

We thank the reviewers for their helpful comments. They have improved the manuscript. We provide extensive point-by-point responses below, including excerpts of the modified text. We have done our best to address all comments in the text, including significant changes to several figures.

Anonymous Referee #1

Received and published: 25 October 2013

General Comment:

Gordon et al. (2013) study the effects of photochemical aging on tail-pipe emissions from 15 light-duty gasoline vehicles (LDGVs) using a smog chamber. The major findings of Gordon et al. (2013) are: (1) PM attributable to LDGV tail-pipe emissions is comprised primarily of secondary nitrate and secondary organics, (2) NMOG emissions during cold-start tests were 3-7 times higher than during hot-start tests with similar increases in SOA formation, (3) SOA formation from LEV1 and LEV2 vehicles is comparable to pre-LEV vehicles despite an order-of-magnitude difference in NMOG emissions, and (4) very high SOA mass yields are required to obtain agreement between the amount of SOA mass that forms versus the fraction of hydrocarbon that reacts. The findings are interesting and important, and I recommend publication after all of my comments have been addressed.

Major Comment:

The results presented in Figures 3 and 6a are surprising, and I am not yet convinced that they make sense. The only way reducing emissions by a factor of 10 can result in SOA being reduced by a factor of 1.5 (38%) is if the majority of species that are removed prior to emission do not form SOA (i.e. they are in the speciated non-SOA precursor class). Page 23194, Line 13-14: "Therefore, oxidation of the speciated precursors can explain the pre-LEV SOA data". This implies that the majority of SOA in pre-LEV vehicles must be attributable to the speciated SOA precursors, and not the other two emission categories. Since the speciated SOA precursor emission class is also reduced by a factor of 10 when going from pre-LEV to LEV-1,2 vehicles (figure 3), the SOA concentrations should go down by a comparable level since all three vehicle classes are using the same fuel. That the SOA concentrations do not go down by a comparable level implies that reducing emissions in the speciated SOA precursors class increases the SOA yields of the species in the unspeciated class. The authors rule out differences in OH exposure and the possibility of particle-phase concentrations influencing partitioning, but they do not give any possible explanation for how this could happen. Stating that the relationship between NMOG and SOA is complex and nonlinear is insufficient.

We respectfully disagree with the reviewer's assumption that vehicles using the same fuel must generate the same relative amounts of individual NMOGs in their emissions. Our data indicate that this is not true; for example, the unspeciated fraction is larger for newer vehicles than for older vehicles. We do not understand mechanistically what is driving these changes, but it has been reported (as we discuss below) that variations in catalysts and engine controls may affect the fraction of certain NMOGs emitted. We have inserted the following additional text to address this issue beginning on line 15 of p. 23197:

While further study will be required to fully elucidate the causes of the unexpected difference between the reductions of NMOG and SOA for the different LEV classes, several possible explanations exist. In general, components of the vehicle system upstream (engine

controls) and downstream (catalyst technologies) of the actual fuel combustion site play crucial roles in determining what is emitted from the tailpipe; thus, even when identical fuels are burned in different vehicles (as in the present study), there is no reason to expect that the emissions profiles should be identical.

Two changes to emission controls during the 1990s (i.e., between pre-LEV and LEV1) could have some impact on the specific NMOGs emitted by different vehicles: spark retard and catalyst formulation. Spark retard, first used extensively with LEV1 vehicles, was introduced to increase the catalyst warm-up rate, but this technique can change the mix of NMOGs released during the warm-up period (1, 2). The higher temperature can lower the amount of unburned fuel emitted, but especially at extensive spark retard it can also increase the amount of partially burned fuel (potentially increasing the unspciated fraction). In addition, during this same time period (pre-LEV to LEV1 transition) Pd began to replace Pt as the main active metal in automotive catalysts. This shift in control technology could also alter the mix of NMOGs emitted from newer vehicles (3, 4). In particular, the catalytic capability of Pt and Pd may differ depending on whether or not the NMOGs have double bonds.

