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Photochemical aging of volatile organic compounds in the Los Angeles basin: Weekday-weekend effect

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[1] During the CalNex (California Research at the Nexus of Air Quality and Climate Change) field study in May–June 2010, measurements of volatile organic compounds (VOCs) were performed in the Los Angeles (LA) basin onboard a NOAA research aircraft and at a ground site located in Pasadena. A weekday-weekend effect in ozone, caused by lower NO_x emissions due to reduced diesel truck traffic in the weekends, has been previously observed in Los Angeles and other cities. Measurements in the Caldecott tunnel show that emission ratios of VOCs do not vary with the day of the week, but measurements during CalNex2010 show a VOC weekday-weekend effect through faster photochemical processing at lower ambient NO_x mixing ratios. Ambient VOC enhancement ratios of long-lived species such as benzene are the same between weekdays and weekends, whereas enhancement ratios of short-lived species, such as trimethyl benzene, are up to a factor of three lower on weekends. Based upon the observed differences in VOC enhancement ratios to CO, we determine that photochemical processing was on average 65%–75% faster on weekends during CalNex2010, which indicates that ambient OH radical concentrations were larger by this factor causing the observed change in VOC composition. A box model calculation based on the Master Chemical Mechanism was used to verify the increase in photochemical processing in the weekends.

1. Introduction

[2] Photochemical smog and air pollution with high ozone levels are a problem for many cities in the United States and elsewhere. In the Los Angeles (LA) basin the air pollution problem has been well documented and studied since the 1950s [*Haagen-Smit*, 1952; *Renzetti*, 1956]. The large population (about 13 million people) and the inefficient ventilation of the basin exacerbate the problem. The levels of ozone, volatile organic compounds (VOCs) and other pollutants have decreased dramatically over the past five

decades in the South Coast Air Basin (Warneke et al., 2012), but the air quality district that encompasses the LA basin is still designated as an ozone nonattainment area.

[3] In the LA basin the main emission sources for the ozone precursors VOCs and NO_x ($NO + NO_2$) are motor vehicle emission. The CARB (California Air Resources Board) emission inventory suggests that in the LA basin in 2008 mobile sources were the dominant emission sources and accounted for 89% of total NO_x, 52% of reactive organic gases, 90% of carbon monoxide (CO), and 30% of $PM_{2.5}$ (particulate matter, less than 2.5 μm) [*California Air Resources Board (CARB)*, 2009]. For most VOCs and CO emissions are dominated by gasoline vehicles [*Harley et al.*, 2001; *Marr and Harley*, 2002a], while NO_x, black carbon, primary $PM_{2.5}$, and primary organic aerosol are dominated by diesel engines [*Ban-Weiss et al.*, 2008b; *Kirchstetter et al.*, 1999], even though heavy-duty, diesel-powered vehicles generally are only a small fraction (<5%) of the total number of on-road motor vehicles in LA [*Chinkin et al.*, 2003; *Marr and Harley*, 2002a]. Significant weekday to weekend differences in traffic patterns exist in LA: gasoline powered passenger vehicles show different peak hours but overall have similar activity on weekends, whereas the heavy-duty diesel truck traffic is significantly reduced on weekends [*Chinkin et al.*, 2003; *Harley et al.*, 2005; *Marr*

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and Harley, 2002b]. Gasoline and diesel fuel sales 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) and a reduction of heavy-duty truck traffic of 40–80% was observed [*Chinkin et al.*, 2003]. The reduced activity of diesel-powered vehicles causes a significant reduction in NO_x and black carbon emissions in the LA basin on weekends [*Harley et al.*, 2005; *Marr and Harley*, 2002a, 2002b]. Most recent estimates from 2010 data show a reduction of 35–50% in NO_x emissions on the weekends [*Pollack et al.*, 2012; *Russell et al.*, 2010]. In contrast, the gasoline powered vehicle emissions of VOCs and CO stay relatively constant on weekends (decrease by $4 \pm 11\%$) and therefore the VOC/NO_x ratio increases by about 43–48% [*Pollack et al.*, 2012].

[4] The combination of faster photochemical processing and therefore more rapid ozone production at higher VOC/NO_x ratios in VOC-limited areas and less O_3 destruction by NO_x titration leads to higher average ozone in urban areas on weekends. This weekday-weekend ozone effect has been studied in LA basin and elsewhere extensively in the past [*Fujita et al.*, 2003a, 2003b; *Marr and Harley*, 2002b; *Murphy et al.*, 2007; *Pollack et al.*, 2012; *Yarwood et al.*, 2008]. *Pollack et al.* [2012] investigated the weekend ozone effect during CalNex 2010 in detail and found that more rapid photochemical processing ($43\% \pm 12\%$) and greater ozone production efficiency (22%–51%) on weekends mainly caused the increase in ozone in the LA basin in the weekends. Here we show that the observed faster photochemical processing on weekends not only has a strong effect on ozone, but also on the mixing ratios and composition of VOCs in the LA basin. This analysis utilizes ground-based and airborne data from CalNex 2010 ("California Research at the Nexus of Air Quality and Climate Change") field project.

2. Measurements

[5] Volatile organic compounds measurements in the LA basin were performed during May and June 2010 during the CalNex campaign onboard the NOAA WP-3 aircraft using a proton-transfer-reaction mass spectrometer (PTR-MS) [*de Gouw and Warneke*, 2007; *Warneke et al.*, 2011]. Whole air samples were also collected periodically throughout each flight [*Schauffler et al.*, 1999] and analyzed postflight by gas chromatography [*Colman et al.*, 2001]. Carbon monoxide (CO) was measured by vacuum UV resonance fluorescence [*Holloway et al.*, 2000]. NOAA WP-3 flights were performed on three weekdays (4 May, 14 May, and 19 May 2010) and three weekends (8 May (Saturday), 16 May (Sunday), and 20 June (Sunday) 2010). Flight tracks for these flights can be found elsewhere [*Pollack et al.*, 2012].

[6] The Caltech/Pasadena ground site, 15 km northeast of downtown Los Angeles was located on the Caltech campus, which is in an urban area. VOC measurements at Pasadena were made using an in situ gas chromatograph equipped with a mass spectrometer (GC-MS), and with a proton-transfer ion trap mass spectrometer, which is an instrument similar to a PTR-MS [*Gilman et al.*, 2010; *Warneke et al.*, 2005]. CO in Pasadena was also measured by vacuum UV

resonance fluorescence [*Holloway et al.*, 2000]. Formaldehyde was measured using the fluorometric Hantzsch reaction (model AL4021) [*Rappenglück et al.*, 2010].

[7] Volatile organic compounds emission ratio measurements were made in the Caldecott tunnel located in the San Francisco Bay area using a GC-MS system from 23 July until 29 July 2010 in the mixed traffic bore of the tunnel. VOC measurements were made with an automated in situ GC-MS at a 30 min time resolution [*Fares et al.*, 2012]. Tunnel measurements provide emission ratios for many compounds including those that are highly reactive or may have secondary sources and will be compared to the enhancement ratios measured in the ambient atmosphere. Especially for short-lived compounds during daytime or compounds with large secondary sources, measured ambient enhancement ratios can differ significantly from the emission ratios.

[8] The CARB routinely reports air quality data, and here we use ozone exceedance days and 8 h maximum CO from various sites in the LA basin [*CARB*, 2011].

3. Emissions and Photochemical Processing of Emissions in the LA Basin

[9] To demonstrate how photochemical processing of emissions progresses in the LA basin, Figure 1 shows the number of ozone exceedance days and the 8 h maximum CO from various CARB sites together with a map indicating the location of all the sites inside the LA basin. Data from the sites highlighted in yellow are used to represent a longitudinal profile of the basin and the ones marked in red a latitudinal profile. CO as an indicator of vehicle emissions shows the highest mixing ratios near downtown LA at the Reseda, Burbank and LA North Main sites, whereas most ozone exceedances are in the east side of the basin at the Redlands site close to Riverside. Here photochemical production during regularly occurring daytime transport from downtown areas to the east is evident in the increasing number of exceedances the further downwind the air travels. Additionally, the large primary emissions of NO_x near downtown further decrease ozone by titration. As a result, very few exceedance days occurred at the LA North Main site during the past several years. Also the north-south profile shows that the main vehicle emissions are located closer to the coast around LA downtown from where they are transported further inland [*Langridge et al.*, 2012]. The longitudinal and latitudinal profiles in the LA basin show that there are large differences in the degree of photochemical processing of the air masses within the LA basin. The emissions in downtown LA are not constant: differences in primary emissions of NO_x are observed between weekends and weekdays during CalNex 2010 and previous studies. This difference in emissions leads to faster ozone production and higher ozone concentrations on the weekends [*Marr and Harley*, 2002a].

