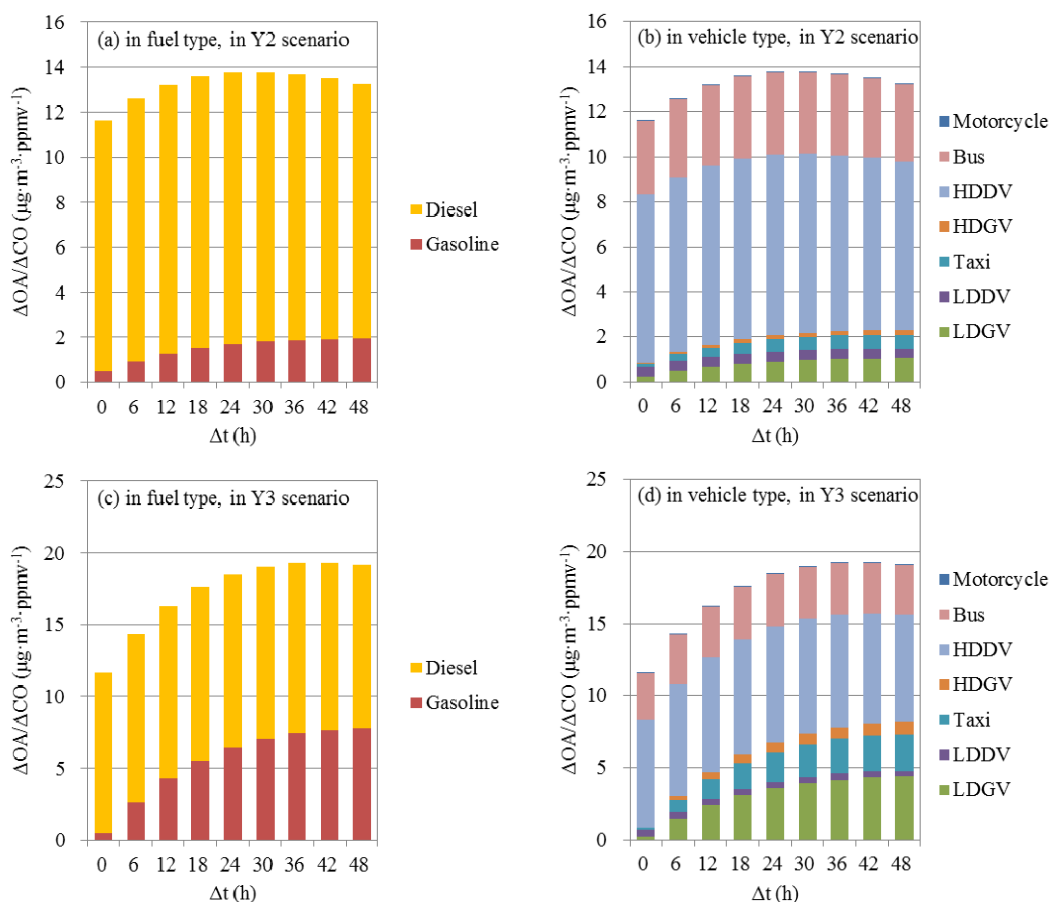
Fig. 8. Contributions of vehicle emissions to OA formation ratios in different vehicle and fuel types in Y2 and Y3 scenarios with the changes of photochemical ages."

2. Specific comments

2.1 There are many abbreviations that are never defined in this manuscript. While some (OA, SOA) are obvious, others (ECE driving cycle) need to be defined in order for the readers to understand the data. There are even some (e.g. PEMS, MARGA) that are defined but are not important to the overall message of the paper and never used again in the manuscript.

Re: Thanks for the comments. We have carefully browsed the full text and added the definitions for the abbreviations. Please check the following changes.

Changes in manuscript:
(6) Section 2.1, page 7981, line 26: replace "The driving cycle of VMAS contains only 1 bag from ECE urban cycle" with "VOC sample was collected from a 1-bag test of the Economic Commission of Europe (ECE) urban cycle".
(7) Section 3.2: add "(tier 1 of low emission vehicle standard in California, US)" behind "LEV-1".

2.2 Abstract line 10: SVOC and LVOC emissions are technically not discussed in this paper. Their reactions do not add OA mass, so it would not be relevant to this study.

Re: Thanks. We removed the contents about SVOC and LVOC. Please see the following changes.

Changes in manuscript:
(2) Abstract, page 7978, lines 9-10: remove "This suggests the requirement for further research on SVOC or LVOC emissions."

2.3 Abstract line 24: "a large number of OA mass" should be "a large amount of OA mass"

Re: Please see the following changes.

