Response to Reviewer Comments on “Emission factor ratios, SOA mass yields, and the impact of vehicular emissions on SOA formation” by Ensberg et al. 2013

We thank the reviewers for providing thorough and insightful comments. We have addressed each comment below, and we feel the quality of the manuscript has improved substantially. Our original analysis assumed that unburned fuel in exhaust emissions is the dominant source of newly formed SOA attributable to vehicular activity. However, Shantanu Jathar and Timothy D. Gordon brought to our attention their recent work which suggests products of incomplete combustion and products of incomplete catalytic converter oxidation may be efficient SOA precursors. Because these data are especially germane to the subject of the present paper, and because we have had extensive discussion with them regarding the incorporation of these data into the manuscript, Shantanu Jathar, Timothy D. Gordon, and Allen L. Robinson have been added as authors of the paper. For the convenience of the editor, we include here the response to the original Short Comment by Shantanu Jathar and Timothy D. Gordon.

Color scheme:

1. Reviewer comments are written in this color. Anonymous reviewers are given the designation R1, R2, etc, and Short Comments are given the designation S1, S2, etc. Each comment is designated with its own number (e.g. first comment from anonymous reviewer 1 and short comment 1 is R1.1 and S1.1, respectively.)
2. Responses to reviewer comments are written in this color.
3. **Text that has been added to the manuscript in response to a reviewer comment is written in this color.**

Anonymous Reviewer 1 (R1):

R1.0 General Comment:

The paper by Ensberg et al. is a well-organized and well-written paper addressing one of the standing issues in urban secondary organic aerosol (SOA) formation. The paper is motivated by lack of a closure between modeling and measurements of SOA as well as recent contradictory findings on the contribution of diesel and gasoline emissions to urban SOA. The paper provides an overview of the recent research in this area and, more importantly, explores some of the plausible reasons for discrepancies in the recently published work related to these two issues. The analysis indicates that uncertainties in the emission factors, drive-cycle dependent emission ratios, or addition of non-vehicular emissions are not enough to explain the observed enhancements in OOA/CO ratios. Conclusions of the paper are that 1) SOA mass yields are significantly higher in the ambient compared to the laboratory, and/or 2) anthropogenic fossil activity other than vehicular emissions contribute significantly to SOA in Southern California. This analysis is highly valuable since the approach taken to address urban SOA formation is different than those of the recent published work and it improves understanding of urban aerosol formation in the Los Angeles Basin. I support its publication in ACP after the following minor comments are addressed.

Specific Comments:

R1.1 Figure 2. When using yields from Figure 2c in the analysis, the assumption is that fuel composition and vehicular exhaust composition are similar. What is the basis for that?

Gentner et al. (2012) validated the assumption that the chemical composition of the non-combusted portion of tail-pipe exhaust is equivalent to liquid gasoline using extensive diagnostics and the chemical mass balance model (See Figures S1-S4 of Gentner et al. 2012). However, Gentner et al. (2012) did not include in the analysis the partially combusted fraction of tail-pipe exhaust on the assumption that these species are not effective SOA precursors. Recent work by Jathar et al. (2013) and Gordon et al. (2013) suggests, in fact, that partially combusted hydrocarbons may be important SOA precursors. We have conducted additional analysis based on the emission factors and aggregate SOA mass yields reported in Jathar et al. (2013) and Gordon et al. (2013), which include products of incomplete combustion and incomplete catalytic converter oxidation. As discussed in the response to S3.1-S3.2, the original conclusions of Ensberg et al. (2013) remain the same.

R1.2. Are the SOA yields plotted in Figure 2b based on yields when all of the parent hydrocarbon in the chamber is used up or do they account for contribution of 2nd generation products as well?

From Supplemental Section 2.3 of Gentner et al. (2012):
"Our derived SOA yields are intended to model the first several generations of photochemical oxidation, which corresponds to the extent of oxidation effectively constrained by experimental measurements. It is highly plausible that the continued increase in ΔOA/ΔCO ratios beyond our predictions is caused by the continued oxidation of multi-generation oxidation products in the gas-phase. In this study, we have refrained from estimating SOA yields for these highly-aged air masses as doing so would require excessive extrapolation with high uncertainties. A re-evaluation of gasoline and diesel SOA yields is encouraged once these data become available."

We have added the following sentence to the manuscript for clarity:

"Based on the level of oxidation effectively constrained by experimental measurements, the SOA mass yields reported by Gentner et al. (2012) are expected to be representative of the first several generations of photochemical oxidation."

R1.3. Are all the errors (e.g., in Eq. 11, 13, 14, etc) propagated uncertainties from each element?

We are not exactly sure what is meant by "each element". The errors in equations 11-14 are based on ~40% total errors in the emission factors (EF_gas,co, EF_dies,co, EF_gas,gpom, EF_dies,gpom), which have been propagated through the relevant arithmetic equations.