[10] Photochemical processing in the LA basin is also clearly evident in the VOC ratios as demonstrated in Figure 2. A time series from a flight on 19 May 2010 of benzene and the C9-aromatics as measured by PTR-MS is shown in Figure 2a. A correlation plot of the C9-aromatics versus benzene for two individual plumes is shown in Figure 2b and very different enhancement ratios (i.e., slopes)
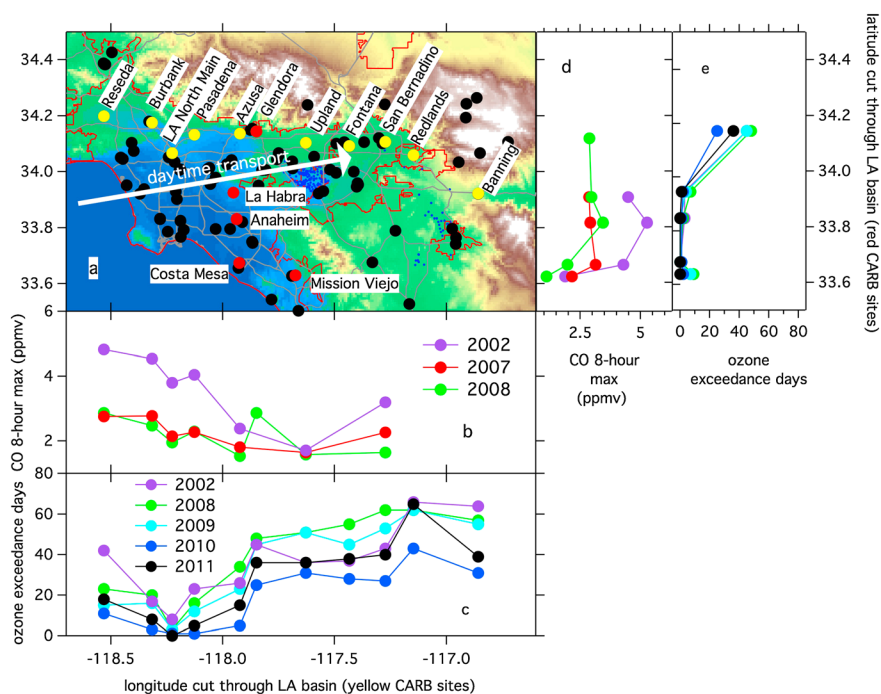
Figure 1. (a) Location of the air quality monitoring sites on a topographic map of the LA basin. Typical daytime transport is indicated with the arrow. (b, c) Longitudinal cut through the LA basin of 8 h maximum CO and ozone exceedance days. (d, e) Latitudinal cut.

are evident. The plume with the larger enhancement ratio was observed during an over-flight of the Pasadena ground site and the other one with the small enhancement ratio was outflow from LA observed outside the basin close to Banning Pass. Enhancement ratios of aromatic VOCs have

been used frequently in the past to determine the progress of photochemical aging and the air mass age [*Calvert*, 1976; *Roberts et al.*, 1984; *Warneke et al.*, 2007]. These ratios can also be called photochemical clocks. Vehicles emit aromatics in certain ratios in an urban environment
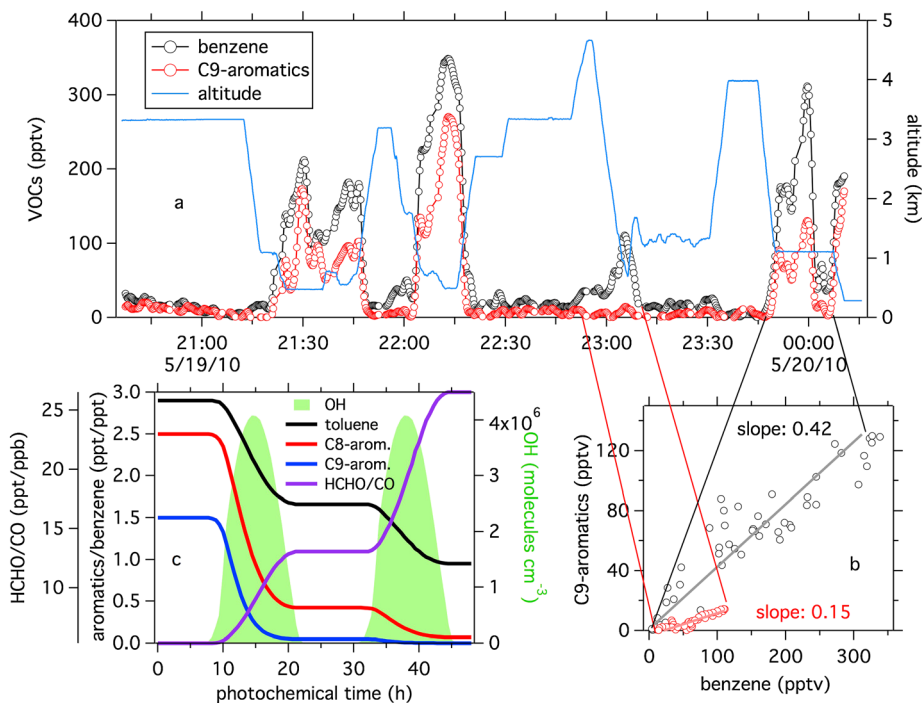

Figure 2. (a) Time series of benzene and the C9-aromatics for a section of a flight in the LA basin. (b) Correlation plot of a fresh and an aged plume of the C9-aromatics versus benzene. (c) Estimation of the enhancement ratios of aromatics and formaldehyde versus photochemical age.

Table 1. Enhancement Ratios (ERs in pptv/ppbv) of Various VOCs to CO for All Weekday and Weekend NOAA WP-3 Flights and Pasadena Ground Site Together With the k_{OH} and Weekday/Weekend (WD/WE) Ratios of the ERs

Compound	k_{OH} [a] ($\times 10^{-12}$)	Aircraft Enhancement Ratios			Pasadena Daytime Enhancement Ratios			Pasadena Nighttime Enhancement Ratios		
		WD	WE	WD/WE	WD	WE	WD/WE	WD	WE	WD/WE
Ethene	9.42 [c]	4.99	3.64	1.37	8.07	5.9	1.37	10.4	11.2	0.93
Propene	13	0.87	0.56	1.56	1.39	0.72	1.92	3.58	4.17	0.86
t-2-Butene	53	0.014	0.012		0.018	0.007	2.66	0.09	0.09	1.06
1-Butene	31.4	0.13	0.056	2.36	0.14	0.083	1.67	0.34	0.39	0.86
13-Butadiene	58				0.053	0.021	2.59	0.34	0.42	0.80
i-Butane	2.1	2.84	3.48	0.82	3.49	3.77	0.93	3.28	4.67	0.70
i-Pentane	3.9	5.78	5.08	1.14	8.9	8.93	1.00	8.28	9.56	0.87
n-Butane	0.92	4.77	4.87	0.98	6.28	7.13	0.88	5.09	6.5	0.78
n-Pentane	2.4	2.41	2.34	1.03	3.64	3.72	0.98	3.4	4.04	0.84
n-Hexane	5.3	0.93	0.70	1.33	1.06	0.90	1.18	1.18	1.38	0.86
n-Heptane	7.2	0.40	0.29	1.38						
Ethane	0.25	11.8	15.7	0.76	13.7	16.6	0.83	17.0	27.1	0.63
Propane	1.11	14.9	13.1	1.14	18.7	16.7	1.12	11.7	15.7	0.74
Benzene	1	1.08	1.06	1.02	1.15	1.19	0.97	1.27	1.53	0.83
Toluene	5.7	3.47	2.29	1.52	2.97	2.23	1.33	3.11	3.6	0.86
Ethylbenzene	7.5	0.48	0.33	1.44	0.49	0.36	1.36	0.56	0.65	0.87
m-Xylene [b]	22.7	0.72	0.44	1.65						
o-Xylene	12.2	0.47	0.28	1.67	0.44	0.3	1.47	0.66	0.75	0.88
p-Xylene	15.2	0.55	0.28	1.99						
mp-Xylene	19				0.98	0.51	1.92	1.75	1.94	0.90
124-Trimethyl benzene	32.5	0.27	0.12	2.23	0.23	0.11	2.09	0.62	0.7	0.89
135-Trimethyl benzene	54.3				0.074	0.025	2.96	0.32	0.35	0.92
123-Trimethyl benzene	32.7	0.07	0.033	2.12	0.12	0.048	2.5	0.25	0.27	0.92
2-Ethyl toluene	13.2	0.097	0.056	1.73	0.067	0.043	1.56	0.12	0.13	0.94
3-Ethyl toluene	22.4	0.20	0.11	1.90						
4-Ethyl toluene	13.6	0.13	0.058	2.16						
3+4ethyl toluene	18				0.17	0.117	1.48	0.34	0.40	0.87
i-Propyl benzene	6.61				0.025	0.02	1.25	0.031	0.035	0.89
n-Propyl benzene	5.71				0.079	0.061	1.30	0.104	0.12	0.87
Acetylene	0.46	5.21	4.35	1.20	7.12	6.41	1.11	6.24	5.27	1.18

