Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass

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[1] Although laboratory experiments have shown that organic compounds in both gasoline fuel and diesel engine exhaust can form secondary organic aerosol (SOA), the fractional contribution from gasoline and diesel exhaust emissions to ambient SOA in urban environments is poorly known. Here we use airborne and ground-based measurements of organic aerosol (OA) in the Los Angeles (LA) Basin, California made during May and June 2010 to assess the amount of SOA formed from diesel emissions. Diesel emissions in the LA Basin vary between weekdays and weekends, with 54% lower diesel emissions on weekends. Despite this difference in source contributions, in air masses with similar degrees of photochemical processing, formation of OA is the same on weekends and weekdays, within the measurement uncertainties. This result indicates that the contribution from diesel emissions to SOA formation is zero within our uncertainties. Therefore, substantial reductions of SOA mass on local to global scales will be achieved by reducing gasoline vehicle emissions. **Citation:** Bahreini, R., et al. (2012), Gasoline emissions dominate over diesel in formation of secondary organic aerosol mass, *Geophys. Res. Lett.*, *39*, L06805, doi:10.1029/2011GL050718.

1. Introduction

[2] Anthropogenic aerosol particles have adverse effects on air quality, visibility, and health as well as direct and indirect effects on climate [*Monks et al.*, 2009]. Among the common aerosol types, organic aerosol (OA) often contributes a large fraction of the submicron aerosol mass [*Zhang et al.*, 2007]. Laboratory experiments have indicated that OA can be formed from photooxidation of precursors present in gasoline fuel and diesel exhaust [*Miracolo et al.*, 2010; *Odum et al.*, 1997] and from biogenic emissions [*Griffin et al.*, 1999]. However, the relative importance of these sources of OA in many regions is poorly understood [*Fuzzi et al.*, 2006; *Monks et al.*, 2009].

[3] Emissions from gasoline and diesel vehicles differ in their chemical characteristics [*Kleeman et al.*, 2008; *Presto et al.*, 2009] and their weekly pattern [*Harley et al.*, 2005; *Marr and Harley*, 2002a]. In the United States, emissions from gasoline vehicles dominate vehicular hydrocarbon and carbon monoxide (CO) emissions [*Harley et al.*, 2001; *Marr and Harley*, 2002b]. Emission factors of nitrogen oxides (NO_x), black carbon (BC), $PM_{2.5}$ (particulate matter, less than 2.5 micron), and primary OA (POA) from diesel engines are, respectively, a factor of 13, 37, 20, and 13 higher than from gasoline, per mass of fuel used [*Ban-Weiss et al.*, 2008]. Gasoline and diesel fuel sale data show that diesel fuel consumption was only 17% of the total fuel consumption on weekdays during May-June 2010 in California (http://www.boe.ca.gov/sptaxprog/spftrpts.htm, see auxiliary material).[1] Because of the health hazards associated with primary particles emitted from diesel vehicles, regulations in California since 1998 are directed to control PM emissions from diesel vehicles (http://www.arb.ca.gov/msprog/onroadhd/onroadhd.htm, and links therein). Traffic counts have indicated that vehicular diesel emissions in California are lower on weekends compared to weekdays by 60–80% while only a 5–10% decrease in gasoline-powered vehicles is observed on the weekends [*Harley et al.*, 2005]. Effects of lower diesel emissions during weekends on NO_x, and subsequently on ozone, have been studied in many urban areas [*Harley et al.*, 2005; *Marr and Harley*, 2002a, 2002b; *Murphy et al.*, 2007; *Pollack et al.*, 2012]. These studies indicate that there is a large decrease in emissions of NO_x and only a small decrease in emissions of VOCs during the weekends. The combination of a more rapid ozone production at higher VOC/NO_x ratios in VOC-limited areas [*Marr and Harley*, 2002a; *Pollack et al.*, 2012] and less O_3 destruction by NO_x titration [*Murphy et al.*, 2007; *Pollack et al.*, 2012] leads to higher average ozone observed in urban areas over the weekend. Analysis of organic and elemental carbon (OC, EC, respectively) measurements in Southern California during summer and fall of 1995 [*Harley et al.*, 2005] and the IMPROVE (Interagency Monitoring of Protected Visual Environments) aerosol samples throughout the U.S. [*Murphy et al.*, 2008] indicate that fine particle EC has a pronounced weekly cycle, with minima occurring on Sunday, while OC concentrations are more constant.

