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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.

1. The authors use 0.45±0.18 g GPOM $(L_{gas})^{-1}$ and 1.01±0.40 g GPOM $(L_{diesel})^{-1}$ 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 $(L_{gas})^{-1}$ 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 $(L_{gas})^{-1}$ 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 $(L_{gas})^{-1}$. 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 $(L_{diesel})^{-1}$ 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 $(L_{diesel})^{-1}$, 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 $(L_{diesel})^{-1}$.

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 $(L_{diesel})^{-1}$.

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.

References

1. May AA*, et al.* (submitted) Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles. *Atmospheric Environment*.
2. Gordon TD*, et al.* (2013) Secondary Organic Aerosol Formed from Light Duty Gasoline Vehicle Exhaust Dominates Primary Particulate Matter Emissions. *Atmospheric Chemistry & Physics Discussions* 13:23173–23216.
3. Kishan S, Burnette, A., Fincher, S., Sabisch, M., Crews, W., Snow, R., Zmud, M., Santos, R., Bricka, S., Fujita, E., Campbell, D., Arnott, W. (2008) *Kansas City PM Characterization Study Final Report*, (U.S. Environmental Protection Agency).
4. May AA*, et al.* (2013) Gas- and particle-phase primary emissions from in-use, on-road gasoline and diesel vehicles. *submitted to Atmospheric Environment*.
5. Gentner DR*, et al.* (2012) Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions. *Proceedings of the National Academy of Sciences* 109(45):18318-18323.
6. Jathar SH*, et al.* (2013) Secondary Organic Aerosol Formation from Photo-Oxidation of Unburned Fuel: Experimental Results and Implications for Aerosol Formation from Combustion Emissions. *Environmental Science & Technology* 47(22):12886-12893.
7. Gordon TD*, et al.* (2013) Secondary Organic Aerosol Production from Diesel Vehicle Exhaust: Impact of Aftertreatment, Fuel Chemistry and Driving Cycle. *Atmos. Chem. Phys. Discuss.* 13:24223-24262.