[a]In cm^3 molecules^{-1} s^{-1} [*Atkinson et al.*, 2005].

[b]Not all compounds were measured both on the aircraft and the ground site.

[c]The significant figures in the table are not justified in many cases given the uncertainty in the data, but they are included for adequate precision, if these results are used in further calculations.

and then the aromatics are oxidized in the atmosphere at different rates according to their respective lifetimes [*Warneke et al.*, 2007]. The rate coefficients for the reactions with OH for all aromatics used here are given in Table 1.

[11] Benzene is the longest-lived VOC (i.e., smallest reaction rate coefficient with OH) considered here, and therefore the ratio of other aromatics to benzene will decrease with photochemical aging. The results of a calculation estimating the evolution of toluene, C8- and C9-aromatics ratios with benzene are shown in Figure 2c. The emission ratios of VOCs were obtained from A. Borbon et al. (A. Borbon et al., Emissions of anthropogenic VOCs in northern midlatitude megacities: observations vs. emission inventories in Los Angeles and Paris, submitted to *Journal of Geophysical Research - Atmospheres*, 2012, doi:2012JD018235), and typical OH concentrations (daytime maximum of 4×10^6 molecules cm^{-3}) were assumed in the LA basin [*Bahreini et al.*, 2012]. Rate coefficients with OH for the C8- and C9-aromatics were averaged according to *de Gouw et al.* [2005]. Neither atmospheric mixing nor additional emissions after emission ($t = 0$) were taken into account in this calculation, and therefore it represents an ideal case. The toluene/benzene ratio evolves most slowly and the C9-aromatics/benzene most rapidly of the photochemical

clocks shown in Figure 2c, which means that toluene/benzene can be used for longer-range transport and C9-aromatics/benzene only for more local transport. The aromatic ratios are a type of photochemical clock that relies on the oxidation of primary emissions. Another type of photochemical clock relies on the photochemical production of secondary compounds such as formaldehyde (HCHO) during aging. HCHO has small, but nonzero, primary emissions [*Ban-Weiss et al.*, 2008a; *Garcia et al.*, 2006], but is produced during photochemical oxidation of primary VOC species. Therefore, the ratio of HCHO to a long-lived species such as CO increases with the processing of the primary emissions [*Warneke et al.*, 2011]. A simple estimate of this increase is also shown in Figure 2c. This clock is not quantitative only qualitative, because HCHO is produced by many different primary VOCs (mostly not aromatics) at different rates and is also photochemically removed.

[12] Using both types of clocks together gives a better estimate of photochemical processing than using either clock alone. In Figures 3a–3c the primary clocks using the aromatics are plotted versus the secondary clock using HCHO. Each data point in the figure is determined from the slope of the respective VOCs from an individual plume or period of enhanced mixing ratios encountered during the CalNex2010
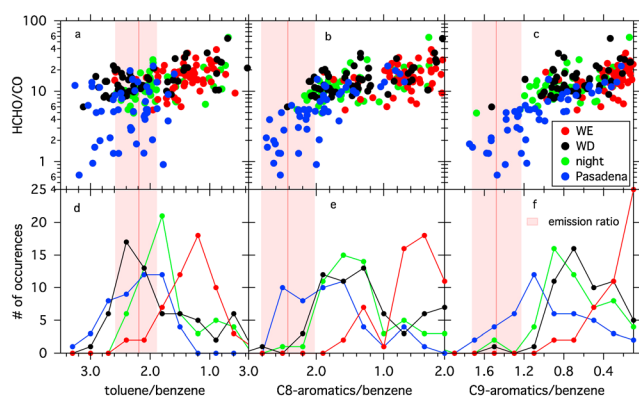
Figure 3. (a–c) Secondary (ΔHCHO/ΔCO) versus primary (Δaromatics/Δbenzene) photochemical clocks color-coded as ground site data or nighttime, weekend, and weekday flight data. Fresh plumes appear in the lower left corner and aged plumes in the upper right corner. (d–f) Histograms of the primary photochemical clocks. The emission ratios and the range from the measurements in the Caldecott tunnel are indicated by the red lines and the red shaded areas.

HCHO/CO ratio. A reason for this could be that the clock is too slow, i.e., toluene is insufficiently removed on the time scale of processing relevant to this site, and the ratio is more influenced by variations in the primary emissions than by photochemical aging. This demonstrates that the right clock should be chosen for different transport times.

[14] In the aircraft measurements in Figure 3 it is clear that the nighttime data and the weekday data have a similar age
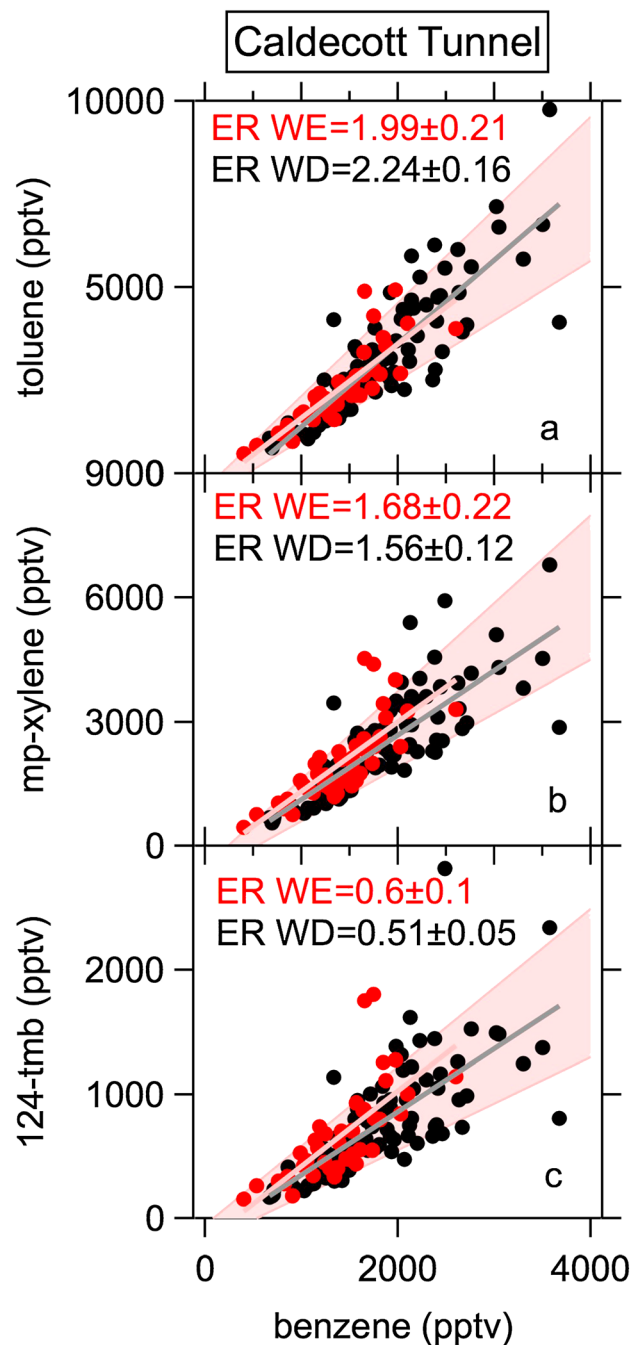
campaign. Figure 2b shows the analysis for two example plumes and all plumes encountered in the area shown in Figure 1 in or close to the LA basin were included in Figure 3. All individual plumes (i.e., periods of increased mixing ratios) encountered at the Pasadena ground site were also used. Fresh emissions are in the lower left corner and photochemical aging will move the ratios toward the upper right corner of the graphs in Figures 3a–3c. Vehicle emission ratios of toluene, C8- and C9-aromatics to benzene from vehicle traffic determined using the measurements in the Caldecott tunnel are also shown in Figure 3. The range of emission ratios is estimated using the variability in the tunnel measurements and are indicated by the shaded red areas in Figure 4. The vehicle emission ratios for the C8- and C9-aromatics agree well with the freshest enhancement ratios observed at the Pasadena ground site (Figure 3). Toluene, on the other hand, sometimes shows larger enhancement ratios than can be explained from the vehicle emission ratios. Furthermore, in Figure 3 the toluene plot shows more scatter for the fresher plumes than do the other two plots. Additional sources for toluene other than vehicle traffic are most likely the cause for the higher enhancement ratios; these additional sources of toluene have been identified as industrial and evaporative emissions in Mexico City [*Karl et al.*, 2009].

