

Interactive comment on “Secondary organic aerosol formation exceeds primary particulate matter emissions for light-duty gasoline vehicles” by T. D. Gordon et al.

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 be-

C8491

tween 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.

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,

C8492

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.

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.

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

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?

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

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.

Kleinman, L. I., Springston, S. R., Daum, P. H., Lee, Y. N., Nunnermacker, L. J., Senum, G. I., Wang, J., Weinstein-Lloyd, J., Alexander, M. L., Hubbe, J., Ortega, J., Canagaratna, M. R., and Jayne, J. : The time evolution of aerosol composition over the Mexico City plateau, *Atmos. Chem. Phys.*, 8, 1559–1575, 2008.

C8493

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 13, 23173, 2013.

C8494