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Airborne and ground-based observations of a weekend effect in ozone, precursors, and oxidation products in the California South Coast Air Basin

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[1] Airborne and ground-based measurements during the CalNex (California Research at the Nexus of Air Quality and Climate Change) field study in May/June 2010 show a weekend effect in ozone in the South Coast Air Basin (SoCAB) consistent with previous observations. The well-known and much-studied weekend ozone effect has been attributed to weekend reductions in nitrogen oxide ($NO_x = NO + NO_2$) emissions, which affect ozone levels via two processes: (1) reduced ozone loss by titration and (2) enhanced photochemical production of ozone due to an increased ratio of non-methane volatile organic compounds (VOCs) to NO_x. In accord with previous assessments, the 2010 airborne and ground-based data show an average decrease in NO_x of 46 ± 11% and 34 ± 4%, respectively, and an average increase in VOC/NO_x ratio of 48 ± 8% and 43 ± 22%, respectively, on weekends. This work extends current understanding of the weekend ozone effect in the SoCAB by identifying its major causes and quantifying their relative importance from the available CalNex data. Increased weekend production of a VOC-NO_x oxidation product, peroxyacetyl nitrate, compared to a radical termination product, nitric acid, indicates a significant contribution from increased photochemical production on weekends. Weekday-to-weekend differences in the products of NO_x oxidation show 45 ± 13% and 42 ± 12% more extensive photochemical processing and, when compared with odd oxygen ($O_x = O_3 + NO_2$), 51 ± 14% and 22 ± 17% greater ozone production efficiency on weekends in the airborne and ground-based data, respectively, indicating that both contribute to higher weekend ozone levels in the SoCAB.

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1. Introduction

[2] Tropospheric ozone (O_3) has adverse health effects on humans (e.g., as a respiratory irritant), is damaging to vegetation, and is a major constituent of smog [*Finlayson-Pitts and Pitts*, 2000; *Jacob*, 1999]. The weekend ozone effect is a phenomenon documented since the 1970s [*Cleveland et al.*, 1974; *Elkus and Wilson*, 1977; *Karl*, 1978; *Levitt and Chock*, 1976] in which ambient, daytime surface ozone concentrations in urban areas tend to be higher on weekends than on weekdays. A weekend ozone effect in the California South Coast Air Basin (SoCAB) has been

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extensively studied [*Blanchard and Tanenbaum*, 2003; *Chinkin et al.*, 2003; *Fujita et al.*, 2003; *Marr and Harley*, 2002b; *Qin et al.*, 2004; *Yarwood et al.*, 2003]. Decreased concentrations of nitrogen oxide (NO_x = NO + NO_2) emissions on weekends are considered to be the dominant cause of increased weekend ozone concentrations [*Lawson*, 2003; *Croes et al.*, 2003; *Blanchard and Tanenbaum*, 2003; *Fujita et al.*, 2003; *Marr and Harley*, 2002a, 2002b; *Murphy et al.*, 2007; *Yarwood et al.*, 2003; *Yarwood et al.*, 2008].

[3] On-road motor vehicles are the dominant emissions source of many pollutants in the SoCAB. According to the 2008 inventory of estimated annual average emissions (Emission Data by Air Basin, California Air Resources Board, accessed May 2011 from http://www.arb.ca.gov/ei/emissiondata.htm) for the SoCAB, on-road motor vehicles contribute 25% of total organic gases, 30% of reactive organic gases, 62% of CO, and 55% of NO_x to the total emissions. Weekday and weekend differences in emissions are commonly associated with differences in fuel combustion products, fuel economy, fuel consumption, and traffic patterns of on-road gasoline and diesel-powered vehicles. Heavy-duty, diesel-powered vehicles generally represent a small portion (<5%) of the total number of on-road vehicles [*Ban-Weiss et al.*, 2008b; *Chinkin et al.*, 2003; *Marr and Harley*, 2002a], but are the dominant on-road source of NO_x and black carbon (BC) emissions [*Ban-Weiss et al.*, 2008b; *Kirchstetter et al.*, 1999]. Light-duty, gasoline-fueled vehicles, which are the majority of the on-road fleet, are the primary on-road source of CO and CO_2 [*Ban-Weiss et al.*, 2008a; *Sullivan et al.*, 2004]. Previous studies [*Chinkin et al.*, 2003; *Dreher and Harley*, 1998; *Harley et al.*, 2005; *Marr et al.*, 2002] demonstrated similar overall activity of gasoline-fueled vehicles on weekdays and weekends in California despite changes in peak travel time, while diesel-fueled vehicle activity was markedly reduced on weekends compared to weekdays. Weekend reductions in the traffic volume of heavy-duty, diesel-fueled vehicles have been reported to be 40 – 80% in the SoCAB [*Chinkin et al.*, 2003]. The large decrease in on-road diesel-fueled vehicle activity on weekends leads to significant reductions in weekend NO_x and BC emissions.