R1.4. As I understand, [OH]~1.5×10^6 molecule cm^{-3} is needed to get to the mentioned exposure of ~58.3×10^9 molecule cm^{-3} s for 0.45 day photochemical age. Considering that most of the vehicular emissions are during the day, shouldn't a higher average OH be considered that is more typical of daytime OH in the summer? This would result in a higher fraction of VOCs reacting in 0.45 days and a lower required SOA yield.

The OH-exposure (integral of OH and exposure time) is the relevant quantity for calculating the fraction of the GPOM that has reacted (e.g. frac = (1 - exp(k* OHexp)), and not the average OH concentration. The average concentration is only used to calculate the correspondence between photochemical age and actual age as needed. Since the OH-exposure is fully constrained by the evolution of the benzene/trimethyl-benzene ratio, assuming a different OH concentration will not impact our results. We chose a value of OH to be 1.5×10^6 molec/cm^3 so that we could create a photochemical age (in days) for reference, and since that same value has been used in many previous studies and is close to daily average values during CalNex, as already mentioned in the text. We have added the following sentence to the manuscript for clarity:

"Note that the OH-exposure, which is fully constrained by the measured evolution of the benzene/trimethyl-benzene ratio, is the only quantity needed for calculating the fraction of VOC that has reacted (e.g. frac = (1 - exp(k × OH-exposure)). Therefore, choosing a different OH radical concentration will not influence our results because the OH exposures remain the same."

R1.5. On p 27793, lines 18-26: authors provide some evidence that indicate vehicular emissions dominate the anthropogenic reactive hydrocarbons in the LA Basin. Why do they conclude then that vehicular emissions might not dominate SOA formation in the area (line 9-10 on P. 27795)?

We mentioned in the manuscript "Although this is not proof, the linear decrease in normalized NMHC concentrations with photochemical age, and the similarity between estimated emission ratios are both consistent with vehicular exhaust being the dominant source of these compounds." It is also possible that a fraction of the light aromatics and C6,C9-11 alkanes originated from different anthropogenic sources that are located in the same general areas as on-road vehicular emissions. Also, since we did not include the larger alkanes (>C12), nor did we include any oxygenated compound emissions, we cannot rule out the possibility that non-vehicular emissions are contributing significantly to the SOA budget in L.A.

R1.6. On. P. 27785, it's indicated that 90% of gasoline and diesel fuel has been identified by recent analytical work. Couldn't the 10% unidentified components of fuel contribute to the unmeasured components of vehicle exhaust which can form SOA?

Additional analysis based on recent smog chamber work by Gordon et al. (2013) and Jathar et al. (2013) suggests that this is not an issue. Specifically, Jathar et al. (2013) showed that unburned diesel fuel and combustion tail-pipe exhaust from diesel-fueled vehicles have similar SOA formation potentials. As shown in Figure 4 of Jathar et al. (2013), the experimentally derived aggregate SOA mass yields for diesel exhaust are very similar to the value reported by Gentner et al. (2012) (Y_{dies} = 15%). With respect to gasoline, Gordon et al. (2013) measured SOA/ΔCO in a smog chamber from tail-pipe exhaust emissions from 15 light-duty gasoline vehicles (LDGVs) taken from the California vehicle fleet. These SOA/ΔCO enhancement measurements are still well below the SV-OOA/ΔCO enhancements measured during CalNex. Since these results are not influenced by the uncertainty associated with the emission factors and aggregate SOA mass yields reported by Gordon et al. (2013) and Gentner et al. (2012), we conclude that the concern raised by the reviewer is not an issue. See response to S3.1-S3.2 for additional details.

Anonymous Reviewer 2:

R2.0 General Comment:
This paper provides an excellent and comprehensive analysis of the combined implications of several measurement and modeling studies of Organic aerosol in the Los Angeles basin, a large metropolitan area with a long record of air pollution issues that are related almost entirely, it is thought, to vehicle emissions. What this paper has done that is novel is to use the large number of measurements provided by a recent multi-million dollar study, along with inventory and regulatory data, to assess whether this is true, and if it is, whether the contributions from diesel and gasoline can be quantified. I am a bit disappointed that it has not generated as much online discussion as I had expected (given the offline discussions that I have heard), as that would have allowed the authors to expand more on many of the underlying limitations of their analysis. I support publication of this paper in ACP. The concise style of the paper is great for brevity, but there are a number of minor points that the author could address in a slightly extended revised version (rather than the present Science-like format) that would provide more context and literature comparisons, especially for their somewhat unexplained adoption of the unpublished Zotter result as a starting point.

Specific Comments:
R2.1. I find the abstract organization is a bit awkward, since it first states that the paper will quantify the diesel and gas fractions and then concludes that large fractions of OA may not be from vehicles at all. Since the latter seems to be a prerequisite for the former's answer to be important, I'd suggest rearranging the order to make it clear that while the initial point of the paper had been to separate the contributions of gas and diesel, in the end the paper could not establish the fraction that was from vehicles (in total) well, and hence the uncertainty of the diesel/gas contributions is large and/or can only be quantified relative to each other.