Changes in manuscript:
(2) Abstract, page 7978, line 24: replace "a large number" with "a large amount".

2.4 Section 2.1: do the HDDT have aftertreatment technologies? A catalyst or a particulate filter?

Re: The HDDT didn't have any aftertreatment technologies. We have added the descriptions for HDDTs and other vehicle types.

Changes in manuscript:
(2) Section 2.1, page 7981, lines 19-20: replace "All MTs were 4-stroke with 125 cc 20 displacement." and "semi-volatility" with "All MTs were 4-stroke with 125 cc displacement and without catalytic converter or any other pollution control device. All gasoline vehicles were equipped with catalytic converters. Diesel vehicles didn't install any aftertreatment device like DPF (Diesel Particle Filter)."

2.5 Section 2.3: if MARGA data are not used in the manuscript, I suggest removing it from the discussion.

Re: We have removed the contents about MARGA.

Changes in manuscript:
(2) Section 2.3, page 7984, lines 24-26: remove "Water soluble ions were measured by a commercial instrument for online monitoring of aerosols and gases (MARGA, model ADI 2080, Applikon Analytical B.V.)."

2.6 Pg. 7987 line 6: how is SOA mass yield defined? It seems like discussion and comparison of average SOA mass yields between different studies is of limited utility. It depends on what species are measured and included in SOA yield calculations. I suggest shortening this discussion.

Re: The SOA mass yield in this study is defined as the ratio of calculated SOA mass to the total mass of identified SOA precursors and unidentified species. Identified non-SOA precursors were

excluded from total VOC emissions. The definition of SOA yield in this study is similar to the effective SOA yield introduced by Gordon et al. So we decide to keep the comparisons with Gordon et al.'s results. To clearly explain the methodology of SOA yield calculations, we add a new section of "SOA yield estimation" in Section 2 "Materials and methods".

Changes in manuscript:

(1) Section 2.1: we insert a new section on "SOA yield estimation". The contents are as follows.

"To investigate the SOA formation potentials of VOC emissions in vehicle exhausts and gas evaporation, we calculated the SOA yields of the exhausts from gasoline, diesel, and motorcycle vehicles and evaporative emissions with the following equation.

$$Y_j = \frac{\sum \left(C_{i,j} \times Y_i \right)}{\sum VOC_j} \tag{3}$$

Where, Y_j is the SOA yield of source j (unitless). $C_{i,j}$ is the weight percent (by carbon) of species i in which can be identified by measurements or references from source j (wtC%). VOC_j is the weight percent (by carbon) of total identified SOA precursors and unidentified species. Identified non-SOA precursors were excluded from total VOC emissions. The weight percentages of identified species were determined by the measurements above. The unidentified species accounted for about 25%, 60%, and 50% in gasoline, diesel, and motorcycle exhausts, repectively. Considering IVOCs which had high SOA formation potentials were not measured in this study, 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. Y_i is the yield of species i under high-NOx condition considering the study was focusing on urban area with high NOx concentration (unitless). The yield for each SOA precursor was referenced from Gentner et al. (2012), which listed the yields of known and estimated compounds using a combination of measured SOA yields derived from laboratory-chamber experiments and approximate SOA yields based on box modeling."

2.7 Pg. 7988 line 9: "analytic method" should be "analytical method"

Re: Thanks. However, the whole section has been changed according to other comments. The sentences with "analytic method" has been removed .Please check the changes in the response to comment No. 1.1-1.3

2.8 Section 3.3: Thousand t is a confusing unit. Perhaps ktonnes?

Re: Thanks. We changed them with k tons. Please see the following changes.

Changes in manuscript:

(3) Section 3.3, page 7988, line 25: replace "thousand t" with "k tons".

(4) Section 2.2.2, page 7983, line 17: replace "30 thousand" with "30,000".

2.9 Pg. 7989 line 13: typo "respetively" should be "respectively"

Re: Thanks. The whole section has been changed according to the response to the comment of No. 1.7(2). The mistake has been revised.

2.10 Section 3.4: % iles should be percentiles. Also, why is 97.5 percentile used? Usually 95th percentile is used.

Re: Thanks. We have revised it. In addition, the whole paragraph has been moved to Section 2.3 to explain the methodology of photochemical age determination. The initial X/E will be higher when we used 97.5 percentile. Please check the following changes.