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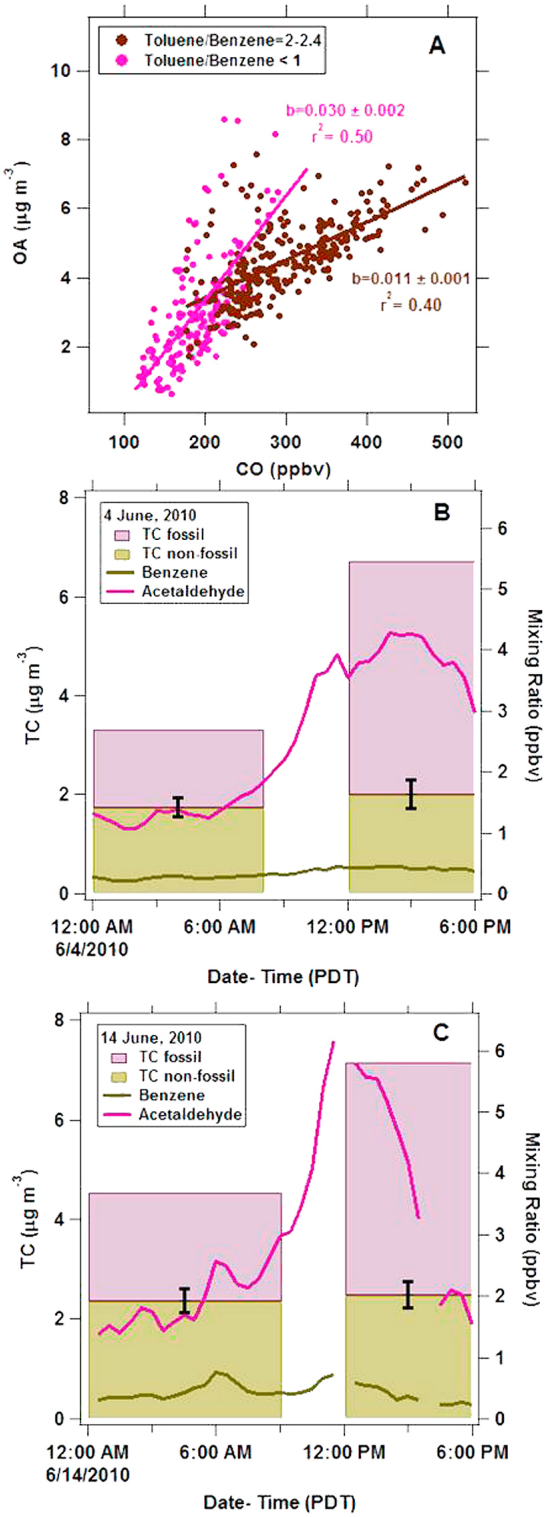

Figure 1. (a) Correlation plot of OA vs. CO in relatively fresh (toluene/benzene = 2–2.4) and aged (toluene/benzene < 1) plumes. (b, c) Average fossil and non-fossil aerosol TC mass from radiocarbon and Sunset OC/EC measurements as well as diurnal profiles of benzene and acetaldehyde measurements at Pasadena on two weekdays during CalNex.

[4] In this study, we first establish that in the LA Basin SOA makes a major contribution to OA mass and that its formation is dominated by fossil sources of carbon. We then use day of the week differences in diesel and gasoline emissions and quantify the relative importance of gasoline and diesel emissions to secondary formation of OA by comparing airborne measurements of OA in the LA Basin between weekends and weekdays. We analyze data collected on 3 weekday (4 May, 14 May, and 19 May 2010) and 3 weekend (8 May (Saturday), 16 May (Sunday), and 20 June (Sunday) 2010) aircraft flights conducted in the LA Basin during daytime, as part of the CalNex ("Research at the Nexus of Air Quality and Climate Change") field project.

2. Measurements

[5] During May and June 2010, the NOAA WP-3D aircraft conducted research flights in California as part of the CalNex field project. Here we analyze only those measurements which were collected in the LA Basin at altitudes lower than 1 km above sea level, between noon and 5:30 pm PDT (Figure S1 in Text S1). Measurements of submicron (50–650 nm) aerosol non-refractory composition aboard the aircraft were made using a compact time-of-flight aerosol mass spectrometer (C-ToF-AMS, referred to as AMS, Aerodyne Inc., Billerica, MA) [*Bahreini et al.*, 2009; *Drewnick et al.*, 2005]. Black carbon (BC) measurements in the size range of 90–700 nm were made by a single-particle soot photometer (SP2, Droplet Measurement Technologies, Inc., Boulder, CO) [*Schwarz et al.*, 2006]. Comparison of total mass estimated from the sum of AMS species and BC against total mass estimated from size distributions measured aboard the aircraft [*Brock et al.*, 2011] produces an average slope of 0.97 (r^2 = 0.88 and 0.97 for weekend and weekday, respectively) (Figure S2 in Text S1). Furthermore, the average weekday slope differs from the average weekend slope by less than 7%, indicating no significant instrumental bias between the weekend and weekday measurements.