We have rewritten a large portion of the abstract so that the emphasis is now on identifying the source of the gasoline/diesel discrepancies and modeling underpredictions. The updated abstract is:

"The underprediction of ambient secondary organic aerosol (SOA) levels by atmospheric models in urban areas is well established, yet the cause of this

underprediction remains elusive. Likewise, the relative contribution of emissions from gasoline- and diesel-fueled vehicles to the formation of SOA is generally unresolved. We investigate the source of these two discrepancies using data from the 2010 CalNex experiment carried out in the Los Angeles basin (Ryerson et al., 2013). Specifically, we use gas-phase organic mass (GPOM) and CO emission factors in conjunction with measured enhancements in oxygenated organic aerosol (OOA) relative to CO to quantify a significant lack of closure between expected and observed organic aerosol concentrations attributable to fossil activity. Two possible conclusions emerge from the analysis to yield consistency with the ambient data: (1) vehicular emissions are not a dominant source of anthropogenic fossil SOA in the Los Angeles basin, or (2) the ambient SOA mass yields used to determine SOA formation potential of vehicular emissions are substantially higher than those derived from laboratory chamber studies."

R2.2. I think the most original aspect of this paper is the use of the dual constraints of the matched yields and propagated errors that are implied by the gas/diesel split. Since this is a subtle and new (for this issue) point, some additional explanation could be merited so that the approach may be more easily interpreted and repeated (and cited) by others.

We are not sure what additional explanation can be added. The approach consists of plotting two quantities (in our case, required and predicted SOA mass yields as functions of fuel usage), and identifying where the quantities intersect as well as where their respective error bars intersect. We feel this is explained clearly in the text. Therefore, we have not modified the manuscript in response to this comment.

R2.3. While it is clear in the manuscript that the study is for LA, it would be instructive and useful for the authors to provide some comparative information about the extent to which similar conditions may/not exist for other metropolitan areas, or at the very least by including the comparison to identify why these results cannot be extrapolated to other areas for which such detailed information and inventories do not yet exist.

We have added the following text to the conclusions section of paper to address this point:

"Ratios of OOA/ΔCO for Mexico City and the Northeast US are similar to or smaller by about a factor of 2 than those observed in LA, as reported by Hayes et al. (2013). Ratios of NMHC/ΔCO for emissions in the Northeast US are very similar to those in the LA area (Borbon et al., 2013), while those in Mexico City are higher by about a factor of 2 (Bon et al., 2011). Therefore similar qualitative discrepancies between predicted and required SOA yields, albeit of somewhat lower magnitude, may exist in these urban areas as well."

R2.4. I think Referee #1 had an important point, and I think that a response that clarifies this point would improve the paper. Has the uncertainty in the 0.45 days value been explored?

Please see response to R.1.4.

R2.5. Section 3.2.1 – how is a “significant contribution” defined?

We have rephrased that text from:

“...in order for vehicular emissions to make a significant contribution to the measured anthropogenic fossil OOA budget, at least one of the following must be true...”

to

“...if the SVOOA/ΔCO enhancements shown in Figure 1C are primarily attributable to vehicular emissions, at least one of the following must be true...”.

R2.6. The authors have used “county” fuel sales; what is the uncertainty associated with this assumption? Are these month totals for June 2010? What is the contribution from fuel in non-LA counties?

These numbers are based on annual fuel sales. With respect to the contribution from non-L.A. counties, Ventura county (12.8% diesel), Los Angeles county (13.2% diesel), and Orange county (10.7% diesel) all have comparable gasoline/diesel fuel sales fractions. Counties downwind of L.A. county have higher diesel fuel sales (e.g. Riverside = 21.4%, San Bernardino = 23.7%), but flow from those areas into Pasadena during the daytime periods that dominate fossil SOA is unlikely due to very consistent wind directions during daytime (e.g. Washenfelder et al., 2011). Therefore the uncertainty associated with this fraction is small for our study. Furthermore, as shown in the analysis presented in our response to S3.1-S3.2 (first figure), large discrepancies exist at virtually all gasoline/diesel splits.

Washenfelder, R. A., et al. (2011), The glyoxal budget and its contribution to organic aerosol for Los Angeles, California, during CalNex 2010, J. Geophys. Res., 116, D00V02, doi:10.1029/2011JD016314.

R2.7. The authors have done a reasonable job of estimating EF uncertainty, but it should be noted that Tables 4-6 are not complete, and there is not “closure” of the compounds for which EF are tabulated and the measured total SV/LV OOA. So the conclusion that SOA yields must be higher than modeled can mean either that compounds are missing (that have non-zero yields) or that the compounds that are included in the models have higher than currently modeled yields. The uncertainty for the missing compounds is more difficult to estimate, especially using tunnel studies not conducted in LA driving conditions.

As discussed in our response to R1.6 and S3.1-S3.2, this issue does not influence the conclusions of Ensberg et al. (2013). Based on the results presented in Gordon et al. (2013), it seems likely that catalytic converters remove a significant fraction of the non-methane hydrocarbons (NMHCs), but not all, and that the ones they leave behind have higher nominal SOA yields. What may be occurring is that catalysts convert many NMHCs into partially oxidized species which are no longer measurable by GCMS and similar total HC analyzers (that also use a GC). Therefore, it is plausible that a considerable fraction of the gas-phase organic compounds in tail-pipe exhaust are not measured by either Gordon et al. (2013) or Gentner et al. (2012), which is why the "apparent yields" (delta SOA/ delta NMHC) reported by Gordon et al. (2013) are so high. However, this explanation is clearly speculative at this point since we don't have such measurements.