[4] Reduced NO_x emissions on weekends can affect ozone levels via two processes: 1) decreased ozone loss by titration and 2) increased ozone production due to an increase in the ratio of volatile organic compounds (VOCs) to NO_x. The chemistry behind these processes has been described in detail [*Finlayson-Pitts and Pitts*, 2000; *Jacob*, 1999; *Murphy et al.*, 2007; *Tonse et al.*, 2008], and is briefly summarized here. The first process, decreased ozone loss by titration, has been considered a dominant cause for higher weekend ozone. Decreased NO_x emissions, emitted mostly as nitric oxide (NO), on weekends leads to decreased ozone loss due to reaction with NO according to (R1), and thus higher mixing ratios of ozone remain.

$$O_3 + NO \rightarrow NO_2 + O_2 \quad \text{(R1)}$$

[5] Recent studies [*Marr and Harley*, 2002a; b; *Yarwood et al.*, 2003; *Tonse et al.*, 2008; *Yarwood et al.*, 2008] indicate that the second process, increased photochemical production of ozone, may play a significant role in increased weekend ozone levels in and downwind of urban areas. Increased weekend VOC/NO_x ratios favor peroxy (HO_2) and alkylperoxy (RO_2) radical formation via (R2) and (R3).

$$OH + CO + O_2 \rightarrow HO_2 + CO_2 \quad \text{(R2)}$$

$$OH + RH + O_2 \rightarrow RO_2 + H_2O \quad \text{(R3)}$$

[6] Nitrogen dioxide (NO_2) is generated via (R4) and (R5) upon oxidation of NO by HO_2 or RO_2, and ozone is produced by photooxidation of NO_2 via (R6) and (R7).

$$HO_2 + NO \rightarrow NO_2 + OH \quad \text{(R4)}$$

$$RO_2 + NO \rightarrow NO_2 + RO \quad \text{(R5)}$$

$$NO_2 + h\nu \rightarrow NO + O \quad \text{(R6)}$$

$$O + O_2 \rightarrow O_3 \quad \text{(R7)}$$

[7] Recycling of OH via (R4) and further reactions of RO propagate the chain reactions for ozone formation.

[8] WD-to-WE differences in reaction products, specifically nitric acid (HNO_3) which is formed via (R8) and peroxyacetyl nitrate (PAN; $CH_3C(O)O_2NO_2$) produced via (R9), are affected by the WD-to-WE differences in NO_x and VOC/NO_x ratio and thus act as indicators for WD-to-WE differences in the relative contribution of titration and photochemical production to observed ozone concentrations.

$$OH + NO_2 \rightarrow HNO_3 \quad \text{(R8)}$$

$$CH_3C(O)O_2 + NO_2 \rightarrow CH_3C(O)O_2NO_2 \quad \text{(R9)}$$

[9] Formation of HNO_3 effectively removes OH radicals from the chain reactions that produce ozone, and thus is a radical termination step. Enhanced formation of HNO_3, which preferentially occurs under the high NO_x conditions more characteristic of weekdays, is an indicator for branching in the OH chemistry toward quenching the ozone formation cycle. On the other hand, an increased VOC/NO_x ratio on weekends shifts the OH chemistry toward enhanced production of RO_2 via (R3). Enhanced production of RO_2 leads to increased formation of VOC-NO_x oxidation products such as PAN via (R9) as well as ozone via (R4 – R7). Rapid thermal decomposition of PAN regenerates RO_2 and NO_2 and promotes continued ozone production. Positive correlation between O_3 and PAN in urban areas has been well established by *Roberts et al.* [1995]; thus PAN formation is an indicator for branching in the HO_2 and RO_2 chemistry favoring the ozone formation cycle. The abundance of HNO_3 relative to PAN provides an indication of the balance between termination and propagation steps in the catalytic ozone formation cycle.

[10] Odd oxygen (O_x = O_3 + NO_2) has also been interpreted in previous studies [*Murphy et al.*, 2007; *Sadanaga et al.*, 2008; *Tonse et al.*, 2008] to isolate the relative contributions from titration and photochemical production to weekday and weekend ozone levels. If we consider titration

only, O_3 is consumed in (R1) only to regenerate NO_2, which undergoes photooxidation via (R6 and R7) back into O_3. Despite depletion of O_3, regeneration of NO_2 in this chemical null cycle conserves the O_x concentration. Net production of ozone and O_x is only achieved by formation of NO_2 via (R2 – R5). Therefore, a lack of WD-to-WE differences in O_x indicate titration as the dominant process affecting differences in ozone, while observed WD-to-WE differences in O_x indicate differences in photochemical production.