[6] Gas phase measurements of volatile organic compounds (VOCs), including benzene, toluene, acetonitrile, formaldehyde, acetaldehyde, and isoprene aboard the aircraft were made online by a proton-transfer-reaction mass spectrometer (PTR-MS) [*de Gouw and Warneke*, 2007; *Warneke et al.*, 2011]. CO mixing ratios were measured by vacuum UV resonance fluorescence [*Holloway et al.*, 2000]. Mixing ratios of nitrogen dioxide and ozone were measured by a cavity ring-down spectrometer (CRDS) [*Wagner et al.*, 2011]. Photolysis rates of various species, including ozone and formaldehyde, were calculated using measurements from an actinic flux spectroradiometer aboard the aircraft [*Stark et al.*, 2007]. All aircraft measurements were averaged to the 10 s sampling time of the AMS.

[7] In addition to the airborne measurements during CalNex, ground-based measurements of gas and aerosol phase species were made in Pasadena, 17 km NE of downtown LA, during 15 May- 15 June, 2010. At this site, total particulate carbon (TC) measurements were made by an EC/OC analyzer (Sunset Laboratory Inc., Tigard, OR) using the EUSAAR2 analytical method [*Cavalli et al.*, 2010]. Radiocarbon measurements were also performed offline on aerosol filter samples, collected every 3–4 h by a Digitel DHA-80 HiVol sampler (DIGITEL Elektronik AG, Hegnau, Switzerland) [*Szidat et al.*, 2004]. Furthermore, VOC measurements of benzene and acetaldehyde were made online by GC-MS analysis [*Goldan et al.*, 2004].

3. Observations and Discussion

3.1. Anthropogenic Contribution to OA

[8] Airborne measurements of OA in the LA Basin show a significant (factor of 3) increase in the enhancement ratio of