Changes in manuscript:

(2) Section 3.4, the 2nd paragraph: move it to Section 2.3 and replace it with

"The evolution of primary VOC emissions to SOA formation is determined by OH exposure in the atmosphere. The OH exposure can be calculated with Eq. (4) developed by de Gouw et al. (2005, 2008).

$$\Delta t \cdot [OH] = \frac{1}{(k_X - k_E)} \times \left[\ln\left(\left[\frac{X}{E}\right]\Big|_{t=0}\right) - \ln\left(\left[\frac{X}{E}\right]\right) \right] \tag{4}$$

Here, Δt is photochemical age (h). $[OH]$ is the average OH radical concentrations (molecules·cm^{-3}). The ratio of m,p-xylene to ethylbenzene (X/E) was considered as a photochemical clock. k_X and k_E are the OH rate constants of m,p-xylene (18.9×10^{-12} cm^3·molecule^{-1}·s^{-1}) and ethylbenzene (7.0×10^{-12} cm^3·molecule^{-1}·s^{-1}) (Yuan et al., 2013). $[X]/[E]|_{t=0}$ and $[X]/[E]$ are initial emission ratio and the ratio after photochemical reaction of m,p-xylene to ethylbenzene. The concentrations of m,p-xylene and ethylbenzene showed good correlations during the observation (Fig. S3). The different diurnal variations of m,p-xylene and ethylbenzene indicated that they are engaged in different chemical reactions in the daytime (Fig. S4). Fig. 3 illustrates the diurnal distributions of the ratios of observed m,p-xylene to ethylbenzene in summer and winter of 2013. The initial emission ratios of m,p-xylene to ethylbenzene were determined by the X/E ratio on 97.5 percentiles, which were 2.17 and 1.68 in summer and winter, respectively.
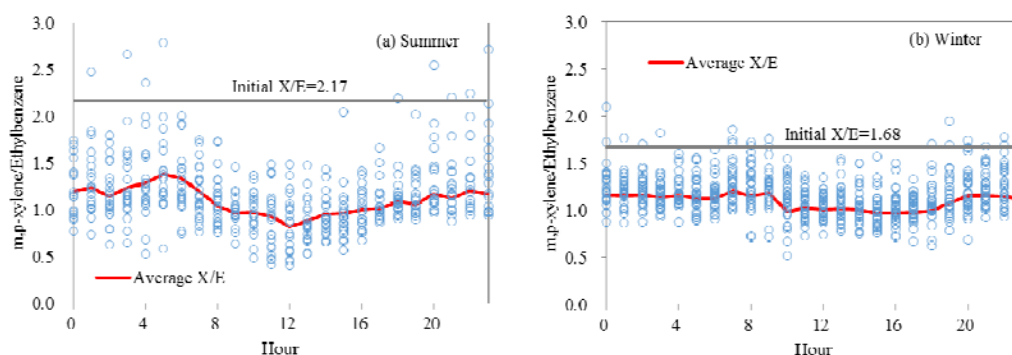

Fig. 3. Diurnal distributions of the ratios of m,p-xylene to ethylbenzene concentrations in summer and winter in the urban atmosphere in 2013."

2.11 Section 3.4: To be more precise, t.[OH] should be referred to as "OH exposure", not photochemical exposure time

Re: Thanks. We have revised it. Please see the following changes.

Changes in manuscript:
(2) Section 3.4, page 7990, line 26: replace "photochemical exposure time" with "OH exposure".
(3) Section 3.5, page 7991, line 26: replace "photochemical exposure time" with "OH exposure".

2.12 Pg. 7990 line 13: a reference should be cited for the OH rate constants

Re: Thanks. We have added a reference for that. Please see the changes in the response of the comment No. 2.10.

2.13 Section 3.5: what is the [OH] used to calculate delta t in Eqn (2)? Are there measurements or estimates of OH to support the value used?

Re: There was no OH measurement conducted due to the lack of measurement devices. So we quoted the 24-hour average [OH] value (3×10^6 molecules·cm^{-3}) from de Gouw et al. (2008). We have added the description in the section. And also, the paragraph of this section has been moved to Section 2.3 to explain the methodology of OA production estimation. Please see the following changes.