[11] Here, we report airborne and ground-based measurements from the CalNex (California Research at the Nexus of Air Quality and Climate Change) field study in May and June 2010. Measurements of O_3 during CalNex confirm the well-documented weekend ozone effect in the SoCAB, while measurements of the NO_x and VOC precursors to ozone formation demonstrate significant reductions in NO_x and an increase in VOC/NO_x ratio on weekends consistent with previous observations. Measurements of O_3, NO_2, and CO from a routine surface monitoring network in the SoCAB provide supporting evidence for these findings. Measurements of a VOC-NO_x oxidation product (PAN), the main radical termination product (HNO_3), and an indicator for net changes in O_3 production (O_x) demonstrate differences in the relative contribution of photochemical production to weekday and weekend ozone levels in the SoCAB. Additional analyses of O_x and oxidized NO_x from the CalNex data set suggest faster photochemical processing and greater ozone production efficiency on weekends.

2. Experimental Description

2.1. CalNex Airborne Measurements

[12] Airborne measurements of trace gases and particulate matter were acquired during the CalNex field study in May and June 2010. An instrumented National Oceanic and Atmospheric Administration (NOAA) P-3 aircraft conducted fourteen daytime research flights over the California SoCAB and Central Valley during CalNex. Seven of the fourteen daytime flights, including four weekdays (4 May, 14 May, 19 May, 24 May) and three weekend days (8 May, 16 May, 20 June), were focused on the SoCAB and are used in this analysis. The instrumental techniques, accuracy, precision, sampling frequency, and references containing further details for the measurement used in this analysis are summarized in Table 1. Airborne CO measurements were provided by vacuum UV resonance fluorescence [*Holloway et al.*, 2000]; airborne CO_2 measurements were provided by wavelength-scanned CRDS [*Chen et al.*, 2010] and by quantum cascade laser spectroscopy (QCLS). Accumulation-mode BC was measured by single-particle soot photometry (SP2) [*Schwarz et al.*, 2010]. PAN [*Roiger*, 2011; *Slusher et al.*, 2004], NH_3 [*Nowak et al.*, 2007, 2010], and HNO_3 [*Neuman et al.*, 2002, 2003] measurements were provided by chemical ionization mass spectrometry (CIMS). Airborne measurements of VOCs were obtained periodically throughout each flight using a whole air sampler (WAS) [*Schauffler et al.*, 1999] and analyzed post-flight by gas chromatography [*Colman et al.*, 2001]. VOCs were also measured in-flight for 1 s sequentially every 17 s using a proton-transfer-reaction mass spectrometer (PTR-MS) [*de Gouw and Warneke*, 2007]. Data from the WAS canister samples were primarily used in this analysis; data from the PTR-MS were additionally considered for toluene and benzene. Airborne measurements of O_3 [*Ryerson et al.*, 1998], NO [*Ryerson et al.*, 2000], and NO_2 [*Pollack et al.*, 2011], were primarily provided by chemiluminescence (CL). A comparison of NO, NO_2, and O_3 measurements by CL and by cavity ring-down spectroscopy (CRDS) on the P-3 shows agreement within the instrument uncertainties [*Wagner et al.*, 2011]; thus, CRDS data are used for the 14 May flight where CL data are not available. Airborne measurements of total reactive nitrogen (NO_y) were also acquired using the CL instrument [*Ryerson et al.*, 1999]. NO_y measurements were not available for the 4 May and 14 May flights, therefore using a calculated sum for NO_y, where $\Sigma NO_y = NO_x + PAN + HNO_3$, provides a more complete data set for this analysis. A range of precisions for ΣNO_y is determined by adding in quadrature the reported precisions for the NO_x, PAN, and HNO_3 measurements (Table 1). A mean accuracy of $\pm 12\%$ for ΣNO_y is determined by averaging the percent accuracies calculated for each data point, which were determined by propagating in quadrature the percent accuracies reported for the NO_x, PAN, and HNO_3 measurements (Table 1). Comparison of measured NO_y to ΣNO_y generally shows agreement within the uncertainties. However, significant differences between measured NO_y and ΣNO_y were consistently observed when high levels of NH_3 and aerosol nitrate were sampled. These differences arise from known interferences with NH_3 [*Fahey et al.*, 1985] and ammonium nitrate aerosol [*Ryerson et al.*, 1999] that lead to an over-estimate of the gas-phase NO_y measurement and a reduction of ΣNO_y as HNO_3 is consumed to form ammonium nitrate. From flight data in the LA basin, we estimate that differences in measured NO_y and ΣNO_y outside the reported uncertainties are observed when NH_3 exceeds roughly 10 ppbv. Therefore, the summed NO_y data and the HNO_3 measurements are additionally filtered by $NH_3 < 10$ ppbv prior to further analysis.