R2.8. Figure 3. I think the “required” Aggregate SOA Mass Yield is from measurements, right? Specifically, 70% of SVOOA based on Zotter/Hayes? This should be clarified in caption. If so, it would be good to repeat both the assignment and uncertainties mentioned by Hayes/Zotter in determining that SVOOA was “fossil-vehicle SOA”.

See response to comment R2.9. Also, we have added the following text to the caption in Figure 3:

“Required yields are based on SV-OOA measurements and ^{14}C measurements reported in Zotter et al. (2013); Hayes et al. (2013)”

R2.9. Perhaps other methods for quantifying fossil SOA should be considered, especially if the Zotter paper is, as listed in the references, still not published. I recommend holding publication of this paper until that critical reference is accepted for publication. Moreover, the authors would be more circumspect to include explicit consideration of other approaches for quantifying fossil SOA, given the substantial uncertainty.

The Zotter paper is currently under revision for JGR.

To our knowledge the ^{14}C method is the only method which can directly determine fossil and non-fossil carbon in organic aerosols, therefore we consider it to be the most reliable starting point. Note that the discrepancy identified in this study will only become more pronounced if, because of uncertainties associated with ^{14}C analysis, more of the OOA factor is actually attributable to vehicular emissions.

R2.10. P. 27795 conclusions “vehicular emissions do not dominate SOA concentrations attributable to anthropogenic fossil activity in Southern California”: I think what is meant here (if above interpretation is correct) is that the amount of SVOOA that is fossil is not as large as stated/implied by Hayes et al. (if that paper is interpreted to say that all SVOOA is fossil SOA). I think it is worth clarifying that this conclusion may be specific to the AMS-PMF method of identifying fossil SOA.

The interpretation of this point by the reviewer is incorrect. Hayes et al. (2013) interpreted SV-OOA as being dominated by urban emissions, some fraction of which are non-fossil, e.g.

from cooking sources. Zotter et al. interpret SV-OOA in this way as well, and uses the ^{14}C measurements to apportion SV-OOA between fossil and non-fossil sources. Since ^{14}C measurements are needed for the apportionment, there is no such thing as an “AMS-PMF method of identifying fossil SOA.” Therefore, there is no need to modify the paper in response to this comment.

R2.11. A similar point is that this approach assumes that emissions from different sources do not interact, i.e. that the emissions of non-vehicle sources do not affect the yields of vehicle sources. This independence underlies the use of single-reactant yields in models, but there is certainly both some laboratory and theoretical evidence to suggest that it may not be sufficient to understand cities as complex as LA.

We are indeed making this assumption, and the text below has been added to make it explicit in the revised paper. We are, however, unsure to which evidence the reviewer may be referring to that may suggest otherwise. To our knowledge when multiple anthropogenic compounds have been studied the yields have been consistent with those of the individual compounds (e.g. Odum et al., 1996; 1997). The added text is:

“We implicitly assume that the yields from Gentner et al., which were mostly obtained from experiments with individual compounds, apply to the complex LA atmosphere, consistent with the limited evidence available for complex precursor mixtures (e.g. Odum et al., 1996; 1997).”

R2.12. Aren’t there also non-fossil sources of CO? How are these accounted? How does this affect the Zotter result?

The Zotter paper does not use CO measurements to reach its conclusions. Those are used in Hayes et al. (2013) and the present work to study OA components and their evolution with photochemical age. Since the background is subtracted, only urban CO sources are relevant. In terms of non-fossil sources of CO, oxidation of biogenic species or other non-fossil VOCs in the basin is one such source, but these are estimated to contribute to ambient CO concentrations minimally (Griffin et al., 2007) and are therefore neglected here. Cooking is not considered an important source of carbon monoxide [Allan et al., 2010; California Air Resources Board, California emission inventory data, 2008, http://www.arb.ca.gov/ei/emsmain/emsmain.htm; Harley et al., 1997]. We have added the following text to the paper in response to this point:

“CO emissions in Los Angeles are attributable almost exclusively to vehicular emissions (Griffin et al., 2007, http://www.arb.ca.gov/app/emsinv/emssumcat.php), with minor contributions from cooking and oxidation of biogenic emissions (Hayes et al., 2013, Allan et al., 2010).

Short Comment by Shantanu Jathar and Timothy D. Gordon:

S3.0 General Comment:
Ensberg et al., present a novel approach combining both bottom-up and top-down measurements to determine the relative importance of gasoline and diesel emissions to SOA formation in the South Coast Air Quality Basin. Although their methodology appears robust, we would like to express a few concerns about their input data. We focus specifically on (1) the gas-phase organic matter (GPOM) emission factors and (2) the SOA yields that are used. Revising these data in accordance with the recently reported values quoted below may impact the authors' conclusions.