[13] Histograms of the primary photochemical clock data are shown in Figures 3d–3f. The ground site in Pasadena shows a large range of photochemical ages albeit lower on average than the aircraft data. Pasadena is, during typical daytime wind patterns, about 3–5 h downwind of downtown LA [*Veres et al.*, 2011; *Washenfelder et al.*, 2011] and is strongly influenced by those emissions, but also fresh local emissions during the night are responsible for many of the plumes in Figure 3. The Pasadena data also show that the toluene/benzene ratio is not well correlated with the

Figure 4. Emission ratios of toluene, *m* + *p*-xylene and 1,2,4-trimethyl benzene to benzene in the Caldecott tunnel, color-coded by weekday (black) and weekends (red). The shaded areas indicate the range of estimated emission ratios. The slopes with one standard deviation are given.
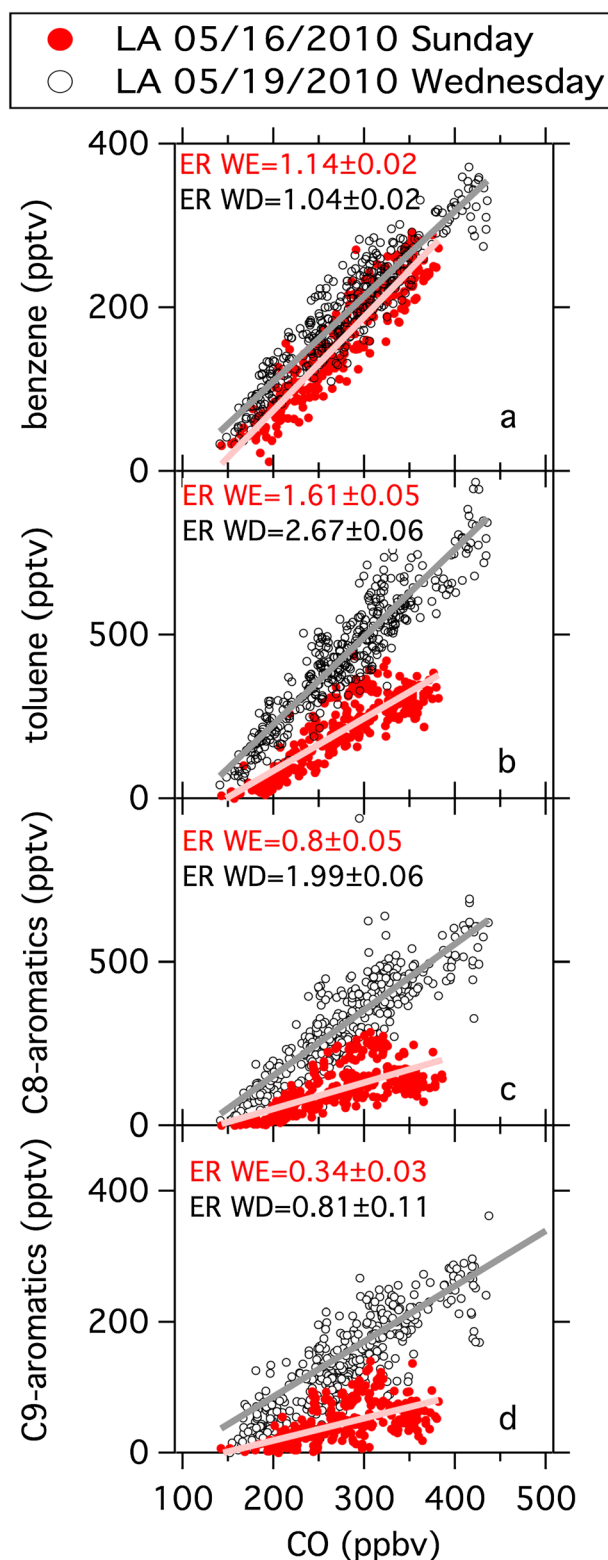
Figure 5. Correlation plots of some aromatics versus CO from a weekday (19 May 2010) and a weekend (16 May 2010) flight of the NOAA WP-3 aircraft. The slopes with one standard deviation are given.

distribution. On the other hand, the weekend data are generally more aged. This greater age on weekends is discussed in the following section.

4. VOC Weekend Effect in the LA Basin

4.1. VOC Emissions Ratios Constant Between Weekends and Weekdays

[15] In Figure 4 the correlation plots of toluene, the C8- and C9-aromatics versus benzene measured in the Caldecott tunnel located in the San Francisco Bay area are shown. Weekday data are in black and weekend data in red. The slope of these plots using all the data yield the emission ratios shown in Figure 3. The emission ratios of the aromatics in the weekends are not significantly different from the weekdays even though there are fewer diesel trucks in the tunnel during the weekends. Together with the similar gasoline vehicle traffic between weekdays and weekends in LA [*Marr and Harley*, 2002b], this suggests that the aromatics emission ratios used in the photochemical clocks do not change significantly on weekends, even while the NO_x emissions are greatly reduced due to the reduced diesel truck traffic [*Harley et al.*, 2005]. Here we assume that the fresh emissions measured in the tunnel in the San Francisco Bay are generally representative of tailpipe emissions in California and therefore can also be used in the LA basin.

4.2. Evidence for Faster Photochemical Processing in the Weekends

[16] In contrast to the tunnel measurements, the ambient VOC data show clear differences between the weekdays and weekends. Figure 5 shows correlation plots of the aromatics versus CO from two example flights during CalNex2010. One flight was on Sunday 16 May 2010 and the other flight three days later on Wednesday 19 May 2010. These flights serve as a typical example for the differences observed between weekends and weekdays. CO, a good tracer for vehicle exhaust combustion, is long enough lived that it does not significantly oxidize during its residence time in the LA basin. The enhancement ratio of benzene, the longest-lived aromatic, to CO is about the same for both days. As was shown for the tunnel measurements earlier, this indicates that the emission ratios of aromatic compounds to CO do not change between the weekdays and weekends. Toluene, the C8- and C9-aromatics on the other hand have smaller enhancement ratios to CO on the weekend compared to the weekday flight, and the differences increase as the lifetime of the compound decreases. The short-lived aromatics observations from the aircraft indicate faster photochemical processing in the weekends as was observed previously in the LA basin [*Bahreini et al.*, 2012; *Pollack et al.*, 2012].