[13] Airborne trace gas data were averaged to 2 s prior to further analysis to minimize the influence of a ± 1 s uncertainty in the time alignment of the measurements and to match the sampling interval of PAN. Before further analysis involving VOC measurements, 1-s trace gas mixing ratios were further averaged over the in-flight sampling duration of each WAS canister (3–8 s) according to canister fill start and stop times. Flight data from the daytime mixed boundary layer (BL) over the Los Angeles (LA) basin between 0.2 and 1 km above ground level (AGL), $33.6° < \text{latitude} < 34.3°$, and $-118.5° < \text{longitude} < -116.8°$ were retained for this analysis (Figure 1). The lower limit on altitude reduces sampling of concentrated emissions during takeoff and landing. Only data acquired between 12:00 – 18:00 Pacific daylight time (PDT), when the planetary BL was well developed and photochemical processing was well advanced, were retained.

2.2. CalNex Ground-Based Measurements

[14] Ground-based trace gas measurements were also acquired during CalNex and are used here to extend the number of weekdays and weekends studied. Ground-based instrumentation (Table 1) was located at the California Institute of Technology in Pasadena from 15 May to 15 June. Ground-based measurements of NO, NO_2, and NO_y were provided by CL; O_3 was measured using UV

Table 1. Summary of Instrument Techniques and Uncertainties for Airborne Measurements Onboard the NOAA P-3 and Ground-Based Measurements at the Pasadena Site During CalNex

Species	Technique (Commercial Instrumentation)	Accuracy	Precision	Frequency	Reference
		CalNex-Aircraft			
O_3	NO/O_3 CL	±2%	±(0.015 to 0.15) ppbv[a]	1 Hz	*Ryerson et al.* [1998]
O_3	CRDS	±3%	±0.12 ppbv	1 Hz	*Wagner et al.* [2011]
NO	NO/O_3 CL	±3%	±(0.01 to 0.05) ppbv[a]	1 Hz	*Ryerson et al.* [2000]
NO	CRDS	±2%	±0.14 ppbv	1 Hz	*Wagner et al.* [2011]
NO_2	UV-LED photolytic conversion to NO followed by CL detection	±4%	±(0.03 to 0.08) ppbv[a]	1 Hz	*Pollack et al.* [2011]
NO_2	CRDS	±2%	±0.09 ppbv	1 Hz	*Wagner et al.* [2011]
NO_y	Au catalyzed thermal conversion to NO followed by CL detection	±12%	±(0.04 to 0.10) ppbv[a]	1 Hz	*Ryerson et al.* [1999]
$\sum NO_y$	Calculated sum of measured NO_x + PAN + HNO_3	±12%[b]	±(0.03 to 0.10) ppbv[b]	1 Hz	
CO	Vacuum UV resonance fluorescence	±5%	±1 ppbv	1 Hz	*Holloway et al.* [2000]
CO_2	Wavelength-scanned CRDS (Picarro, model 1301-m)	±0.10 ppmv	±0.15 ppmv	1 Hz	*Chen et al.* [2010]
CO_2	QCLS	±0.10 ppmv	±0.15 ppmv	1 Hz	
BC	SP2	±40%	±25%	1 Hz	*Schwarz et al.* [2010]
PAN	Thermal decomposition-CIMS using I^- reagent ion	±20%	±0.005 ppbv	0.5 Hz	*Roiger* [2011], *Slusher et al.* [2004]
NH_3	CIMS using protonated acetone dimer reagent ion	±30%	±0.2 ppbv	1 Hz	*Nowak et al.* [2007], *Nowak et al.* [2010]
HNO_3	CIMS using SiF_5^- reagent ion	±15%	±0.012 ppbv	1 Hz	*Neuman et al.* [2002], *Neuman et al.* [2003]
VOCs	WAS	±10%	±2%	~72 cans per flight	*Colman et al.* [2001], *Schauffler et al.* [1999]
VOCs	PTR-MS	±20%	±10%	1 Hz	*de Gouw and Warneke* [2007]
		CalNex-Pasadena			
O_3	UV differential absorption (Thermo Environmental Instruments, model 49c)	±4%	±4%	1 min^{-1}	
NO	CL (Thermo Electron Instruments, model 42i-TL)	±4%	±4%	1 min^{-1}	
NO_2	Photolysis (Air Quality Designs, model BLC) followed by CL (Thermo Electron Instruments, model 42i-T)	±6%	±6%	1 min^{-1}	
NO_y	Mo conversion followed by CL (Thermo Electron Instruments, model 42i-TL)	±4%	±4%	1 min^{-1}	
CO	Vacuum UV fluorescence (Aerolaser, 5001)	±4%	±0.13 ppbv	1 min^{-1}	*Gerbig et al.* [1999]
CO_2	Non-dispersive IR absorption	±0.12 ppmv	±0.01 ppmv	1 min^{-1}	*Peischl et al.* [2010]
VOCs	GC-MS	±20%	±10 pptv	30 min^{-1}	*Gilman et al.* [2010]

[a]Range of imprecision determined from 1 Hz counting statistics.