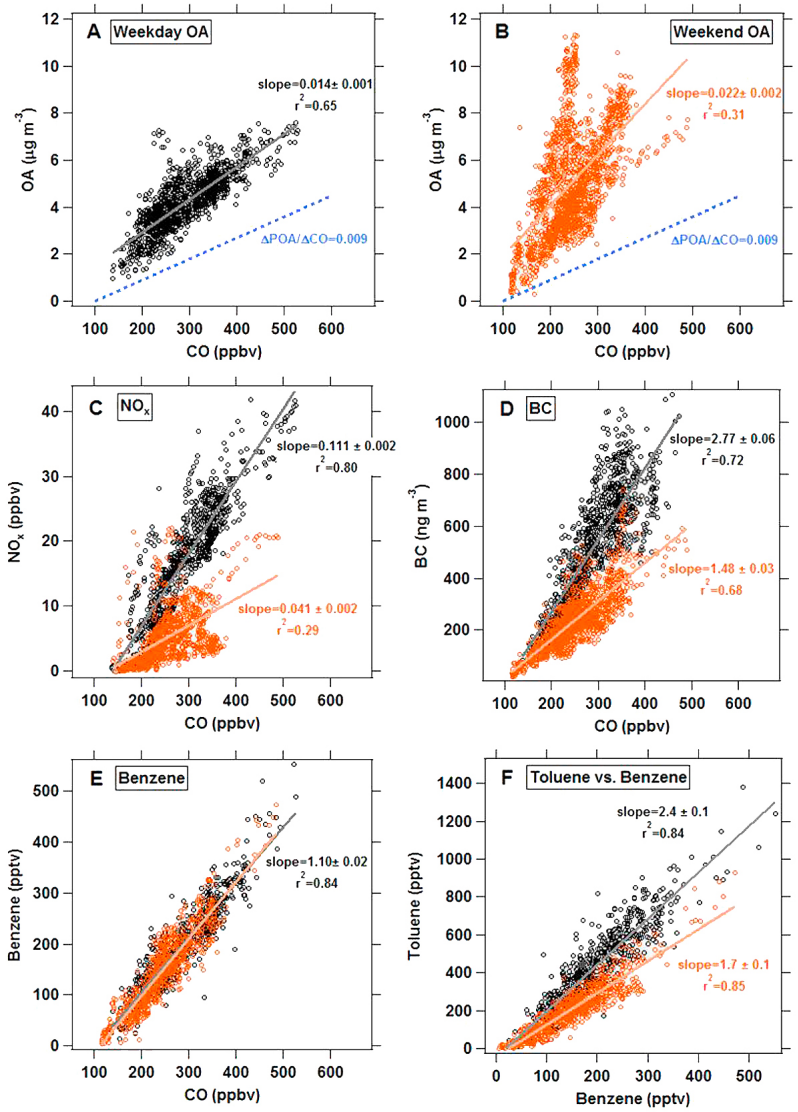

Figure 2. Weekday (black circles) and weekend (orange circles) correlation plots of (a, b) OA vs. CO, (c) NO_x vs. CO, (d) BC vs. CO, (e) benzene vs. CO, and (f) toluene vs. benzene. Data were limited to altitudes lower than 1000 m over the LA Basin, and obtained between noon and 5:30 pm PDT. The dashed lines in Figures 2a and 2b indicate estimated urban ΔPOA/ΔCO [*de Gouw et al.*, 2008].

OA with respect to CO (ΔOA/ΔCO) with an increase in photochemical processing (i.e., decrease in the ratio of toluene/benzene) (Figure 1a). Consistent with previous studies [*Docherty et al.*, 2008; *Turpin and Huntzicker*, 1991; *Williams et al.*, 2010], this indicates a dominant contribution of SOA to the observed OA in the Basin. Furthermore, diurnal profiles of TC measurements in Pasadena reveal that there is a significant increase in TC mass coincident with the increase in secondary pollutants like acetaldehyde when the processed emissions from LA arrive at Pasadena (Figures 1b and 1c). Considering that BC was <15% of the TC mass (Figure 2d), TC closely represents OC during CalNex. In addition, the afternoon increase in TC mass is predominantly due to the increase in the fossil fraction, suggesting that photooxidation of anthropogenic organic compounds is the major contributor to SOA within the city plume [*Zhang et al.*, 2011].

[9] Lack of a significant contribution from biogenic VOCs to OA mass in the LA Basin is also apparent in the long-term measurements (http://www.arb.ca.gov/aqd/aqdcd/aqdcddld.htm) of OC and CO, a marker for primary combustion emissions, since anthropogenic emissions have decreased over the last decades with technological improvements in mobile sources [*Ban-Weiss et al.*, 2008] while the biogenic emissions are not expected to show a significant long-term trend. These measurements indicate that CO and OC have decreased by 3–6% per year in the last 10 years whereas OC/CO ratios have not decreased significantly (Figure S3 in Text S1). In addition, comparison of airborne fine particle volume measured from the NOAA P3 research aircraft on the west side of the LA basin on 13 May 2002 (a Monday) with similar measurements in 2010 indicates that the ratio of Δvolume/ΔCO has stayed the same within the measurement uncertainties despite a factor of two reduction in CO and VOCs (not shown) from 2002 to 2010 (Figure S4 in Text S1). Considering the

small contribution of biomass burning (confirmed by low acetonitrile mixing ratios of 90 ± 22 pptv) to the 2010 data set, the above observations indicate that OA in the LA Basin is controlled by secondary processing of anthropogenic emissions.