[17] Diurnal variations separated into weekdays and weekends of CO, benzene, 1,2,4-trimethyl benzene (124-tmb) and the 124-tmb/benzene ratio from the Pasadena ground site are shown in Figures 6a–6d. High nighttime mixing ratios due to low mixing heights and slow photochemistry are observed for all compounds on all days. Pasadena, being about 3–5 h downwind of LA downtown, generally receives the rush hour emissions from that region between 10 A.M. and 2 P.M., which can be seen in the maxima of the longer-lived species CO and benzene [*Veres et al.*, 2011; *Washenfelder et al.*, 2011]. The short-lived compounds such as 124-tmb and the ratio of 124-tmb to benzene have a minimum in the afternoon, when the boundary layer is the highest and the photochemical processing the fastest [*Veres et al.*, 2011]. Faster photochemical processing on weekends is reflected in smaller midday concentrations and a smaller midday 124-tmb/benzene ratio on
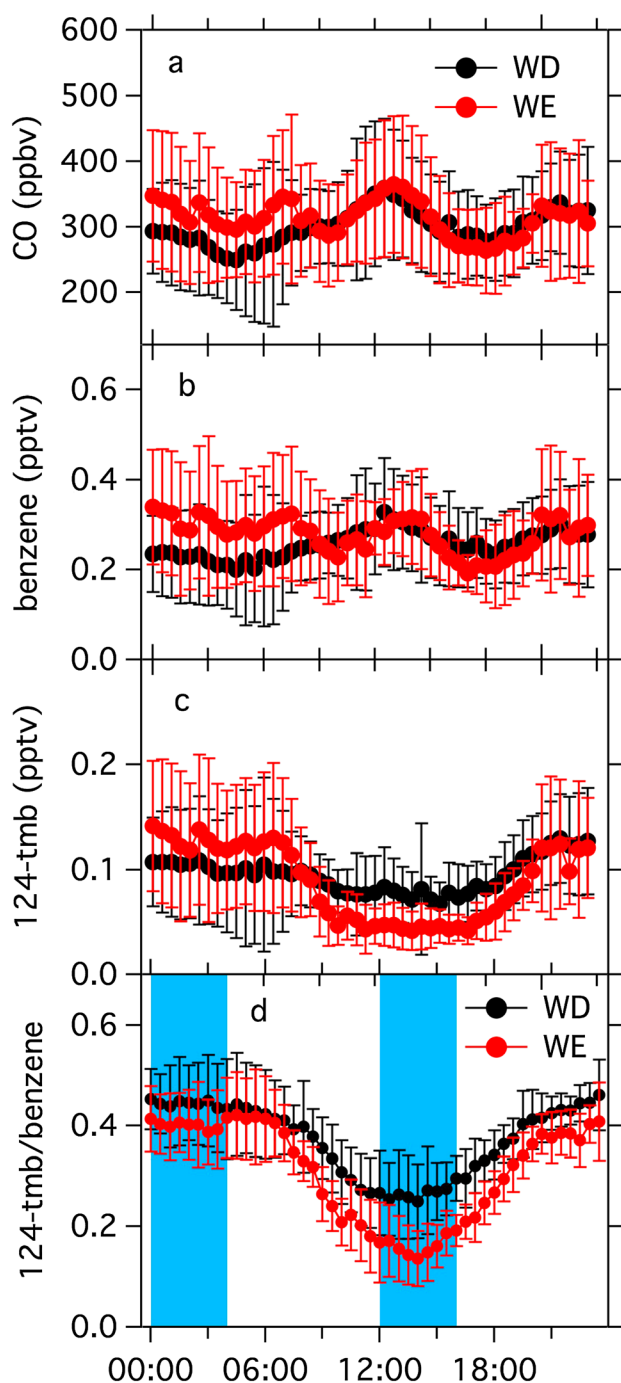
Figure 6. Diurnal variations of (a) CO, (b) benzene, (c) 1,2,4-trimethyl benzene (124 tmb), and (d) the 124-tmb/benzene ratio at the Pasadena ground site for weekdays and weekends. The blue shaded areas indicate the times that were used to represent daytime (12–4 P.M. LT) and nighttime (12–4 A.M. LT).

weekends. Figures 7a–7h show correlation plots of some aromatics with CO for the nighttime (12 A.M.–4 A.M.) and daytime (12 P.M.–4 P.M.) periods (indicated by the shaded areas in Figure 6d) and slopes are given in Table 1. During nighttime in the absence of photochemical processing, the enhancement ratios are identical for the weekends and weekdays. During daytime, differences due to photochemical processing are

observed, where the differences in enhancement ratios to CO are larger for the shorter-lived compounds. Thus, at the ground site as well as from the aircraft, faster photochemical processing was observed during weekends.

[18] Here it should be mentioned that biogenic VOCs like isoprene and its oxidation products were also observed on the aircraft and at the ground site and were generally consistent with the faster photochemical processing in the weekends, but they showed very different diurnal and spatial variations than anthropogenic VOCs. Discussing the biogenic VOCs in detail is beyond the scope of this paper.

4.3. Quantification of the Difference in Degree of Processing During Weekends

[19] The difference in enhancement ratios between the weekdays and weekends for all VOCs measured during CalNex2010 is investigated in Figure 8. The enhancement ratios for many VOCs are given in Table 1. They were determined from the slope of the correlation plots identical to those shown in Figure 5, but here we used whole air samples data from all the weekday and weekend flights (not only the example flights), and for the Pasadena data identical to Figure 7 for daytime and nighttime data. The ratios of the weekday to weekend enhancement ratios, also given in Table 1, are plotted in Figure 8 versus the rate coefficient with OH. A clear relationship between the OH rate coefficient of the individual compounds and the decrease in enhancement ratio on weekends exists for the aircraft data and the daytime data in Pasadena. Nighttime data in Pasadena, with no significant photochemical processing, show no trend with OH rate coefficients.

[20] The first-order loss of a VOC such as toluene can be described with the following equation if mixing and dilution are neglected:

$$[\text{toluene}] = [\text{toluene}]_0 \times e^{-k_{\text{toluene}}[\text{OH}]t} \qquad (1)$$

where [toluene] is the concentration of toluene after processing time t, $[\text{toluene}]_0$ is the concentration at the time of emission, k_{toluene} the rate coefficient for the reaction with OH and [OH] the concentration of OH. The enhancement ratio of toluene to CO during weekdays at the time t is then

$$\left(\frac{[\text{toluene}]}{[\text{CO}]}\right)_{\text{WD}} = \left(\frac{[\text{toluene}]}{[\text{CO}]}\right)_0 \times e^{(-k_{\text{toluene}}+k_{\text{CO}})[\text{OH}]t} \qquad (2)$$

where [CO] is the concentration of CO at the time t and $([\text{toluene}]/[\text{CO}])_0$ is the emission ratio of toluene to CO. The use of VOC ratios to CO at least approximately corrects for the neglect of mixing and dilution. The emission ratio from vehicle traffic can be determined from the measurements in the Caldecott tunnel. Here we assume that the emission ratio is identical to the enhancement ratio measured in Pasadena at night, which is justified by the good comparison of the tunnel and Pasadena nighttime enhancement ratios for the aromatics in Figure 3. On weekends photochemical processing is faster than during the week and therefore the enhancement ratio of toluene on the weekends can be expressed by

$$\left(\frac{[\text{toluene}]}{[\text{CO}]}\right)_{\text{WE}} = \left(\frac{[\text{toluene}]}{[\text{CO}]}\right)_0 \times e^{(-k_{\text{toluene}}+k_{\text{CO}})[\text{OH}]t\times A} \qquad (3)$$