Furthermore, catalysts are optimized to reduce emissions of regulated pollutants (NO_x, NMOG, and CO), not SOA precursors. Catalysts are typically developed using surrogate emissions comprised of small hydrocarbons, such as propene—many of which do not produce SOA in the atmosphere. Control experiments in which the chamber was injected with (1) clean air instead of vehicle exhaust (i.e., dynamic blank experiments) and (2) exhaust from vehicles emitting sub-ambient (below the minimum detection limit of our instruments) particle and NMOG concentrations demonstrate that the SOA production observed during the chamber experiments was not significantly affected by contamination or by the propene used to adjust VOC/NO_x ratios.

In addition to these two intrinsic differences (spark retard and catalyst formulation) among the vehicles studied, it is also possible that an artifact of our analysis could explain the difference between the reductions of NMOG and SOA for the different LEV classes. Our NMOG classification scheme (SOA precursor, non-precursor, unspciated) is coarse, and compounds within the SOA precursor class have a wide range of reaction rates with OH (minimum $k_{OH} = 1.14 \times 10^{-13}$, maximum $k_{OH} = 5.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Thus if among two vehicles with identical masses of SOA precursor emissions, one vehicle's SOA precursor emissions include a larger share of compounds with fast reaction rates, that vehicle should have a greater yield than the other.

Minor Comments:

1. The authors currently state that OH levels were inferred from the decay of individual hydrocarbons. The authors need to clarify how OH and OH-exposure were calculated. I recommend the authors calculate the OH-exposure using the methods of Parrish et al. (2007) and Kleinman et al. (2008), and see if the results presented in Figure 6c remain the same. Also, shouldn't SOA formation depend exponentially, not linearly, on OH exposure? Instead of using measurements from the end of 3 hours of photo-oxidation, the authors should take all

measurements from different experiments at the same OH-exposure. This will remove the uncertainty about how much differences in OH-exposure influence experiment-to-experiment variability.

We have added the following text to the MS:

“OH exposures (OH multiplied by time) were calculated based on the loss of VOCs via reaction with OH as described by the rate law:

$$\frac{d}{dt}[VOC] = -k[OH][VOC]$$

After integrating from t_0 to t , OH exposure is given by

$$[OH] \cdot t = -\frac{1}{k} \ln \left(\frac{[VOC]_t}{[VOC]_0} \right)$$

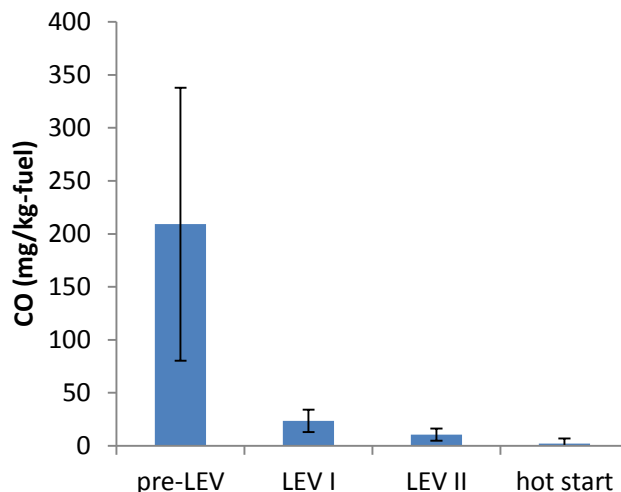
We calculated the OH exposure according to the equation above using concentrations of three to six different VOCs (toluene, benzene, xylenes, trimethylbenzene, propene and butanol) measured with a PTR-MS which were then fit to derive our OH exposure estimate.”

Figure 6a now includes SOA production after 5×10^6 molecules cm^{-3} h in addition to SOA production after 3 h of photo-oxidation. As expected (and discussed in text), this figure shows that there is a more pronounced reduction in SOA with LEV class when measurements are taken at the same photochemical age.

We recalculated OH exposures using the ratios of VOCs as suggested by the reviewer for at least 3 experiments from each of the LEV classes. Recalculated OH exposures did differ from the original estimates in some cases. These differences are due to the fact that our approach is averaging estimates from three to six tracers while the Parrish approach is based on only two. The recalculated OH exposures for pre-LEV experiments were somewhat lower than the original estimates. LEV-1 estimates match reasonably well between the two approaches. Recalculated OH exposures for some LEV-2 experiments were somewhat higher than originally estimated while some were somewhat lower. In general, if the revised estimates were used, the reduction in SOA production after equivalent OH exposure with LEV class shown in the revised Figure 6a would likely be modestly accentuated. Nevertheless, our conclusion (p. 23197, lines 9-11) that “newer (LEV1 and LEV2) vehicles produced less SOA than older (pre-LEV) vehicles (per mass of fuel burned), but the differences were much smaller than the order of magnitude reduction in NMOG emissions” remains valid.