[b]A mean accuracy for ΣNO_y of ±12% is determined by averaging the percent accuracies calculated for each data point; which is determined by propagating in quadrature the percent accuracies of the NO_x, PAN, and HNO_3 measurements. A range of precisions for ΣNO_y is determined by adding in quadrature the precisions of the NO_x, PAN, HNO_3 measurements.

differential absorption. Measured values for NO_y are used in the analysis of the ground-based data owing to minimal differences observed between the measured and calculated sum of NO_y, which result from less interference from NH_3 and ammonium nitrate aerosol at this specific sampling location. Ground-based measurements of CO were provided by vacuum UV resonance fluorescence [*Gerbig et al.*, 1999]; CO_2 was measured via non-dispersive IR absorption [*Peischl et al.*, 2010]. VOCs were measured for 5 min every 30 min using a gas chromatograph with mass spectrometric detection (GC-MS) [*Gilman et al.*, 2010]. Additional measurements of CO [*Andrews and Novelli*, 2010] and CO_2 [*Andrews and Lang*, 2010] were obtained from flask samples acquired at the Mt. Wilson Observatory (Figure 1) during the same time period. Flask samples were taken twice daily at roughly 04:00 and 16:00 PDT.

[15] Trace gas measurements from the CalNex-Pasadena site were averaged over 1 min prior to analysis, and were further averaged over the sampling duration of the GC-MS according to start and stop times before analysis involving the VOC measurements. For best comparison with the airborne data, only trace gas measurements acquired between 12:00 – 18:00 PDT from the CalNex-Pasadena site and from the afternoon Mt. Wilson Observatory flasks were retained. National holidays have been excluded leaving 21 weekdays (Monday through Friday) and 10 weekends (Saturday and Sunday) for both sites between 15 May and 15 June, 2010.

2.3. SoCAB Network Measurements

[16] Measurements of O_3, NO_2, and CO from the South Coast Air Quality Management District (AQMD) monitoring network were considered to further supplement this analysis. Trace gas data are available from the Web-based Air Quality and Meteorological Information System accessible via the California Air Resources Board (CARB) Web site (http://www.arb.ca.gov/aqmis2/aqdselect.php). Hourly averages from more than 20 locations in the SoCAB (Figure 1) as well as hourly averages from the monitoring

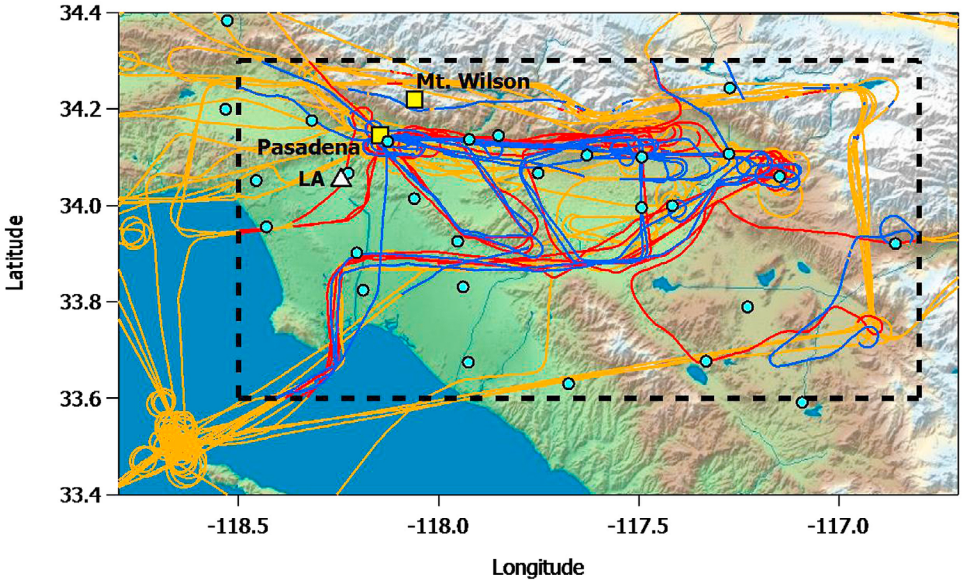

Figure 1. NOAA P-3 flight tracks (orange) from the seven daytime flights conducted in the SoCAB. Airborne data from the mixed BL (between 0.2 and 1 km AGL) in the LA basin (dashed box) are colored to indicate data from the four weekday (blue) and three weekend (red) flights used in this analysis. Additional measurements were acquired from ground-based instrumentation located at the CalNex-Pasadena ground site and flask samples taken at Mt. Wilson Observatory (yellow squares). Surface measurements from 20+ sites in the South Coast Air Quality Monitoring District (cyan circles) supplement the CalNex observations. The downtown LA area (white triangle) is indicated as a point of reference.

site located at S. Wilson Avenue (34.13° latitude, −118.13° longitude) in Pasadena were selected. For best comparison with the CalNex airborne and ground-based data, only afternoon (12:00 – 18:00 PDT) measurements during 15 May to 15 June were used from the AQMD data sets.