Changes in manuscript:
(2) Section 3.5, the 2nd paragraph: move to Section 2.3 and replace with

"OA production is determined by the loss terms and formation rates of OA concentration after POA emissions exhaust into the atmosphere. de Gouw et al. (2008) introduced a method to explain the OA evolution during photochemical aging of urban plumes as shown by Eq. (5).

$$\frac{\Delta OA}{\Delta CO} = \frac{\Delta POA}{\Delta CO} + \frac{\Delta SOA}{\Delta CO} \tag{5}$$
$$= ER_{POA} \times \exp(- L_{OA} \cdot \Delta t) + ER_{VOC_j} \times Y_j \times \frac{P_{OA}}{L_{OA} - P_{OA}} \times [\exp(- P_{OA} \cdot \Delta t) - \exp(- L_{OA} \cdot \Delta t)]$$

Here, *ΔOA/ΔCO* is the ratio of OA formation versus CO emission after photochemical reaction (µg·m^{-3}·ppmv^{-1}). ER_{POA} is the primary emission ratio of OA to CO emission (µg·m^{-3}·ppmv^{-1}). ER_{VOCj} is the primary emission ratios of VOC (including SOA precursors and unidentified species) from source *j* to CO emission in the unit of ppbv^{-1}·ppmv^{-1}. Y_j is the SOA yield of source *j*, which is determined by Eq. (3). L_{OA} and P_{OA} are the loss and formation rate of organic aerosol, respectively. We used the empirical parameters derived by de Gouw et al. (2008), which were 0.00677 h^{-1} and 0.0384 h^{-1}, respectively. *Δt* is the photochemical age calculated by equation (4). Because there is no OH measurement in Shanghai, we reference the 24-h average OH concentration (3×10^6 molecules·cm^{-3}) from de Gouw et al. (2005)."

Other changes in manuscript:
(1) Section 1: To clearly explain the main points of this manuscript, we make some revisions in

"Introduction" section. The changes are as follows.

Page 7981, lines 5-12: replace "In this study, we first investigated …… in the urban atmosphere of Shanghai." with "In this study, we first constructed a vehicular emission inventory of Shanghai for the year of 2012. Then the SOA yields of VOCs emissions from different vehicle types were discussed based on the new measurements of VOCs species from a fleet of vehicles in Shanghai. Finally, we calculated the inventory-based vehicular OA production with the ambient observation data to evaluate the OA contribution of vehicle emission. The main purpose of this study is to discuss: (1) the contribution of vehicle emission to OA in urban Shanghai; (2) the relative contributions of gasoline and diesel vehicles to vehicle derived OA."

(2) Section 1, page 7980, lines 5-8: remove "Considering the importance of vehicular gas-phase precursors to SOA formation prediction, May et al. (2014) investigated the VOC emissions from 64 light-duty gasoline vehicles, 2 medium-duty diesel vehicles and 3 heavy-duty diesel vehicles with varying levels of aftertreatment."

(3) Section 2: to better explain the methodologies of this manuscript, we reorganized the section of "Materials and methods". The first section mainly introduced the method of vehicle emission inventory compiling, which included four sections. The contents are as follows.

"2.1.1 Methodology of emission inventory compilation

We developed emission inventories for the pollutants including VOCs, CO, EC, and OC with the IVE (International Vehicle Emission) model for Shanghai, China. The methodology of the model has been introduced by Wang et al. (2008). Vehicle kilometers of travel (VKT), vehicle flow distribution, driving pattern, fleet composition and emission factor of each vehicle type were 5 key parameters for the development of vehicle emission inventory. Vehicle emissions can be calculated with Eq. (1).

$$E = \sum_t \left\{ VKT \times f_{[t]} \times EF_{[t]} \times \sum_d \left[f_{[dt]} \times K_{[dt]} \right] \right\} \qquad (1)$$

Where, E is emission amount of each vehicle type (g). VKT is Vehicle kilometers of travel of each vehicle type (km). $f_{[t]}$ is the fleet composition of the specific technology of each vehicle type (%), such as fuel type, engine size, and emission standard. $EF_{[t]}$ is the emission factor of each vehicle technology (g·km^{-1}). $f_{[dt]}$ is the fraction of the driving pattern (%). $K_{[dt]}$ is the correction factor of each driving pattern determined by the model (unitless). Evaporative emissions are also calculated with Eq. (1). $EF_{[t]}$ will be evaporative emission factor of each vehicle technology as the evaporative emissions are calculated.

2.1.2 Road traffic data survey

VKTs and their weights on 3 road types (including highway, arterial road, and residential road) were surveyed from transportation for the year of 2012. VKTs on each road type were further separated into 7 vehicle types by the use of video camera surveys. The distributions of each vehicle type were surveyed on various road types with video cameras from March to May. About 4000 valid hours were obtained on 15 roads covering 3 road types. Survey days included weekdays and weekends and each day covered 24 h. The results show that light-duty vehicles (including light-duty cars, light-duty trucks, and taxis) are the major vehicle types on the road, accounting for 56% of the total flows. Heavy-duty vehicles (including heavy-duty bus, heavy-duty truck, and city bus) comprise 19% of the whole VKTs in Shanghai. GPS data were used to determine the driving patterns of various vehicle types. The driving patterns

were determined by the average speeds and VSP (Vehicle Specific Power) distributions. We installed GPS units on light-duty cars, taxis, buses, and heavy-duty trucks to record the driving speeds and altitudes second by second. About 150 hours of valid GPS data were collected in this study. The data covered 2831 km of roads and were composed of 3 road types and 4 vehicle types. VSP of each vehicle and road type can be calculated with Eq. (2) introduced by Jimenez (1999).