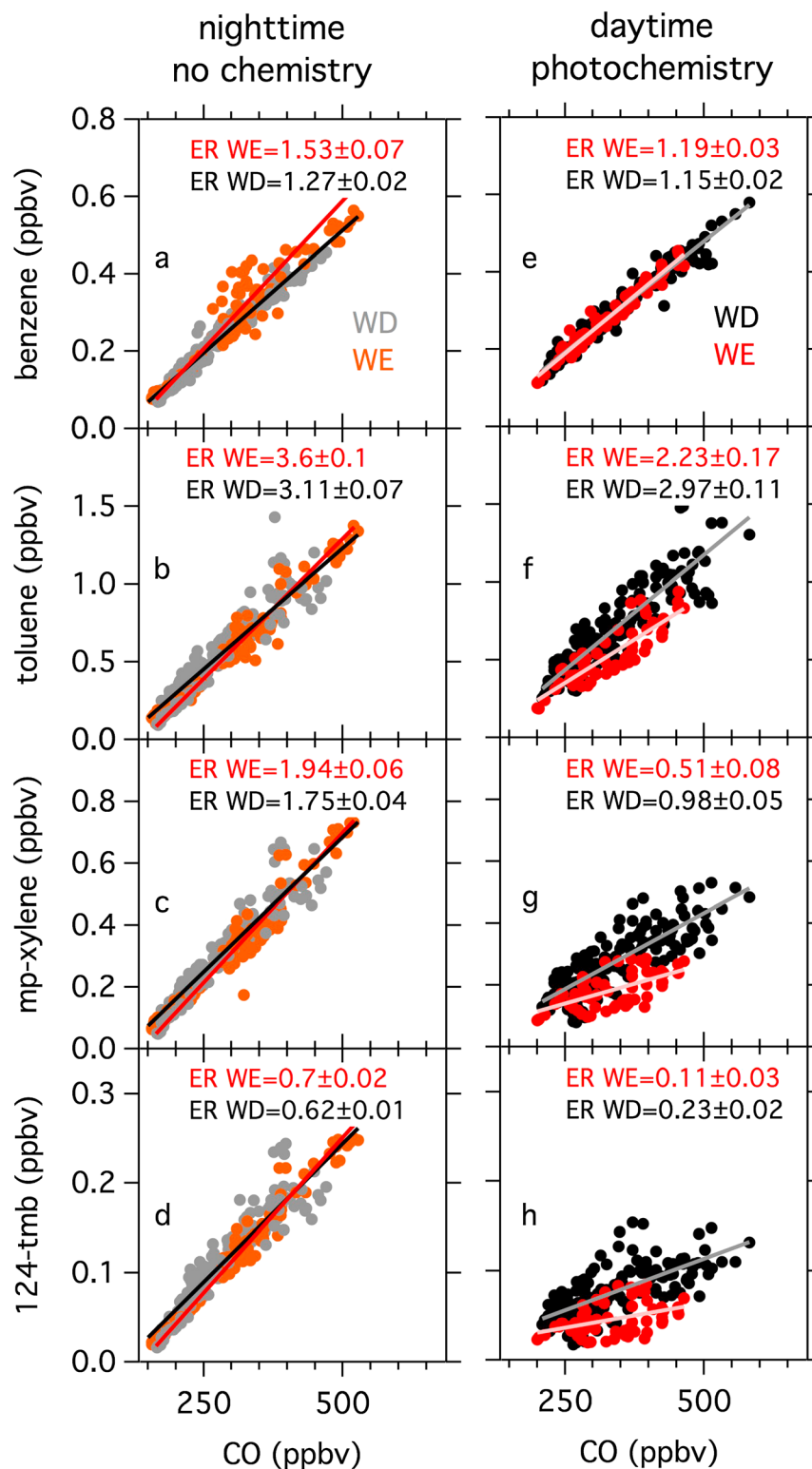where A is the ratio of [OH] on weekends compared to weekdays.

Figure 7. Enhancement ratios of some aromatics with CO from weekdays and weekends (Saturday and Sunday) at the Pasadena ground site for daytime (12–4 P.M. LT) and nighttime (12–4 A.M. LT) data. The slopes with one standard deviation are given here and in Table 1.

[21] The enhancement ratio on weekends can be calculated from the emission ratio and the observed weekday enhancement ratios by assuming different values of the factor A. The solid lines in Figure 8 represent linear fits for this calculation using A values of 1, 1.65, and 1.75, which best describe the Pasadena nighttime and daytime and the flight data, respectively. Thus, the Pasadena data imply that during the transport time from downtown LA OH
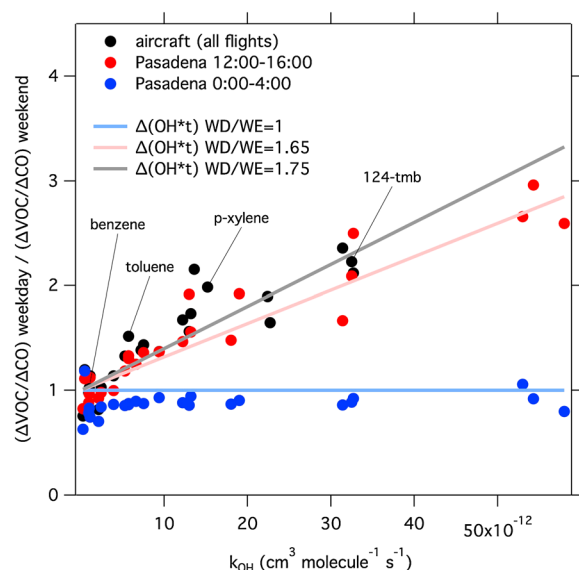
Figure 8. The ratio between weekends and weekdays in enhancement ratios of all measured VOCs with CO versus their rate coefficient with respect to OH together with a calculation using equations (2) and (3) of the difference using 1, 1.65, and 1.75 times faster chemistry in the weekends than in the weekdays.

concentrations were on average 65% higher on weekends compared to the same time period during weekdays, and for the aircraft data the average OH encountered by the sampled air parcels was 75% higher on weekends. If the aircraft had flown different flight patterns on weekdays versus weekends, this result could be misleading, but very similar patterns were followed on weekends and weekdays [*Pollack et al.*, 2012]. The 65%–75% faster chemical processing is somewhat smaller than estimated by *Bahreini et al.* [2012], but they considered only the toluene/benzene ratio for their determination, which shows a stronger weekday/weekend difference than most other compounds used here.

[22] A 65%–75% increase in OH concentrations at a 35%–50% decrease in NO_x emissions seems large, but there are three possible reasons for this larger increase: (1) the main reason was shown in *Pollack et al.* [2012], who demonstrated that the decrease in NO_x emissions in the LA basin causes a strong increase in photochemical processing speed as can be seen in an increase in $(PAN + HNO_3)/NO_y$ ratio (43% $\pm$ 12%), which is the result of higher OH on the weekends. In simple terms, OH is a function of its sources and sinks, where a major sink is NO_2, which was lower on the weekends by 34–46%. The dominant source for OH during CalNex2010 was ozone [*Young et al.*, 2012], which was higher on the weekends by about 30%. (2) Looking at Figure 5 and *Pollack et al.* [2012] there might be a small decrease in VOC emissions on the weekends leading to some increase in the oxidative power in the weekends, and (3) another minor effect could be carryover NO_x from the previous day or days. This could increase the NO_x concentrations throughout the week, so that NO_x drops from Fridays to Saturdays and even further on Sundays [*Murphy et al.*, 2007; *Russell et al.*, 2010]. This effect causes a larger difference in NO_x concentrations than the difference in NO_x emissions between the weekdays and weekends.

[23] The observations during CalNex 2010 cover only a limited time period and therefore limited statistics and could be influenced by unusual meteorology during this time period. *Pollack et al.* [2012] have compared the weekend ozone increase during CalNex 2010 with the previous 5 years from the CARB monitoring network and found that CalNex 2010 was very similar compared to the long-term observations, which indicates that the results from CalNex are likely representative of typical conditions in the LA basin.

4.4. Box Model Simulation of the Weekend Increase in Photochemical Processing

[24] A set of box model simulations demonstrates this weekend NO_x effect on OH concentrations. Model simulations are performed using the Dynamically Simple Model of Atmospheric Chemical Complexity [*Emmerson and Evans*, 2009], constrained to the mean observed concentrations of H_2O, CO, CH_4, C_3H_8, i-C_4H_{10}, n-C_4H_{10}, i-C_5H_{12}, n-C_5H_{12}, n-C_6H_{14}, n-$C_{10}H_{22}$, n-C_9H_{20}, n-$C_{11}H_{24}$, CH_3OH, C_2H_5OH, C_2H_2, and i-propanol. These constraints were identical to calculations in *Young et al.* [2012, 2013] and *Washenfelder et al.* [2011]. For simplicity, other observed VOCs are lumped with the most abundant in that compound class, such that C_2H_4 represents the average sum of all alkene concentrations; acetone represents all ketones; and toluene represents all alkyl-benzenes. NO_x is emitted into the box as a fixed NO emission. In the base simulation the NO emissions are scaled to best match (within ~11%) the average diurnal NO_x observations (Figure 9a). O_3 is constrained to the observed campaign average diurnal concentration in 30 min time bins (Figure 9b). Photolysis frequencies are calculated using the total ultraviolet (TUV) radiation model [*Madronich et al.*, 1998], and the calculated photolysis frequencies are then scaled to the campaign average $j(O^1D)$ and $j(NO_2)$ observations. The model chemistry scheme is generated by the Master Chemical Mechanism V3.2 [*Jenkin et al.*, 1997; *Saunders et al.*, 2003] and contains detailed inorganic chemistry and a near explicit degradation scheme for the 16 constrained VOCs, resulting in 1179 species and 4599 reactions. The model is integrated forward with a time step of 600 s for 10 days. To represent the nonchemical loss of species either through deposition or mixing, and thus prevent the accumulation of unconstrained species within the model, a lifetime with respect to a physical first-order loss of 24 h ($k_{loss} = 1.15 \times 10^{-5}$ s^{-1}) is applied to all calculated species.