2. How do CO emissions during cold start compare to CO emissions during hot start? How do CO emissions compare between vehicle classes? I recommend adding a component to Figure 6d normalizing all quantities by CO as opposed to primary PM, CVS POA, or kg-fuel combusted. This will make it easier to compare the data shown in Figure 6 to results from various field campaigns, and because the semi-volatile nature of POA may influence the ratios shown in Figure 6d.

CO emissions from older vehicles and during cold start are much greater than from newer vehicles and hot start. The data are summarized in the figure below (included in tabular form in Table S.6 of the revised supplemental information). These CO data were used to construct the plot of SOA/CO in Figure 6e (new) as per the reviewers' request.



3. Page 23181, Line 18: “NO_x levels were between 0.1 and 2.4 ppmv”. Why were the NO_x levels so high?

Some of the vehicles had high tailpipe emissions. For example, high levels were observed during experiments with the LEV1-6 vehicle (specifically during LEV1-6.1). This is the vehicle with the known emissions control system failure; we presume that the oxygen sensor in the vehicle was not functional. Several of the pre-LEV vehicles also had very high NO_x emissions.

4. Page 23183, Line 19-20: “We imposed a 5 : 1 upper bound on the ratio of OA on the wall to suspended OA”: Why did you impose this upper bound? Is there any physical reason why the wall-bound OA concentration can't be more than five times higher than the suspended OA concentration?

We were mistaken in saying that the 5:1 limit was binding in half the experiments. In fact, this limit was reached during only two experiments (pre-LEV-3.2 and pre-LEV-3.3, duplicates with the same vehicle) out of the 29 reported in this paper. We have corrected this mistake in the MS.

There is not a physical basis for the 5:1 limit. As we note in the text, with the $\omega = 1$ correction the loss of organic vapors scales with the ratio of the mass of particles on the walls to particles in suspension. The two vapor loss estimates diverge as more particle mass is lost to the chamber walls, increasing the uncertainty in the wall-loss-corrected SOA mass as an experiment progresses. We chose this ratio as the point beyond which the uncertainty was too great for the values to be considered reliable. If we had chosen a higher limit (or no limit) this would not change any of the conclusions of the paper. We have now changed the text to the following: “With one vehicle (experiments pre-LEV-3.2 and pre-LEV-3.3) we imposed a 5:1 upper bound

on the ratio of OA on the wall to suspended OA. In our judgment OA estimates beyond this ratio become too uncertain; therefore, we assumed that these two experiments were complete when this ratio was reached. If we had chosen a higher limit (or no limit), our estimate of the SOA production from this vehicle would have been greater, but this would not change any of the conclusions of the paper.”

5. The subfigures in Figure 4 need to be larger. I recommend regrouping them to be 2 by 2 instead of 4 by 1.

Done.

References:

Parrish, D. D., Stohl, A., Forster, C., Atlas, E. L., Blake, D. R., Goldan, P. D., Kuster, W. C., and de Gouw, J. A. : Effects of mixing on evolution of hydrocarbon ratios in the troposphere, *J. Geophys. Res.-Atmos.*, 112(D10), D10S34, 2007.

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Anonymous Referee #2

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Overview

This manuscript presents new information about the SOA-forming potential of light-duty gasoline vehicles (LDGV). With dynamometer experiments, the authors characterize emissions of non-methane hydrocarbons and primary organic aerosol from 15 vehicles that cover a range of model years. SOA was formed by reaction in a smog chamber post-emission. The authors strived to make the chamber representative of ambient conditions, but were faced with practical challenges that led them to seed the chamber with ammonium sulfate and propene to control the VOC/NO_x ratio. The major findings are succinctly summarized by Reviewer 1. The manuscript is well-written and presents new information about SOA-forming potential of LGDV under laboratory conditions. I share the concerns noted by the other reviewer and recommend publication only after the concerns of Review 1 and the additional questions listed below are addressed.