$$VSP(kW \cdot t^{-1}) = v \times [1.1a + 9.81 \times (a \cdot \tan(\sin(grade))) + 0.132] + 0.000302 \times v^3 \quad (2)$$

Where, v is vehicle speed (m·s^{-1}). a is vehicle acceleration (m·s^{-2}). $grade$ is vertical rise/slope length. Table 1 shows the daily VKT and average speeds of various vehicle and road types in 2012.

Table 1. Daily VKT and average speeds of various vehicle and road types in Shanghai in 2012.

Road types	Daily vehicle kilometers traveled (million km)								Average speed (km·h^{-1})
	Light-duty car	Light-duty truck	Taxi	Heavy-duty bus	Heavy-duty truck	City bus	Motor-cycle	Total	
Highway	38.3	0.62	3.96	3.10	11.82	0.23	0.00	58.04	57.9
Arterial road	22.6	2.93	6.16	1.12	4.73	1.58	5.29	44.41	36.0
Residential road	18.3	3.11	8.92	0.89	1.90	1.38	4.15	38.64	28.5
Total	79.2	6.66	19.04	5.11	18.45	3.19	9.44	141.09	43.0

2.1.3 Fleet composition data survey

Fleet composition data were used to separate the VKT of each vehicle type (as shown in Table 1) into the fractions of specific technologies, such as fuel type, engine size, and emission standard. The data were determined by the ratios of the populations of specific technologies in the vehicle information database from the Vehicle Management Department of Public Security Bureau of Shanghai. We call this "static" fleet. Light-duty cars and taxis were mainly composed of gasoline vehicles, which occupied 98% and 97%, respectively. Diesel vehicles dominated in light-duty truck, heavy-duty bus, heavy-duty truck, and city bus, comprising 56%, 91%, 89%, and 98%, respectively. Euro 2 vehicles were the majority of light-duty cars and light-duty trucks, accounting for 51% and 68%, respectively. Heavy-duty buses and trucks were mainly composed of Euro 2 and Euro 3 diesel vehicles, which comprised 40% and 45% of each vehicle type. However, the fraction of each specific technology should be changed with its occurrence frequency in the real-world. Generally, older vehicles show less occurrence frequency than newer vehicles, which means the annual mileage of older vehicle should be less than the newer one. For this reason, we considered to adjust the fleet compositions according to their real-world annual average mileages. About 30,000 vehicles were surveyed at 4 inspection stations in this study. Vehicle age and odometer reading were recorded for each vehicle. The survey data showed that the annual average mileages of light-duty truck, heavy-duty bus, and heavy-duty truck tended to decrease with the increase of their vehicle ages. The "adjusted" fleet compositions were determined by the multiplication of vehicle populations and their surveyed annual mileages. Fig. 1 shows the static and adjusted fraction by each vehicle type in Shanghai. It is indicated that the adjusted fractions of the older vehicles with pre-Euro and Euro 1 emission standard for light-duty truck, heavy-duty bus, heavy-duty truck, and city bus were much smaller than those of the static ones. Correspondingly, the adjusted fractions of the newer vehicles with Euro 3 emission