[25] Two modified model simulations were performed: (1) 40% reduction in NO emissions and (2) reduction in NO emissions to achieve 44% reduction in NO_x mixing ratios. For the simulation with the 40% reduction in the modeled NO emission a 148% increase in calculated peak OH concentration were modeled together with a 65% reduction in the model daily average NO_x mixing ratios due to the increase in NO_x oxidation. Increasing the O_3 concentration by 30% further, as is observed on the weekends [*Pollack et al.*, 2012], increases the calculated OH concentration by an additional 15%, and reduces NO_x by an additional 3%. The second simulation, which reduces the NO emission to achieve a 44% reduction in NO_x mixing ratios (~23% NO emission reduction), increases calculated peak OH by 83% as shown in Figure 9c. Simulating the same 44% reduction in NO_x concentration with a 30% increase in O_3 (achieved
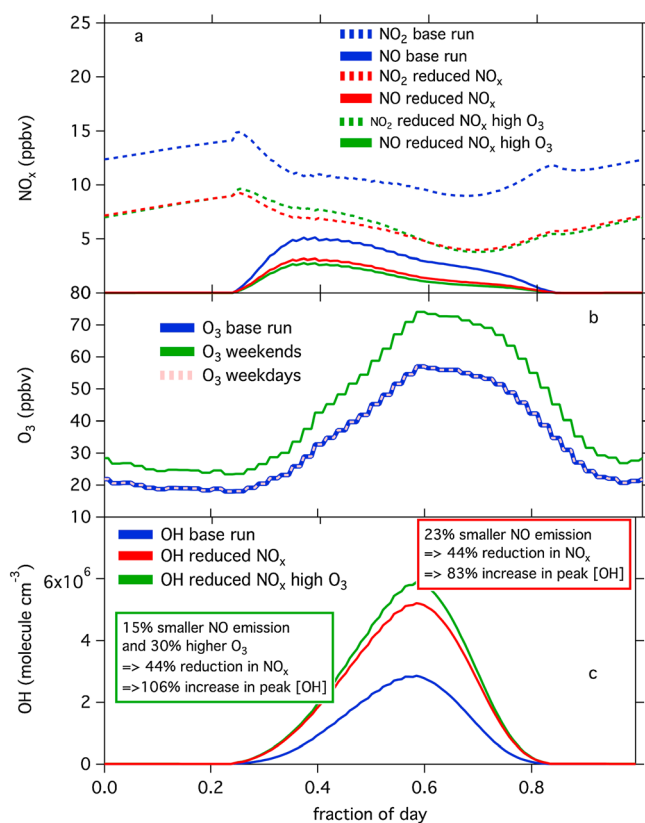
Figure 9. NO_x, O_3 and [OH] box model calculation results: NO emissions are reduced to yield a 44% reduction in NO_x mixing ratios. O_3 was constraint to weekday and weekend values in separate model runs. The weekend [OH] increase is 83% and 106% for the separate model runs.

through a 15% reduction in NO emission) results in a 106% increase in calculated peak OH. The change in modeled OH for both simulations is larger than the 65–75% increase calculated above from observed VOC ratios, and is likely due to the simplified model constraints resulting in an under-prediction of OH sinks within the model. Although these model simulations overpredict the increased oxidation observed in the VOC ratios, they clearly highlight the nonlinear response of OH to changes in emissions of NO_x in the LA basin.

5. Conclusion

[26] Within the LA basin, also called the South Coast air basin, large differences in the degree of photochemical processing of emissions exist: the highest primary emissions are located near the downtown LA area from where they are transported further east toward Riverside while being photochemically processed and mixed with fresh emissions. Most ozone exceedances occur downwind from downtown LA, where few occur. Here we show that photochemical aging of VOCs is not only dependent on location in the basin, but also dependent on the day of the week. A large reduction in diesel truck traffic on weekends results in lower NO_x emissions, which in turn increases OH concentration and consequently leads to faster photochemical processing of VOCs.

[27] Measurements during CalNex 2010 in the LA basin show that the weekend effect is not only observed for NO_x and ozone, but also strongly affects short-lived VOC mixing ratios. Afternoon enhancement ratios of the short-lived VOCs relative to the longer-lived CO or benzene are significantly smaller during the weekends due to the faster photochemical processing. Changes in VOC emissions do not affect these enhancement ratios, because constant emission ratios between weekdays and weekends are seen in the Caldecott tunnel and nighttime measurements at the Pasadena ground site. The magnitude of the difference in the weekday versus weekend enhancement ratios for a particular VOC depends on the lifetime of that VOC with respect to OH oxidation. For longer-lived compounds, such as benzene, no difference between weekdays and weekends are observed in the ambient enhancement ratios, whereas for short-lived compounds, such as 1,2,4-trimethyl benzene, enhancement ratios can approach a factor of three higher during the week. For the CalNex2010 period photochemical processing of VOCs was on average 65%–75% faster, and therefore OH concentrations were 65%–75% higher, on weekends compared to weekdays.

[28] The increase in photochemical processing in weekends was reproduced by box model calculations. The simulation that reduces NO emissions by 23% to achieve a reduction in NO_x mixing ratios by 44% has a peak [OH] increase of 83%, which is higher than observed using the measured VOC ratios, likely because of the simplified VOC mixture in the box model.

References

Atkinson, R., D. L. Baulch, R. A. Cox, J. N. Crowley, J. R. F. Hampson, R. G. Hynes, M. E. Jenkin, J. A. Kerr, M. J. Rossi, and J. Troe (2005), Summary of Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry, *IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry*, *Web Version November 2005*(http://www.iupac-kinetic.ch.cam.ac.uk/).

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.

Ban-Weiss, G., J. Mclaughlin, R. A. Harley, A. Kean, E. Grosjean, and D. Grosjean (2008a), Carbonyl and nitrogen dioxide emissions from gasoline- and Diesel-powered motor vehicles, *42*(11), 3944–3950, *Environ. Sci. Technol.*

Ban-Weiss, G. A., J. P. McLaughlin, R. A. Harley, M. M. Lunden, T. W. Kirchstetter, A. J. Kean, A. W. Strawa, E. D. Stevenson, and G. R. Kendall (2008b), Long-term changes in emissions of nitrogen oxides and particulate matter from on-road gasoline and diesel vehicles, *Atmos. Environ.*, *42*, doi:10.1016/j.atmosenv.2007.09.049.

Calvert, J. G. (1976), Hydrocarbon involvement in photochemical smog formation in Los Angeles atmosphere, *Environ. Sci. Technol.*, *10*, 256–262.

CARB (2009), http://www.arb.ca.gov/ei/maps/statemap/abmap.htm.

CARB (2011), http://www.arb.ca.gov/knowzone/history.htm.

Chinkin, L. R., D. L. Coe, T. H. Funk, H. R. Hafner, P. T. Roberts, P. A. Ryan, and D. R. Lawson (2003), Weekday versus weekend activity patterns for ozone precursor emissions in California's South Coast Air Basin, *J. Air Waste Manage. Assoc.*, *53*(7), 829–843.

Colman, J. J., A. L. Swanson, S. Meinardi, B. C. Sive, D. R. Blake, and F. S. Rowland (2001), Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem.*, *73*(15), 3723–3731.

Emmerson, K. M., and M. J. Evans (2009), Comparison of tropospheric gas-phase chemistry schemes for use within global models, *Atmos. Chem. Phys.*, *9*(5), 1831–1845, doi:10.5194/acp-9-1831-2009.

Fares, S., J. H. Park, D. R. Gentner, R. Weber, E. Ormeno, J. Karlik, and A. H. Goldstein (2012), Seasonal cycles of biogenic volatile organic compound fluxes and concentrations in a California citrus orchard, *Atmos. Chem. Phys. Discuss.*, *12*(7), 17987–18027, doi:10.5194/acpd-12-17987-2012.