2.4. Data Analyses

[17] Weekday and weekend abundances of trace gases from the CalNex airborne data sets were determined by averaging the mean mixing ratios determined for each of the four weekday and three weekend flights. Mean abundances from the CalNex-Pasadena, AQMD-Pasadena, and AQMD-SoCAB surface data sets were calculated by averaging the mean mixing ratios determined for each of the 21 weekdays and 10 weekend days sampled between 15 May and 15 June. The corresponding uncertainties reported for each mean represent confidence limits calculated using the 1σ standard deviation and the corresponding number of weekdays and weekend days sampled in each data set. The reported uncertainties reflect day-to-day variability in the daily mean mixing ratios measured during the CalNex intensive and additionally, for the ground-based measurements, may include influence from concentrated emission sources nearby the specific sampling locations. Confidence limits for WD-to-WE differences and WD-to-WE ratios of mean abundances are calculated by propagating the uncertainties in the means in quadrature [*Taylor*, 1997].

[18] For correlation analysis, the selected airborne and ground-based data were fit using a linear least squares (LLS) [*Press et al.*, 1988] orthogonal distance regression (ODR) [*Boggs et al.*, 1987] weighted by the inverse square of the precision of the measurements (Table 1). The regression slopes from the airborne data involving directly emitted species, such as NO_y, BC, VOC, CO, and CO_2, are interpreted as emissions ratios integrated over all sources in the LA basin, while regression slopes involving the same measurements from ground-based data are interpreted as emissions ratios from a potentially different mixture of basin-wide and local sources. Regression slopes involving secondary pollutants are referred to as enhancement ratios. A total uncertainty for each emission or enhancement ratio was calculated from the quadrature sum of the uncertainty in the regression slope and the calibration uncertainties of the respective measurements [*Taylor*, 1997]. Uncertainties in WD-to-WE ratios were determined by propagation of the total uncertainties from each emission or enhancement ratio. The x-intercepts of the LLS fits of NO_y and BC to CO and to CO_2 provide a measure of the background mixing ratios of long-lived species, such as CO and CO_2, in the LA basin. LLS ODR fits of airborne and ground-based VOCs to NO_x were forced through the origin, consistent with the minimal upwind background mixing ratios of these species compared to enhancements observed in the SoCAB.

3. Results and Discussion

3.1. Weekend Effect in Ozone

[19] A time series of airborne ozone observations from the CalNex intensive in May and June 2010 (Figure 2a) shows higher ozone mixing ratios on weekends (red squares) in comparison to weekdays (blue circles). Mean ozone abundances of 56 ± 5 ppbv and 78 ± 2 ppbv (Table 2) were determined from the average of the four weekday and three weekend flights, respectively. An average weekend-to-weekday (WE-to-WD) difference of 22 ± 6 ppbv demonstrates a significant weekend effect in ozone observed in the

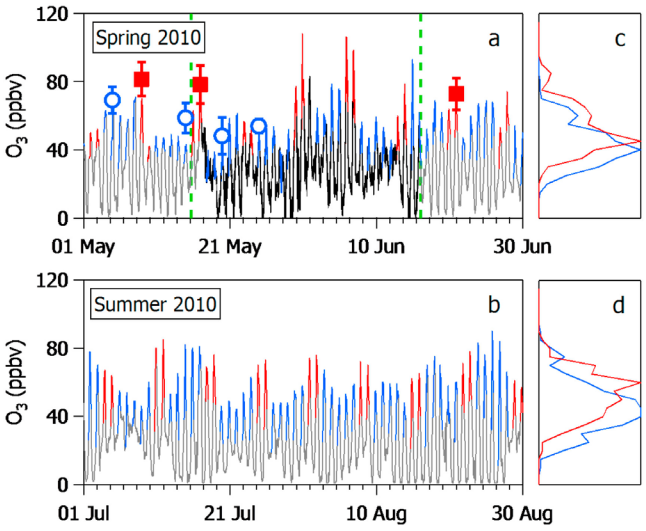

Figure 2. (a) Time series of ozone measured from the CalNex-Pasadena (black line) and AQMD-Pasadena (gray line) ground sites during May and June 2010. Weekday (blue) and weekend (red) measurements isolated to daytime observations between 12:00 – 18:00 PDT are shown for both the CalNex-Pasadena and AQMD-Pasadena data sets. The 15 May to 15 June sampling period at the CalNex-Pasadena site is denoted by the vertical green dashed lines. Symbols represent the average and 1σ standard deviation of airborne ozone from the four weekday (blue circles) and three weekend (red squares) flights. (b) Time series of ozone sampled from the AQMD-Pasadena site during July and August following the CalNex intensive. (c, d) Histogram of weekday (blue) and weekend (red) ozone mixing ratios observed at the AQMD-Pasadena site during spring and summer 2010. The *x*-axes have been normalized to give an equal mode for each distribution.