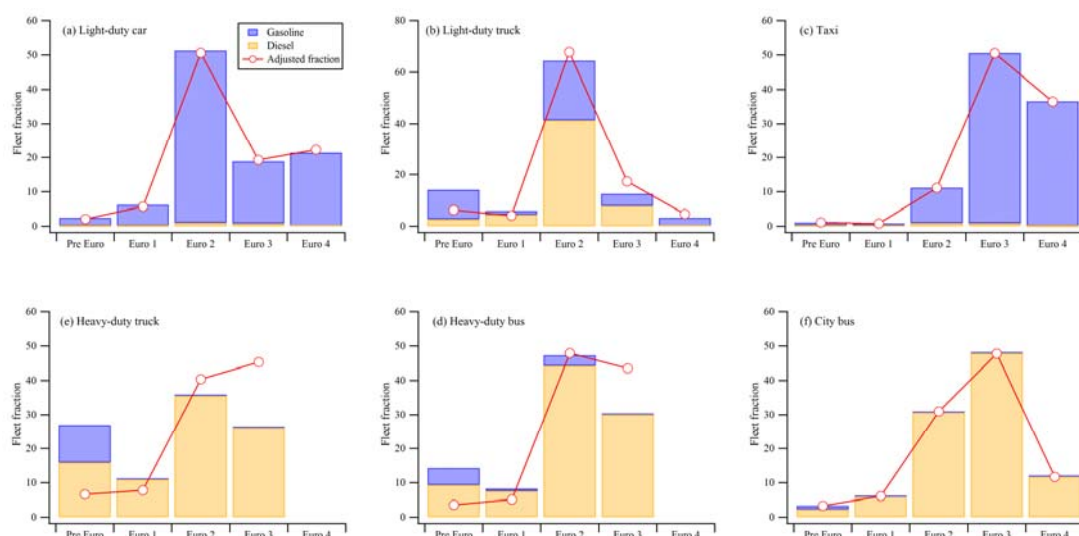standard increased a lot compare with the static ones.

Fig. 1. Static and adjusted fractions of each vehicle type in Shanghai.

2.1.4 Vehicle emission factors

The emission factors of each vehicle technology were modeled with the IVE model. However, most of the default emission factors in the model are based on the measurements in the US. To localize the emission factors in this study, we collected the published emission factors based on the real-world measurements in the previous studies to adjust the modeled emission factors. The measurements were all conducted with Portable Emission Measurement Systems (PEMS) under designed driving routes in the cities of China. The cities included Shanghai, Beijing, Guangzhou, Xi'an, Shenzhen, Jinan, and Yichang (Chen et al., 2007; Huo et al., 2012a; Huo et al., 2012b; Wu et al., 2012; Huang et al., 2013). Fig. 2 shows the comparisons of the adjusted emission factors with the measured ones. The evaporative emission factors were not adjusted due to the lack of measurement data. Default factors in the model were used to calculate evaporative emissions in this study. It is indicated that the adjusted emission factors of each vehicle type generally fit well with the measured results. The emission factors are reliable to be used to establish the emission inventory.
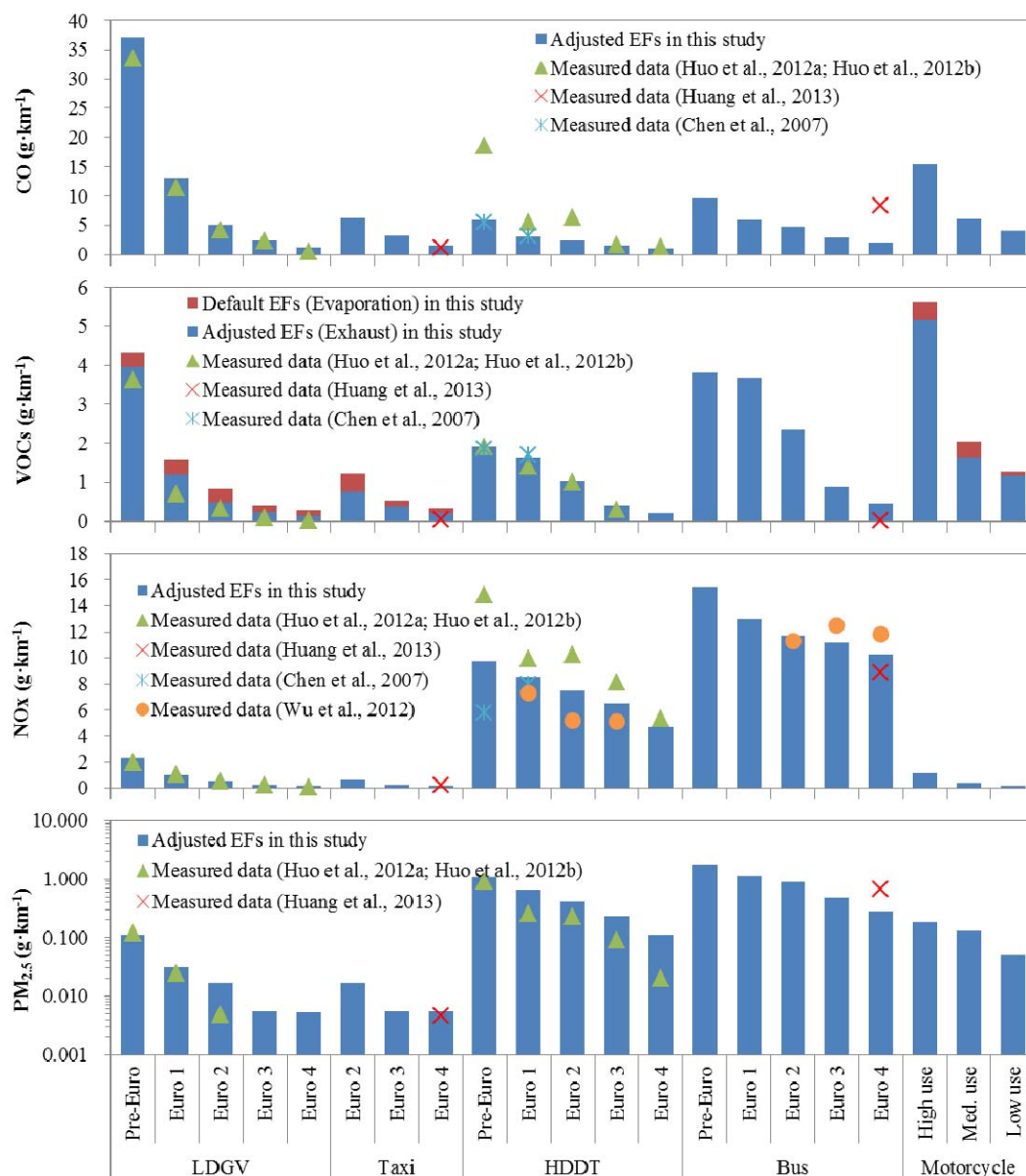
Fig. 2. Adjusted emission factors of various vehicle types (blue bars) and their comparisons with measured emission factors in the previous studies (dots)."