3.2. Differences in Weekday-Weekend Enhancement Ratios

[10] Because of the different emissions from gasoline and diesel sources on weekends compared to weekdays, we use the airborne weekday-weekend data to distinguish the contribution of gasoline and diesel emissions to OA formation. On both weekdays and weekends, enhancements of OA with respect to CO (ratio of ΔOA/ΔCO) were much higher than the literature values of the enhancement ratios of primary OA (ΔPOA/ΔCO) [*de Gouw et al.*, 2008], demonstrating the importance of secondary production of OA on both weekdays and weekends (Figures 2a and 2b). Consistent with a reduction in diesel emissions on weekends [*Pollack et al.*, 2012], $\Delta NO_x/\Delta CO$ is decreased by 63 ± 5% on weekends compared to weekdays (Figure 2c, uncertainties represent standard deviations of the linear least-square regression fits). Similarly, the ΔBC/ΔCO in the LA Basin is decreased by 47 ± 3% on weekends compared to weekdays (Figure 2d). Consistent with other observations in the South Coast Air Basin, average weekend CO mixing ratios in Pasadena during CalNex are lower by only 4 ± 11% compared to weekday values [*Pollack et al.*, 2012]. Since nearly all of the CO emissions are from gasoline vehicles [*Harley et al.*, 2001], these observations are consistent with traffic data showing that gasoline emissions on weekends do not differ significantly from weekdays. Contrary to NO_x, BC does not undergo chemical loss in the atmosphere. Thus, using BC enhancement ratios (Figure 2d), emission factors of BC from gasoline and diesel vehicles [*Ban-Weiss et al.*, 2008], and fuel-use data, we estimate that there is a 54 ± 5% average reduction in diesel emissions on weekends compared to weekdays (see auxiliary material). Furthermore, we estimate that diesel vehicles contribute 87 ± 1% and 76 ± 3% of BC during weekdays and weekends, respectively. Note that these estimates are based on BC emission factors from studies in 2006. With the new particle filter requirements on diesel trucks traveling through the ports in California, BC emission factor from the modified diesel trucks may be lower by 50% [*Dallmann et al.*, 2011]. If these new emission factors represent the basin-wide diesel emissions, diesel contribution to BC during the week will be lower (77 ± 2%). Therefore, the analysis presented here depicts the upper estimate for diesel contributions.

3.3. Effects of Photochemical Processing on SOA Formation

[11] The 57% higher ΔOA/ΔCO ratio observed on the weekends (Figures 2a and 2b) indicates that OA production per CO emitted is higher on the weekends despite the smaller contribution from diesel emissions. A question that arises is what fraction of the higher SOA on weekends is due to changes in photochemistry resulting from the lower NO_x emissions as opposed to changes in emissions on the weekends. The enhancement ratios of benzene with respect to CO are similar regardless of the day of the week (Figure 2e). Consistent with previous studies, this indicates that gasoline vehicles are the dominant source of CO and light, single-ring-aromatic VOCs including benzene and toluene [*Marr and Harley*, 2002b; *Warneke et al.*, 2007]. Because of the higher reactivity of toluene with OH radicals compared to benzene, the lower ratio of toluene/benzene observed on the weekends (Figure 2f) confirms that faster photochemical processing of VOCs occurs during the weekends [*Pollack et al.*, 2012]. The actual rate of photochemical processing is not important for this analysis; however, the relative speed of photochemical processing due to OH during the weekends compared to weekdays is estimated by two independent methods (see auxiliary material). Both methods indicate that the rate of photochemical processing is higher on weekends, by factors of 1.9 ± 1.2 and 2.8 ± 1.0. High VOC/NO_x ratios can also increase SOA production yields [*Ng et al.*, 2007]; however, assuming 25 pptv of HO_2, >95% of the observed weekend NO mixing ratios are still above the threshold (~20 pptv NO) below which SOA yields are expected to increase significantly [*Henze et al.*, 2008].

[12] To separate the role of faster photochemistry from emission differences on the weekends compared to weekdays, we use observed ratios of toluene/benzene to segregate OA and CO data by different degrees of photochemical processing, with the highest ratios indicative of the least processing (Figure 3). Lack of a significant difference in the slopes of the fitted lines to OA vs. CO in each panel indicates that similar enhancements in OA are observed on weekends and weekdays, for similar degrees of photochemical processing, despite the lower diesel emissions on weekends. Further, ΔOA/ΔCO ratios for the least processed plumes (toluene/benzene = 2–2.4) are most similar to literature ΔPOA/ΔCO ratios while ΔOA/ΔCO ratios increase by a factor of 1.5 for the plumes with toluene/benzene = 1–1.6.

3.4. Diesel Exhaust Contribution to SOA Formation

[13] The similar OA enhancements on weekends, when diesel emissions are low, allow us to calculate an upper limit to the contribution of diesel emissions to SOA formation. We assume that the POA mass does not change significantly with photochemical processing and subtract the estimated urban ratio of ΔPOA/ΔCO ($0.009 \pm 0.002\ \mu g\ m^{-3}\ ppbv^{-1}$ [*de Gouw et al.*, 2008]) from the observed ΔOA/ΔCO ratios in Figure 3. Using the subtracted values, we calculate the ratio of weekday to weekend ΔSOA/ΔCO for each photochemical processing category shown in Figure 3. The average ratio of weekday to weekend ΔSOA/ΔCO, weighted by the propagated uncertainties, is 0.90 ± 0.43, which indicates that on average the contribution from diesel emissions to SOA formation is zero within the uncertainties. Using the estimate of ΔPOA/ΔCO [*de Gouw et al.*, 2008], POA emission factors [*Ban-Weiss et al.*, 2008], and fuel use data, we estimate that diesel engine emissions contribute 70 ± 2% of the POA in the LA Basin. Because diesel emissions contribute to POA, but not detectably to SOA, as photochemical processing and SOA formation proceeds, the contribution of diesel emissions to total OA decreases [*Chirico et al.*, 2010].