Specific Comments:
S3.1. The authors use 0.45±0.18 g GPOM (Lgas)-1 and 1.01±0.40 g GPOM (Ldiesel)-1 as base GPOM emission factors. The gasoline base value is low by factor of two compared to estimates derived from the California ARB's EMFAC emissions model and estimates from a recent test campaign comprising 64 gasoline vehicles (model years 1987-2012). In addition, the diesel base value is high by about 30% compared to estimates from a recent test campaign comprising 5 medium- and heavy-duty diesel vehicles. GPOM emissions from EMFAC for diesel vehicles are comparable or even lower than those from the recent experiments.

a. We used EMFAC 2011 to look at annual statewide totals of ROG (exhaust) from on-road gasoline vehicles in California (categories: LDA, LDT1/2, LHD1/2, MDV). We find that ROG (exhaust) emission factors for pre-LEV, LEV1 and LEV2 vehicles are 7.5, 1.1 and 0.117 g (Lgas)-1 respectively. When considered together the ROG (exhaust) emission factor is 1.05 g Lgas-1, which is more than twice the base value used in their work.

b. Recent work by Carnegie Mellon University on on-road gasoline vehicles (1, 2) reports median emission factors for non-methane organic gases (NMOG) of 4.5, 1.3 and 0.4 g (Lgas)-1 for pre-LEV, LEV1 and LEV2 vehicles, respectively. These data agree closely with emissions data from the Kansas City Study (3). According to EMFAC 2011 pre-LEV, LEV1 and LEV2 vehicles consume 7, 36 and 57% of gasoline, respectively—from which we calculate a fleet average NMOG emission factor of 1.01 g (Lgas)-1. This value is, again, more than twice the base value used by Ensberg et al.

c. May et al. recently measured GPOM emissions of 1.0 and 0.003 g (Ldiesel)-1 for DPF- and non-DPF-equipped heavy-duty diesel vehicles (4). Combining these values with the fractions of DPF- and non-DPF-equipped heavy-duty diesel vehicles in the South Coast Air Basin (69% and 31%, respectively) we calculate a fleet average GPOM of 0.69 g (Ldiesel)-1, which is about 30% less than the base value used by Ensberg et al. May et al. also show that the GPOM from EMFAC is ~0.6 g (Ldiesel)-1.

We suggest that the authors increase their gasoline GPOM base value to 1.0 g Lgas-1 and reduce their diesel GPOM base value to 0.69 g (Ldiesel)-1.

This analysis has been added to the manuscript. Here we note that the suggested value of EFnmog,gas = 1.01 g NMOG L-gas^{-1} includes all species, including speciated non-SOA precursors (Gordon et al., 2013). Also, based on the results presented in Gordon et al. (2013), a similar calculation for the fleet-average CO emission factor yields:

EFco,gas = 21.6 g CO L-gas^{-1}

Note that the EFco,gas is ~50% larger than the value reported by Gentner et al., 2012 (EFco,gas = 14.7 g CO L-gas^{-1}). We will add a sensitivity analysis that includes the proposed diesel emission factor (EFnmog,dies = 0.69 g NMOG (L-diesel)$^{-1}$).

S3.2. The authors used the work of Gentner et al. (5) to determine SOA yields for gasoline and diesel emissions. Gentner et al. (5) used the compositions of the fuels and published SOA yields of individual compounds to determine the SOA formation from gasoline and diesel fuel. Recently, Jathar et al. (6) conducted smog chamber experiments and measured SOA yields for unburned gasoline and diesel. We suggest that Ensberg et al. use the experimentally measured SOA yields (and the associated uncertainty) to estimate SOA yields for gasoline and diesel emissions.

Furthermore, we have argued elsewhere that combining SOA yields of individual fuel components is not always an accurate surrogate for the SOA yields of combustion emissions (7). Following Gentner et al. (5), the authors assume that the SOA potential of on-road gasoline emissions is similar to unburned gasoline, i.e. the SOA yields are 0.023±0.007. Gordon et al. (2) show (in Figure 7) that the SOA yields for pre-LEV vehicles are similar to those from unburned gasoline but those for LEV1 (6-30%) and LEV2 (15-50%) vehicles are much higher. Jathar et al. (6) capture this same result in Figure 4 of their publication and suggest that unburned gasoline should not be used as a model-system to estimate SOA formation from on-road gasoline emissions. We suggest that the authors use these experimentally measured yields (in addition to those proposed by Gentner et al. (5)) to re-do the analysis (Figure 3) and re-evaluate their conclusions accordingly.