(4) Section 2.1: we changed it to Section 2.2, which included 3 sections. Section 2.2.1 is "VOC sampling". Section 2.2.2 is "VOC analysis". Section 2.2.3 is "SOA yield estimation". Section 2.2.1 is the first two paragraphs in the original manuscript. Section 2.2.2 is the 3rd paragraph. The contents of Section 2.2.3 has been introduced in the response to the comment of No. 2.6.

(5) Section 2.3: the section has been changed to section 2.3.1. Other two sections were introduced in this section. Section 2.3.2 is "OA production estimation". The contents of this section has been introduced in the response of comment No. 2.10 and comment No. 2.13. Section 2.3.3 is "Determination of vehicular OA contribution". The contents are as follows.

"The observed ΔOA/ΔCO in the atmosphere represents the ratio of total POA emissions and their SOA formation to total CO emissions from all sources, which can be explained by Eq. (6) as follows.

$$\left(\frac{\Delta OA}{\Delta CO}\right)_{obs} = \frac{POA_{total} + SOA_{total}}{CO_{total}} = \frac{(POA_{veh} + SOA_{veh})}{CO_{total}} + \frac{(POA_{oth} + SOA_{oth})}{CO_{total}} = \frac{OA_{veh}}{CO_{total}} + \frac{OA_{oth}}{CO_{total}} \quad (6)$$

The contribution of vehicular OA to total OA production in the atmosphere can be determined by the ratio of OA_{veh}/CO_{total} to $(\Delta OA/\Delta CO)_{obs}$. Here, $(\Delta OA/\Delta CO)_{obs}$ is the ratio of observed ΔOA (Obs, OA-OA$_{background}$) to observed ΔCO (Obs, CO-CO$_{background}$) in the unit of $\mu g \cdot m^{-3} \cdot ppmv^{-1}$. OA_{veh}/CO_{total} is the ratio of vehicular POA emission and SOA formation to total CO emissions, which can be calculated by Eq. (5). ER_{POA} and ER_{VOCj} in Eq. (5) should be substituted by the ratios of vehicular POA and VOC emissions to total CO emissions from vehicle and other sources. The total amount of CO emission was 1.2×10^6 tons according to the annually updated emission inventory in Shanghai for the year of 2012. Iron & steel manufacturing was the major source of CO emission, which accounted for 54% of the total. The sector produced 19.7×10^6 and 18×10^6 tons of pig irons and crude steels, and consumed more than 10×10^6 tons of coal in 2012. Vehicles were the second largest source, accounting for 27.8% of the total. Detailed information is shown in Fig. S5. However, considering the observation site was located in the urban area and most of the large CO emission sources were located at the surrounding areas (about 30-50 km from city center), 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."

(6) Section 4 "Conclustion": based on the changes in the main text, we rewrite Section 4 as follows.