Major comments

Page 23182 – The significance of the statement “There was no evidence of organic particle signal at m/z 28 (CO⁺)” is missing. Were other OA signals present? If so, which ones were used to generate the OA time series in figure 4C?

Our statement was intended to provide some methodological detail on how the OA was determined from the AMS spectra. We explain that essentially all of the m/z 28 signal was due to N₂, and none of it was attributable to particle phase CO⁺ in the background or the SOA. This conclusion was drawn using the AMS particle time of flight method described in the text accompanying figure S1 in the supplemental information for Presto, A. A., M. A. Miracolo, et al.

(2009). "Intermediate-Volatility Organic Compounds: A Potential Source of Ambient Oxidized Organic Aerosol." *Environmental Science & Technology* 43(13): 4744-4749, which can be found at http://pubs.acs.org/doi/suppl/10.1021/es803219q/suppl_file/es803219q_si_001.pdf There were many other OA m/z present in the spectra. The primary organic aerosol was characterized by a large contribution from reduced hydrocarbon species (C_xH_y), with m/z 43 generally the most abundant. Additional POA ions included those from the series of C_nH_{2n+1} (m/z 43, 57, etc.) and the series of C_nH_{2n-1} (m/z 41, 55, etc.). The SOA included many of the same ions, but m/z 44 was more pronounced.

Page 23187 line 23, discussion of Figure 4C – “The SOA production increased linearly with OH exposure” but then dropped off around 6×10^6 molecules cm^{-3} . What is the significance of the deviation from linearity?

We attribute this deviation from linearity to uncertainty in the OH exposure data. The GC-MS samples from the chamber after 3 hours of irradiation indicate that there are still elevated levels of alkanes, aromatics and other SOA precursors in the chamber; thus, the fact that the OH exposure levels off later in the experiment (around 5×10^6 molecules cm^{-3} h in this case) suggests that OA production is oxidant-limited rather than precursor-limited. This conclusion is supported by the observation that the rates of VOC consumption decreases as a function of time. OH levels generally decreased by about a factor of ten after the first hour of the experiment as the HONO was consumed by photolysis.

Page 23188 - What conclusions are drawn from blanks and what are the implications of the blank experiments? What is the variability across multiple blank experiments?

The primary purpose of the blank experiments was to ensure that SOA formation was due to vehicle emissions rather than some other source; the fact that very little SOA was formed when the chamber was filled with CVS air with no vehicle emissions (i.e., a dynamic blank) shows that the SOA production observed during vehicle tests was not substantially influenced by desorption of organics from the transfer line, the exogenous propene addition or VOCs in the background air. In addition to the two true dynamic blank experiments, we treated the nine hot-start experiments with the DPF equipped diesel vehicles as dynamic blanks as well because the emissions for the latter were below ambient levels. The variability across the 11 blank experiments is shown in in Figure 5. The median \pm stdev SOA production from the blanks is $1.4 \pm 1.3 \mu g m^{-3}$. While Figure 5a shows that there is some variability in SOA production, it does not appear to be restricted to either the true dynamic blanks (“blank.1” and “blank.2”) or the DPF blanks (“DPF1.1”, “DPF1.4”, etc.), as there were instances in both blank categories w/ relatively high (e.g., “blank.1” and “DPF1.14”) and low (e.g., “blank.2” and “DPF1.10”) SOA formation.

The variability in NMOG is not possible to calculate because it is below the detection limit for 6 of the 9 DPF blanks and the 2 dynamic blanks. For the last three DPF blanks (DPF2.8, DPF2.7, DPF2.12) the median NMOG (12 mg/kg) is about a factor of 30 smaller than the NMOG from the cleanest cold-start experiment (LEV2-5.1, 409 mg/kg). Hence, both the median and the variability in NMOG for the blanks are negligible in comparison to the vehicle experiments.

Page 23191 line 22 – The statement “Vehicle emissions are mainly composed of saturated species” is not supported by reference and contradicts the data in Figure 3 that shows unsaturated hydrocarbons (e.g. single-ring aromatics) are 20-26% of NMOG emissions.