SoCAB during the time period sampled by these aircraft flights. Ozone measurements from the CalNex ground site at Pasadena, which consist of a substantially larger sampling of weekdays and weekends than the airborne data set, provide further evidence for the observed weekend ozone effect in the SoCAB during CalNex. A time series of the CalNex-Pasadena ozone observations between 15 May and 15 June (Figure 2a, black line) shows several weekends (red) with higher ozone mixing ratios than weekdays (blue). The CalNex-Pasadena observations result in an average ozone abundance of 47 $\pm$ 2 ppbv on weekdays and 65 $\pm$ 5 ppbv on weekends, corresponding to a WE-to-WD difference of 18 $\pm$ 5 ppbv (Table 2). Despite significant differences in the mean weekday and weekend ozone abundances determined from the CalNex airborne and ground-based measurements, large WE-to-WD differences are consistently observed. Differences in meteorological conditions, background ozone concentrations in air masses transported into the SoCAB, downward transport of ozone from aloft, and, for ground-based measurements, potential point source emissions nearby the specific sampling locations are all contributing factors to the mean abundances and the day-to-day variability in ozone.

[20] The relatively small number of days in the CalNex airborne and ground-based observations represents a statistically limited data set. In this section we show that the weekend effect inferred from examination of airborne data and data from a single surface location during CalNex is consistent with ozone measurements from the AQMD surface monitoring network spanning a longer period of time. A time series of ozone measured at the AQMD-Pasadena site during May and June 2010 (Figure 2a, gray line) overlaid with airborne and ground-based measurements shows agreement between the CalNex and monitoring network observations. Consistently higher mixing ratios of ozone are observed on weekends (red) compared to weekdays (blue)

Table 2. Mean Mixing Ratios for O_3, O_x, NO_x, CO, and CO_2 Measured on Weekdays (WD) and Weekends (WE) and Their Corresponding 1σ Confidence Limits[a]

Parameter		CalNex-Aircraft	CalNex-Pasadena	AQMD-Pasadena	AQMD-SoCAB	Mt. Wilson Flasks
O_3 (ppbv)	WD	56 $\pm$ 5	47 $\pm$ 2	41 $\pm$ 2	50 $\pm$ 2	
	WE	78 $\pm$ 2	65 $\pm$ 5	57 $\pm$ 3	61 $\pm$ 3	
	Δ(WE-WD)	22 $\pm$ 6	18 $\pm$ 5	16 $\pm$ 4	11 $\pm$ 4	
O_x (ppbv)	WD	65 $\pm$ 5	63 $\pm$ 3	57 $\pm$ 2	60 $\pm$ 2	
	WE	81 $\pm$ 3	77 $\pm$ 4	67 $\pm$ 4	68 $\pm$ 4	
	Δ(WE-WD)	16 $\pm$ 6	14 $\pm$ 5	10 $\pm$ 5	8 $\pm$ 5	
NO_y or NO_2[b] (ppbv)	WD	15.1 $\pm$ 2.4	24.7 $\pm$ 1.6	17.0 $\pm$ 1.2	10.5 $\pm$ 0.6	
	WE	8.4 $\pm$ 1.0	16.2 $\pm$ 1.8	9.3 $\pm$ 1.2	7.5 $\pm$ 0.8	
	WD-to-WE ratio	1.80 $\pm$ 0.36	1.52 $\pm$ 0.19	1.82 $\pm$ 0.27	1.41 $\pm$ 0.17	
CO (ppmv)	WD	0.26 $\pm$ 0.04	0.32 $\pm$ 0.02	0.43 $\pm$ 0.02	0.25 $\pm$ 0.03	0.21 $\pm$ 0.01
	WE	0.24 $\pm$ 0.04	0.31 $\pm$ 0.03	0.41 $\pm$ 0.03	0.24 $\pm$ 0.04	0.21 $\pm$ 0.02
	WD-to-WE ratio	1.09 $\pm$ 0.24	1.04 $\pm$ 0.11	1.05 $\pm$ 0.08	1.04 $\pm$ 0.20	1.02 $\pm$ 0.12
CO_2 (ppmv)	WD	404 $\pm$ 2	411 $\pm$ 2			399 $\pm$ 1
	WE	403 $\pm$ 2	411 $\pm$ 3			399 $\pm$ 2
	WD-to-WE ratio	1.00 $\pm$ 0.01	1.00 $\pm$ 0.01			1.00 $\pm$ 0.01

[a]CalNex-aircraft data reflect averages over the four weekdays and three weekend days sampled, while CalNex-Pasadena and AQMD measurements reflect averages over the 21 weekdays and 10 weekend days sampled between 15 May and 15 June 2010. WE-to-WD differences are reported for O_3 and O_x; WD-to-WE ratios are reported for NO_x, CO, and CO_2. Confidence limits for WD-to-WE differences and WD-to-WE ratios are calculated by propagating the reported uncertainties for each mean in quadrature.

[b]CalNex averages use the airborne calculated sum of NO_y and ground-based measurements of NO_y; AQMD averages use measurements of NO_2.