"To evaluate the OA contribution of vehicle emissions in the urban atmosphere of Shanghai, we developed a vehicular emission inventory and estimated the SOA yields of gasoline, diesel, and motorcycle exhausts and gas evaporation based on measured C2-C12 VOC species and referenced S/IVOC species from Gentner et al. (2012). Higher contents of aromatic were measured in this study and other studies in China compared with the results from the US and European. Loose limit to aromatic contents in the standard of gasoline fuel in China should be responsible for the high aromatic contents, which resulted in larger SOA yield of gasoline exhaust than the results reported by Gentner et al. (2012) based on the same method. However, the estimated yield was still much lower than the results from smog-chamber experiments (Gordon et al., 2014a), which implied the unidentified species were considerable to SOA formation.

Vehicles dominated the POA emissions and OA productions in the urban atmosphere of Shanghai. Their contributions to OA productions were about 40% and 60% in summer and winter, respectively. The rest of the contributors could be the non-fossil VOC emissions from solvent use, chemical and petrochemical industrials, etc. and the underestimated SOA productions from unidentified VOC or IVOC species in the exhausts. At present, vehicles are experiencing rapid growth trends in the cities of China. Primary emissions and secondary formation of OA derived from vehicles will lead to further deterioration of fine particle pollution in the urban area. Reduction of primary PM emissions and SOA precursors from vehicle exhausts will be helpful to improve the air quality in the cities of China. The results also indicate diesel exhausts dominate the POA emissions in the urban area. Therefore,

strengthening the primary PM emission control of diesel vehicles, especially for the older diesel vehicles with loose emission standards as shown by Fig. 2, plays an important role in OA pollution prevention. Now China is conducting the large-scale elimination of "yellow-labeled" diesel vehicles whose emission standards were lower than Euro 3. It can be expected to effectively reduce the OA pollution caused by diesel vehicles. On the other hand, gasoline exhausts have high potential impacts on SOA formation in the urban area. Tightening the limit of aromatic contents in gasoline fuel will be meaningful to reduce the SOA contributions of gasoline vehicles.

There are still some uncertainties need to be improved in the future. First is the SOA mass yield. More experiments on SOA yields of vehicle exhausts in China will be helpful to the SOA formation potentials of different vehicle types. Especially for gasoline exhausts, the estimated SOA yield was much lower than the experiment results in the US. Vehicular OA contributions will increase about 4%-5% if we replace the estimated SOA yield of gasoline exhaust to the experiment result. It will be meaningful to find out their actual SOA yield and key precursors for urban OA pollution control. Emission inventory is another important source of uncertainty in this study. To reduce the uncertainty of vehicular emission inventory, we localized the vehicle mileage and emission factor data based on the traffic surveys in Shanghai and real-world measurements in some cities of China. However, the CO emission inventories of other sources shown in Fig. S5 still have large uncertainties according to the previous study (Huang et al., 2011). More accurate emission inventory will be helpful to reduce the uncertainty of vehicular OA contribution in this study. However, it can be concluded that vehicle emissions are the most important contributors to OA pollution in the cities of China. Another implication is the potential roles of IVOCs in vehicle exhausts are very important on the SOA formation in the urban area. Therefore, further studies need to pay more attentions to determine the contributions of IVOC emissions to OA pollution in China."

(7) Abstract: based on the changes in the main text, we rewrite this section as follows.

"VOC species from vehicle exhaust and gas evaporation were investigated by chassis dynamometer and on-road measurements of 9 gasoline vehicles, 7 diesel vehicles, 5 motorcycles, and 4 gas evaporation samples. The SOA mass yields of gasoline, diesel, motorcycle exhausts, and gas evaporation were estimated based on the mixing ratio of measured C2-C12 VOC species and references IVOC species. High aromatic contents were measured in gasoline exhaust and contributed more SOA yield comparatively. A vehicular emission inventory was compiled based on a local survey of on-road traffic in Shanghai and real-world measurements of vehicle emission factors from previous studies in the cities of China. The inventory-based vehicular OA productions to total CO emissions were compared with the observed $\Delta OA/\Delta CO$ in the urban atmosphere. The results indicate that vehicles dominate the POA emissions and OA productions, which contributed about 40% and 60% of OA mass in the urban atmosphere of Shanghai. Diesel vehicles, which accounted for less than 20% of VKT, contribute more than 90% of vehicular POA emissions and 80%-90% of OA mass derived by vehicles in urban Shanghai. Gasoline exhaust could be an important source of SOA formation. Tightening the limit of aromatic content in gasoline fuel will be helpful to reduce its SOA contribution. IVOCs in vehicle exhausts have great contributions to SOA formation in the urban atmosphere of China. However, more experiments need to be conducted to determine the contributions of IVOCs to OA pollution in China."