[14] We use the standard deviation of the weekday to weekend ratio of ΔSOA/ΔCO to estimate an upper limit of 47% for the contribution of diesel engine emissions to total SOA on weekdays in the LA Basin and a lower limit of zero (see auxiliary material). Note that because of the lower diesel emissions on the weekends, weekend ΔPOA/ΔCO is most likely lower than the value assumed here. An alternative calculation that uses a lower anthropogenic ΔPOA/ΔCO based on the data from the CalNex ground site produces a maximum weekday contribution from diesel engine emissions to SOA of 20% (see auxiliary material). The estimates presented here represent conservative upper limits; on average diesel contribution to SOA is zero within the uncertainties. We cannot detect a diesel engine signature in the SOA measurements in

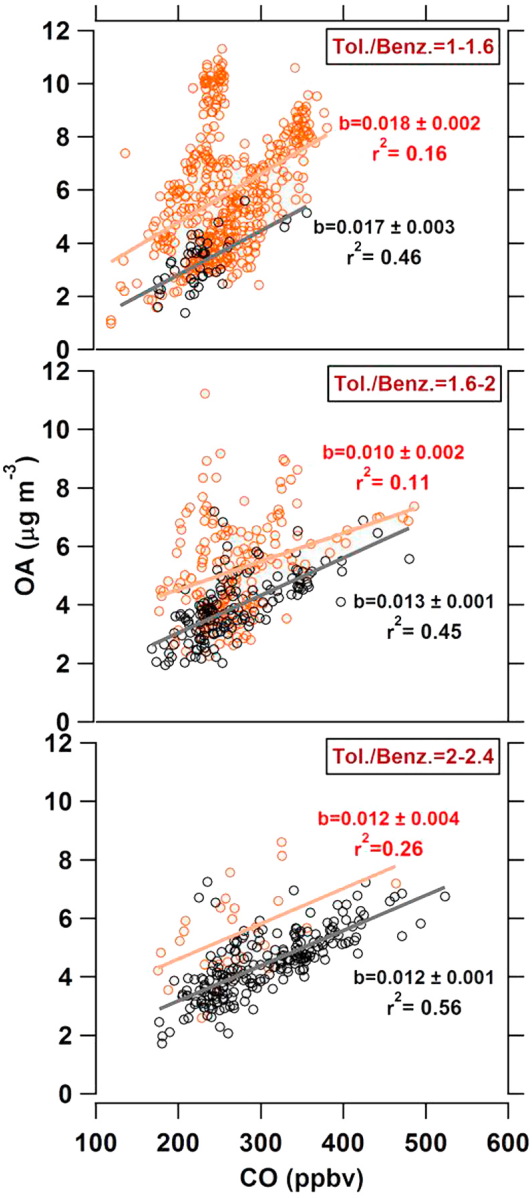

Figure 3. Correlation plots of OA vs. CO for different ratios of toluene to benzene (Tol./Benz.).

the LA Basin, while in contrast weekday enhancements in BC from diesel engine emissions are clearly evident.

4. Implications

[15] Our study suggests that, for more accurate modeling of SOA formation in urban areas, future research should be directed at identifying specific species in the exhaust of gasoline engines that are responsible for SOA formation. Studies targeted at understanding SOA formation from mobile sources with different after-treatment technologies would also be valuable. Our analysis suggests that the ratio of SOA to POA from gasoline emissions may reach a factor of ~3 at OH exposure of 5×10^7 molecule cm^{-3} h. A global estimate of primary OC (POC) from on-road gasoline emissions is 904 Gg/yr [*Bond et al.*, 2004]. Assuming that production of SOA relative to POA from gasoline exhaust follows the same trend as in LA, and using a ratio of 1.2 for POA/POC [*Aiken et al.*, 2008], we estimate that within a day of processing, SOA from gasoline exhaust emissions may reach 4 Tg/yr, which is ~16% of recent global estimates of biogenic SOA [*Andreae and Rosenfeld*, 2008; *Monks et al.*, 2009]. Our observations suggest that a decrease in the emission of organic species from gasoline engines may significantly reduce SOA concentrations on local and global scales.

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