We have conducted the following analyses, which have been added to the manuscript, using the emission factors and SOA mass yields reported in Gordon et al. (2013). We first calculate a fleet-average LDGV NMOG emission factor based on the values reported by Gordon et al. (2013):
EF_preLEV,nmog = 4.5 g NMOG L-gas^{-1}
EF_LEV1,nmog = 1.3 g NMOG L-gas^{-1}
EF_LEV2,nmog = 0.4 g NMOG L-gas^{-1}

EFnmog,gas =0.07*EF_preLEV,nmog +0.36*EF_LEV1,nmog +0.57*EF_LEV2,nmog

EFnmog,gas = 1.01 g NMOG L-gas^{-1}

Note that this EFnmog,gas includes all NMOG emissions, including speciated non-SOA precursors. Similarly for CO:

EFco,gas = 21.6 g CO L-gas^{-1}

To facilitate a consistent comparison with the analysis presented in Gentner et al. (2012), the SOA mass yields presented in Gordon et al. (2013) have been rescaled based on the total NMOG tail-pipe emissions and not the fraction of NMOG emissions that is expected to be comprised of SOA precursors. Therefore, the SOA mass yields used in this analysis are roughly half as large as those reported in Figure 7 of Gordon et al. (2013).

From Gordon et al.:
Y_preLEV = (2%)×(0.38 g SOA precursor /g NMOG) = 0.8%
Y_LEV1 = (6%-33%)×(0.51 g SOA precursor /g NMOG)=10% (average, (3%+16%)/2)
Y_LEV2 = (15%-50%)×(0.49 g SOA precursor /g NMOG)=16% (average, (7%+25%)/2)

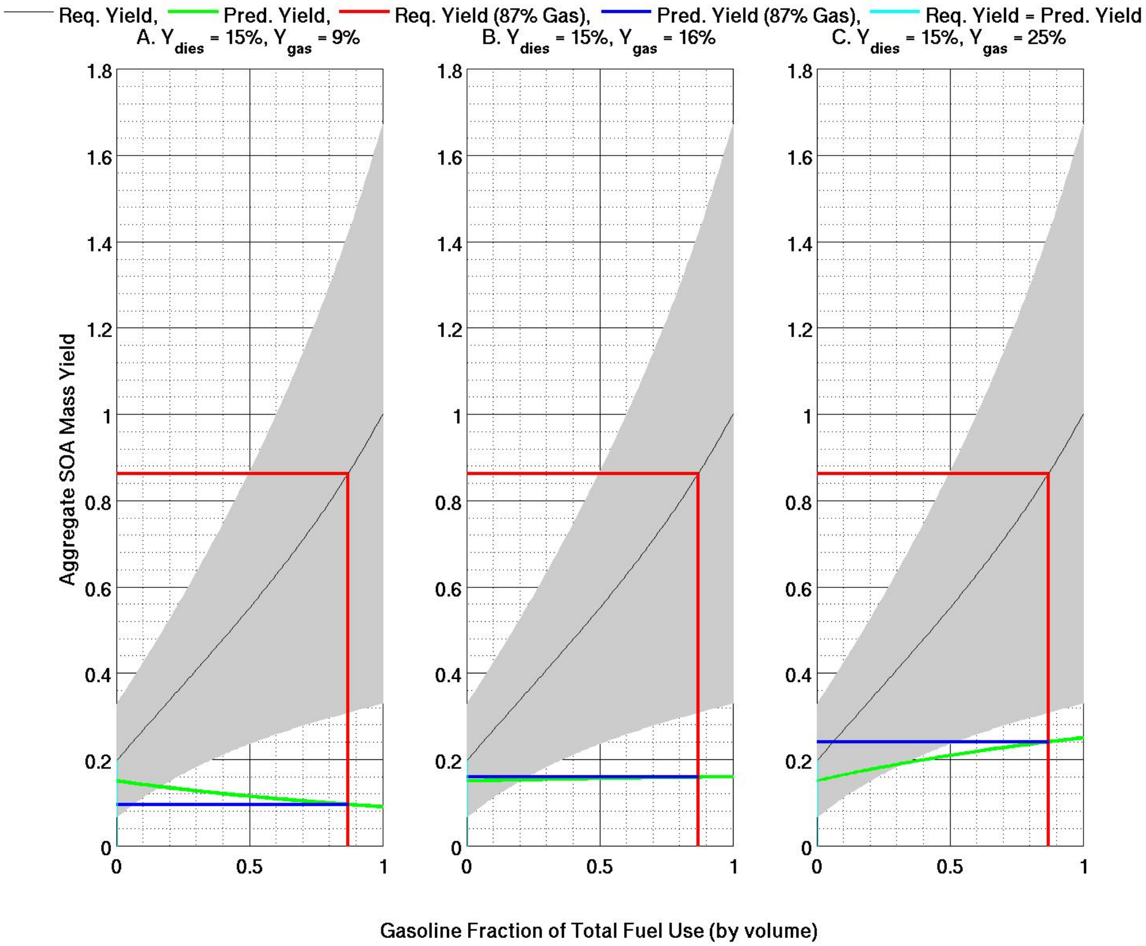
where the SOA-precursors/NMOG conversion factors are taken directly from Figure 3 of Gordon et al. (2013). Using these values, a fleet-average SOA emission factor can also be approximated:

EF_fleetSOA,gas = Y_preLEV*0.07*EF_preLEV,nmog +Y_LEV1*0.36*EF_LEV1,nmog + Y_LEV2*0.57*EF_LEV2,nmog