Figure 3 shows that vehicle emissions are composed of 20-26% of speciated SOA precursors, not unsaturated HCs. The complete list of the compounds included in the “speciated SOA precursor” class is provided in the SI. While it is true that this list includes a number of aromatics and unsaturated HCs, a large percentage of the compounds is alkanes. The emissions profile of Schauer et al. ("Measurement of Emissions from Air Pollution Sources. 5. C1–C32 Organic Compounds from Gasoline-Powered Motor Vehicles." *Environmental Science & Technology* 36(6): 1169-1180. 2002) also shows the large contribution of branched alkanes to vehicle emissions.

Figure 5 – What does it mean if the effective SOA yield is greater than 100%? From section 3.3, it appears that this means that an impossible fraction of organic emissions must be converted to SOA to explain the chamber data.

Yes, the reviewer’s interpretation is correct. Effective SOA yields greater than 100% in Figure 7 indicate that speciated SOA precursors alone are incapable of explaining the observed SOA. That is why we invoked the second SOA yield case in which we include the unspeciated NMOG as a SOA precursor. When unspeciated NMOG is included, the SOA yields are more realistic (i.e., more comparable to SOA yields from single precursor lab studies).

Missing details

Page 23179 line 5, please list the names of “basic gases” that were measured.

We state in lines 6-9 that total hydrocarbons, methane, CO and CO₂ were measured and describe the techniques used to measure them. We neglected to include a description of our NO_x measurement. We have added the following: “...NO_x by chemiluminescence and carbon monoxide...”

Equation 1, what MW was used for NMOG and why?

The gas chromatography measurements from CARB provided the NMOG in ppmC, so the molecular weight used in our calculations was 14, the MW of the CH₂ group. Note that in most cases the CO and NMOG terms in Equation 1 were negligible (<1% of carbon emissions). For a few of the older vehicles with incomplete combustion these terms were modestly more important but still <10% of carbon emissions.

Are data in Figure 5 blank subtracted?

No, and we now state in the caption of Figure 5, “Measured wall-loss-corrected SOA concentration (assuming no blank correction)...” We also state in the text (lines 19-21, p. 23188): “The average wall-loss-corrected SOA mass (assuming no blank correction) for all the cold-start UC chamber experiments plotted in Fig. 5a is $12 \pm 8.4 \mu\text{g m}^{-3}$ which is within the range of typical urban PM concentrations.”

Why are DPF experiments used as background in the study of LDGV?

In order to increase the sample size of our blanks we included the DPF experiments. We believe that this choice was justified because the emissions from these vehicles were cleaner than ambient L.A. air. We state on p. 23188, “Both primary particle and NMOG emissions from the hot-start DPF-equipped vehicle experiments were extremely low, often below ambient levels.”

The equation used to calculate the effective SOA yields and mass closure should be included in the body of the main document, in section 3.3.

We now include this as Equation 2, shown below.

$$Y = \frac{M_{SOA}}{\sum M_{VOC_{reacted}}} = \frac{M_{SOA}}{\sum (M_{VOC_i}) \cdot (1 - \exp(-k_i[OH]t))}$$

where M_{SOA} is the mass of SOA produced, t is photo-oxidation time and M_{VOC_i} , k_i and $[OH]$ are the mass, OH reaction rate of the i th VOC and OH concentration at time t .

Suggestions to improve clarity

Page 23182 lines 7-8 “the measured mass fraction of carbon in the gasoline was 0.85 kg-C kg-fuel-1 (Table S3).”

Done.

Page 23182, line 26: “the measured loss of sulfate seed particles.”

Done.

Page 23193, line 18 “the percentage of organic emissions”

Done.

References

1. Lupescu JA, Chanko TB, Richert JF, & Mauti AA (2009) The Effect of Spark Timing on Engine–Out Hydrocarbon Speciation and Hydrocarbon Trap Performance. *SAE Int.* (01-1068).
2. Russ S, Thiel M, & Lavoie G (1999) SI engine operation with retarded ignition: Part 2-HC emissions and oxidation. *SAE transactions* 108(4):1532-1538.
3. Kummer J (1975) Oxidation of CO and C₂H₄ by base metal catalysts prepared on honeycomb supports. *Adv. Chem. Ser* 143:178.
4. McCabe RW, Siegl WO, Chun W, & Perry J (1992) Speciated Hydrocarbon Emissions from the Combustion of Single Component Fuels. II. Catalyst Effects. *Journal of the Air & Waste Management Association* 42(8):1071-1077.