Fujita, E. M., W. R. Stockwell, D. E. Campbell, R. E. Keislar, and D. R. Lawson (2003a), Evolution of the magnitude and spatial extent of the

weekend ozone effect in California's South Coast Air Basin, 1981-2000, *J. Air Waste Manage. Assoc.*, *53*(7), 802–815.

Fujita, E. M., D. E. Campbell, B. Zielinska, J. C. Sagebiel, J. L. Bowen, W. S. Goliff, W. R. Stockwell, and D. R. Lawson (2003b), Diurnal and weekday variations in the source contributions of ozone precursors in California's South Coast Air Basin, *J. Air Waste Manage. Assoc.*, *53*(7), 844–863.

Garcia, A. R., R. Volkamer, L. T. Molina, M. J. Molina, J. Samuelson, J. Mellqvist, B. Galle, S. C. Herndon, and C. E. Kolb (2006), Separation of emitted and photochemical formaldehyde in Mexico City using a statistical analysis and a new pair of gas-phase tracers, *Atmos. Chem. Phys.*, *6*, 4545–4557.

Gilman, J. B., et al. (2010), Ozone variability and halogen oxidation within the Arctic and sub-Arctic springtime boundary layer, *Atmos. Chem. Phys.*, *10*(21), 10223–10236, doi:10.5194/acp-10-10223-2010.

de Gouw, J. A., and C. Warneke (2007), Measurements of volatile organic compounds in the earths atmosphere using proton-transfer-reaction mass spectrometry, *Mass Spectrom. Rev.*, *26*(2), 223–257.

de Gouw, J. A., et al. (2005), Budget of organic carbon in a polluted atmosphere: Results from the New England Air Quality Study in 2002, *J. Geophys. Res.*, *110*, D16305, doi:10.1029/2004JD005623.

Haagen-Smit, A. J. (1952), Chemistry and physiology of Los Angeles smog, *Ind. Eng. Chem.*, *44*, 1342–1346.

Harley, R. A., S. A. McKeen, J. Pearson, M. O. Rodgers, and W. A. Lonneman (2001), Analysis of motor vehicle emissions during the Nashville/Middle Tennessee ozone study, *J. Geophys. Res.*, *106*(D4), 3559–3567.

Harley, R. A., L. C. Marr, J. K. Lehner, and S. N. Giddings (2005), Changes in motor vehicle emissions on diurnal to decadal time scales and effects on atmospheric composition, *Environ. Sci. Technol.*, *39*(14), 5356–5362.

Holloway, J. S., R. O. Jakoubek, D. D. Parrish, C. Gerbig, A. Volz-Thomas, S. Schmitgen, A. Fried, B. Wert, B. Henry, and J. R. Drummond (2000), Airborne intercomparison of vacuum ultraviolet fluorescence and tunable diode laser absorption measurements of tropospheric carbon monoxide, *J. Geophys. Res.*, *105*(D19), 24, 251–24, 261, doi:10.1029/2000JD900237.

Jenkin, M. E., S. M. Saunders, and M. J. Pilling (1997), The tropospheric degradation of volatile organic compounds: A protocol for mechanism development, *Atmos. Environ.*, *31*(1), 81–104, doi:10.1016/s1352-2310 (96)00105-7.

Karl, T., E. Apel, A. Hodzic, D. D. Riemer, D. R. Blake, and C. Wiedinmyer (2009), Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity, *Atmos. Chem. Phys.*, *9*(1), 271–285.

Kirchstetter, T. W., B. C. Singer, R. A. Harley, G. R. Kendall, and J. M. Hesson (1999), Impact of California reformulated gasoline on motor vehicle emissions. 2. Volatile organic compound speciation and reactivity, *Environ. Sci. Technol.*, *33*(2), 329–336, doi:10.1021/es980374g.

Langridge, J. M., et al. (2012), Evolution of aerosol properties impacting visibility and direct climate forcing in an ammonia-rich urban environment, *J. Geophys. Res.*, *117*, D00V11, doi:10.1029/2011JD017116.

Madronich, S., R. L. McKenzie, L. O. Bjorn, and M. M. Caldwell (1998), Changes in biologically active ultraviolet radiation reaching the Earth's surface, *J. Photochem.Photobiol. B-Biol.*, *46*(1-3), 5–19, doi:10.1016/ s1011-1344(98)00182-1.

Marr, L. C., and R. A. Harley (2002a), Spectral analysis of weekday-weekend differences in ambient ozone, nitrogen oxide, and non-methane hydrocarbon time series in California, *Atmos. Environ.*, *36*(14), 2327–2335, doi:10.1016/ s1352-2310(02)00188-7.

Marr, L. C., and R. A. Harley (2002b), Modeling the effect of weekday-weekend differences in motor vehicle emissions on photochemical air pollution in central California, *Environ. Sci. Technol.*, *36*(19), 4099–4106, doi:10.1021/es020629x.

Murphy, J. G., D. A. Day, P. A. Cleary, P. J. Wooldridge, D. B. Millet, A. H. Goldstein, and R. C. Cohen (2007), The weekend effect within and downwind of Sacramento - Part 1: Observations of ozone, nitrogen oxides, and VOC reactivity, *Atmos. Chem. Phys.*, *7*(20), 5327–5339.

Pollack, I. B., et al. (2012), Airborne and ground-based observations of a weekend effect in ozone, precursors, and oxidation products in the California South Coast Air Basin, *J. Geophys. Res.*, *117*, D00V05, doi:10.1029/2011JD016772.

Rappenglück, B., P. K. Dasgupta, M. Leuchner, Q. Li, and W. Luke (2010), Formaldehyde and its relation to CO, PAN, and SO2 in the Houston-Galveston airshed, *Atmos. Chem. Phys.*, *10*(5), 2413–2424.

Renzetti, N. A. (1956), Ozone in the Los Angeles atmosphere, *J. Chem. Phys.*, *24*(909).

Roberts, J. M., F. C. Fehsenfeld, S. C. Liu, M. J. Bollinger, C. Hahn, D. L. Albritton, and R. E. Sievers (1984), Measurements of aromatic hydrocarbon ratios and NO_x concentrations in the rural troposphere: Estimates of air mass photochemical age and NO_x removal rate, *Atmos. Environ.*, *18*, 2421–2432.

Russell, A. R., L. C. Valin, E. J. Bucsela, M. O. Wenig, and R. C. Cohen (2010), Space-based Constraints on Spatial and Temporal Patterns of NOx Emissions in California, 2005-2008, *Environ. Sci. Technol.*, *44*(9), 3608–3615, doi:10.1021/es903451j.

Saunders, S. M., M. E. Jenkin, R. G. Derwent, and M. J. Pilling (2003), Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, *3*, 161–180.

Schauffler, S. M., E. L. Atlas, D. R. Blake, F. Flocke, R. A. Lueb, J. M. Lee-Taylor, V. Stroud, and W. Travnicek (1999), Distributions of brominated organic compounds in the troposphere and lower stratosphere, *J. Geophys. Res.*, *104*(D17), 21, 513–21, 535.

Veres, P. R., et al. (2011), Evidence of rapid production of organic acids in an urban air mass, *Geophys. Res. Lett.*, *38*, L17807, doi:10.1029/ 2011GL048420.

Warneke, C., J. A. de Gouw, E. R. Lovejoy, P. C. Murphy, W. C. Kuster, and R. Fall (2005), Development of proton-transfer ion trap-mass spectrometry: On-line detection and identification of volatile organic compounds in air, *J. Am. Soc. For Mass Spectrom.*, *16*(8), 1316–1324.

Warneke, C., et al. (2007), Determination of urban volatile organic compound emission ratios and comparison with an emissions database, *J. Geophys. Res.*, *112*, D10S47, doi:10.1029/2006JD007930.

Warneke, C., et al. (2011), Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results, *Atmos. Meas. Tech.*, *4*(10), 2345–2358, doi:10.5194/ amt-4-2345-2011.

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.

Yarwood, G., J. Grant, B. Koo, and A. M. Dunker (2008), Modeling week-day to weekend changes in emissions and ozone in the Los Angeles basin for 1997 and 2010, *Atmos. Environ.*, *42*(16), 3765–3779, doi:10.1016/j. atmosenv.2007.12.074.

Young, C. J., et al. (2012), Vertically Resolved Measurements of Nighttime Radical Reservoirs; in Los Angeles and Their Contribution to the Urban Radical Budget, *Environ. Sci. Technol.*, *46*(20), 10965–10973, doi:10.1021/ es302206a.