Y_fleet,gas = EF_SOA,gas / EFnmog,gas = 9%

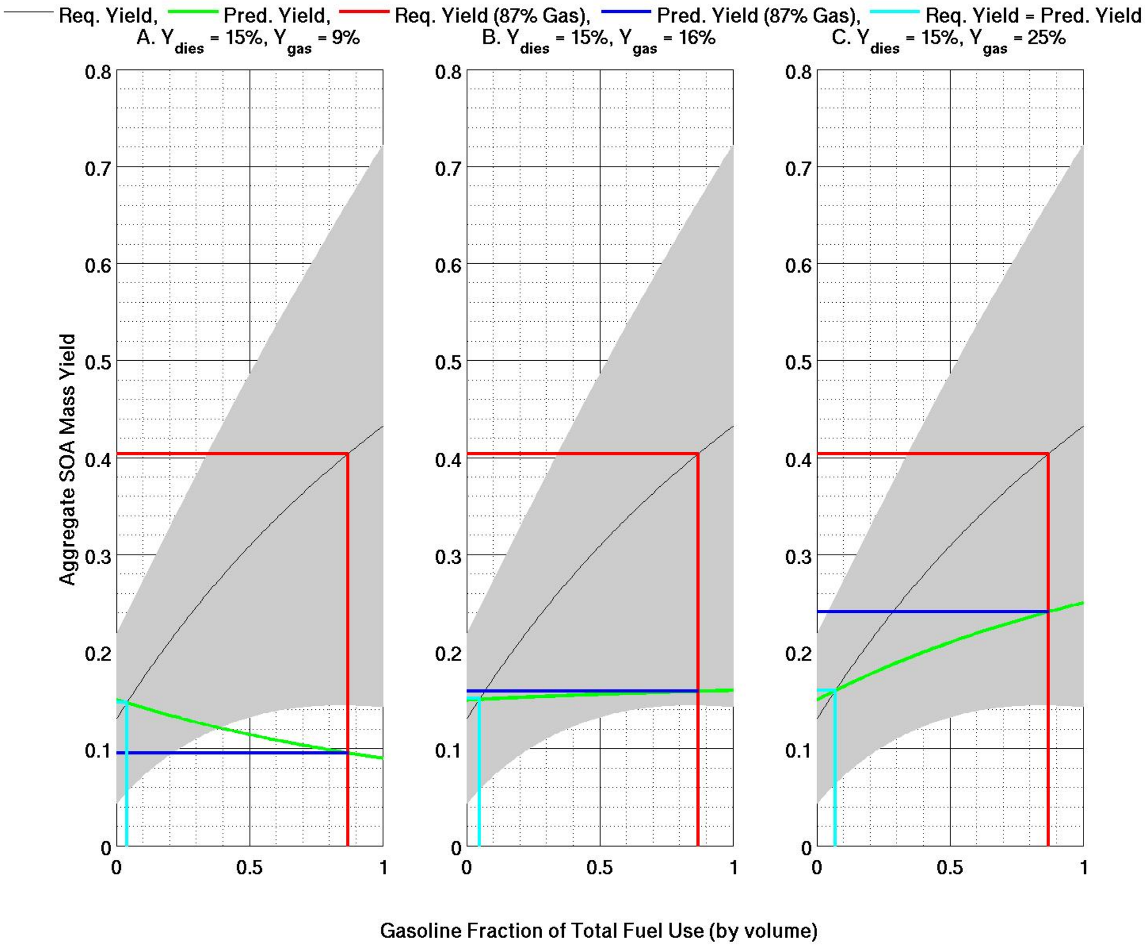
This yield is roughly 4 times larger than the yield for liquid gasoline reported by Gentner et al. (2012).

To account for the uncertainty associated with the SOA yield scaling technique used above, and to determine the upper limit of the SOA formation potential of gasoline vehicles, we have conducted similar analyses assuming Ygas = 16% and Ygas = 25%, which are the upper limits of the LEV1 and LEV2 vehicle classes, respectively, reported by Gordon et al. The resulting panels are:



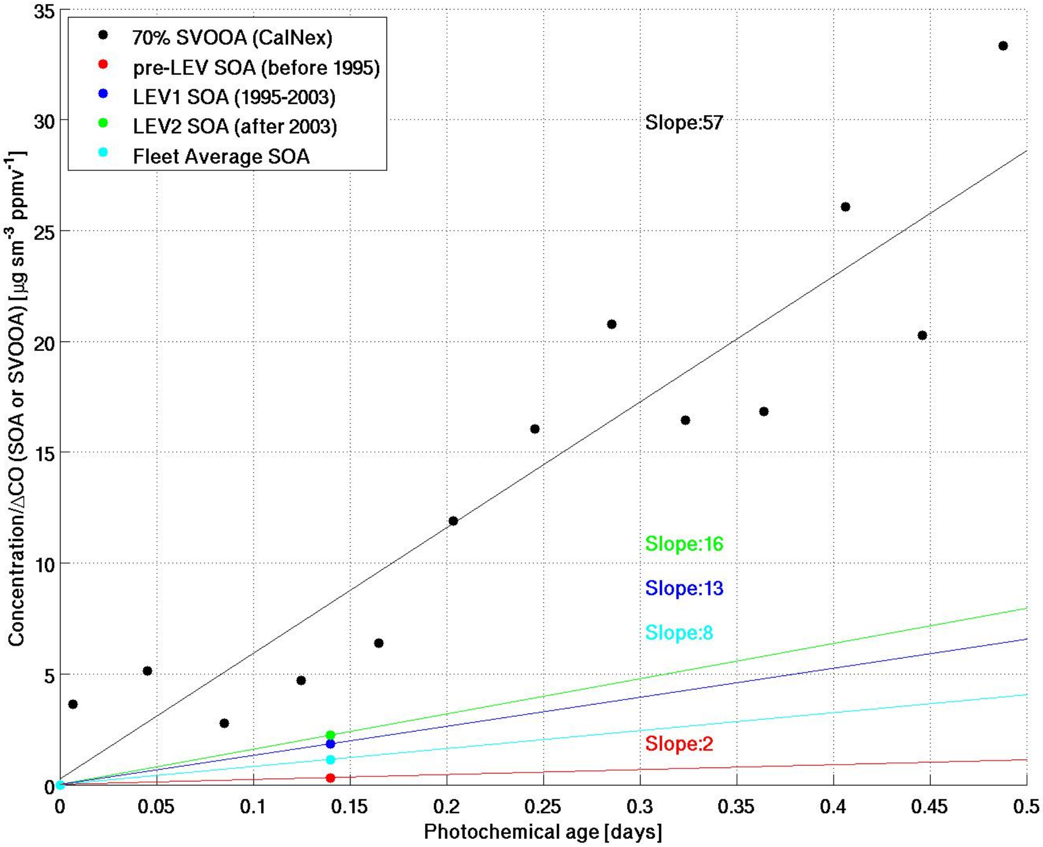
Since the impact of predicted yield uncertainty is demonstrated via sensitivity analyses, the predicted-yield error bars are excluded from this figure. The results presented in subplot (A) of this figure are qualitatively identical to those presented in Figure 3 of Ensberg et al. (2013). Furthermore, although the agreement is slightly better in subplots (B) and (C), the predicted and required yields still differ by more than factor of 3 even when using the highest yields reported Gordon et al. Also note that at no fuel usage do the actual predicted and required yields intersect.

To account for the uncertainty associated with calculating the fraction of emitted NMOG that has undergone chemical reaction after 0.45 days of photochemical aging, an additional sensitivity analysis was conducted in which 100% of the emitted NMOG is assumed to have reacted. The resulting panel is:



As shown in this figure, assuming 100% conversion of NMOG effectively reduces the required SOA mass yields by a factor of ~2. The predicted yields shown in subplot (C) of this figure are still lower than the required yields by a factor of ~1.7. We emphasize that there is a significant lack of closure between expected and observed organic aerosol concentrations attributable to fossil-fuel emissions even when assuming 100% NMOG conversion and an LDGV fleet-averaged SOA mass yield of 25%. Both assumptions are expected to be very unrepresentative of ambient conditions in California.

A more straightforward way to assess the impact of partial combustion and incomplete catalytic conversion on SOA formation from gasoline exhaust is to compare the SOA/ΔCO enhancement ratios measured by Gordon et al. (2013) directly to the SV-OOA/ΔCO enhancement ratios measured at the Pasadena ground site during the CalNex field campaign:



As shown in this figure, the SOA/ΔCO enhancements for all three LDGV vehicle classes are lower than the CalNex measured value at 0.14 days of photochemical aging. Average SOA/ΔCO enhancement slopes (units μg SOA m^{-3} /ppmvCO/day) are calculated for each vehicle class by extending a straight line from the origin through the measured data points. As shown in the figure, the average SVOOA/ΔCO enhancement slope (57 μg SVOOA m^{-3} /ppmvCO/day) is ~7 times larger than the fleet-average SOA/ΔCO enhancement slope (8 μg SOA m^{-3} /ppmvCO/day), and ~ 3.5 times larger than the LEV2 vehicle class slope. Note that the results presented in this figure are self consistent, and therefore are not influenced by the uncertainty associated with the emission factors and aggregate SOA mass yields reported by Gordon et al. (2013) and Gentner et al. (2012). However, they are susceptible to other factors. For instance, Gordon et al. (2013) do not account for loss of organic vapors directly to chamber walls (Matsunaga and Ziemann, 2010). Although highly uncertain, as acknowledged by Gordon et al. (2013), accounting for vapor-phase wall loss would increase their estimated SOA production.

Based on this analysis, a robust conclusion is that either the SOA mass yields for vehicular tail-pipe exhaust are significantly higher than what has been recently reported, or non-vehicular source categories contribute significantly to the anthropogenic fossil OOA budget measured at the Pasadena ground site. For the latter possibility to be true, the non-vehicular fossil emissions must be comprised of compounds other than those listed in Table 6.

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