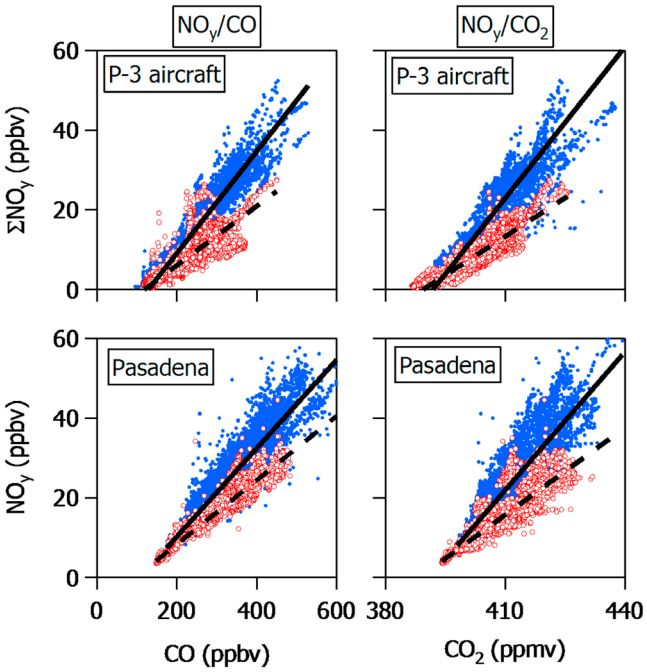

Figure 3. Plots of ΣNO_y versus (top left) CO and (top right) CO_2 using CalNex airborne data, and plots of measured NO_y versus (bottom left) CO and (bottom right) CO_2 using ground-based data from the CalNex-Pasadena site. Weekday (blue dots, solid lines) and weekend (red circles, dashed lines) emissions ratios in Table 3 are inferred from slopes derived from LLS ODR.

(Figures 2a and 2c). Average ozone abundances determined for the AQMD-Pasadena site result in a similar WE-to-WD difference as that observed at the CalNex-Pasadena site, while average ozone for the broader AQMD-SoCAB network leads to half the WE-to-WD difference observed from the basin-wide airborne observations (Table 2). The airborne data likely reflect the greater contrast between relatively clean air sampled near the coast and the more photochemically processed air, which is preferentially sampled by the inland surface sites (Figure 1). Regardless, mean ozone abundances determined from all of the data sets reveal large (11 to 22 ppbv) WE-to-WD differences in ozone during May and June 2010.

[21] Further evidence of a weekend ozone effect in the SoCAB is illustrated by a time series of ozone sampled at the AQMD-Pasadena site during July and August 2010 following the CalNex intensive (Figure 2b). The time series and corresponding histogram (Figure 2d) demonstrate higher ozone mixing ratios are observed on weekends compared to weekdays. Mean ozone mixing ratios of 48 ± 2 ppbv on weekdays and 55 ± 2 ppbv on weekends were determined for 01 July to 30 August, and correspond to a WD-to-WE difference of 7 ± 3 ppbv. In addition, WD-to-WE differences were calculated for 2005 to 2009 using hourly data for the AQMD-Pasadena site. For consistency, the data are limited to the same sampling dates as the CalNex intensive (15 May to 15 June) and to the same time of day (12:00 – 18:00 PDT). Over the five year period, average weekday ozone mixing ratios ranged from 38 to 49 ppbv while average weekend ozone mixing ratios ranged from 51 to 70 ppbv. The corresponding WD-to-WE differences ranged from 13 to 21 ppbv between 2005 and 2009 and displayed no particular increasing or decreasing trend. Regular observation of a weekend ozone effect throughout the spring and summer in 2010 as well as over the previous five years in the monitoring network data supports our interpretation of the CalNex airborne and ground-based observations.

3.2. Weekend Effect in Ozone Precursor Species

3.2.1. NO_x Emissions

[22] Plots of ΣNO_y versus CO and ΣNO_y versus CO_2 using the airborne data (Figure 3), where ΣNO_y represents the calculated sum of airborne measurements of NO_x + PAN + HNO_3, illustrate significant WD-to-WE differences in precursor emissions in the mixed BL of the LA basin. As in previous studies [*Murphy et al.*, 2007; *Parrish et al.*, 2002], NO_y is used here as a more conserved measure of NO_x. Slopes of the LLS ODR fits are interpreted as emissions ratios (Table 3) since NO_y, CO, and CO_2 are approximately conserved species inside the LA basin on the time scale since emission of ~1 day that is considered here. R^2 values from one-sided LLS fits range from 0.66 to 0.91. Larger emissions ratios were consistently observed on weekdays compared to weekends. From the airborne data, WD-to-WE ratios of 1.72 ± 0.32 for NO_y/CO and 1.97 ± 0.34 for NO_y/CO_2 correspond to an average decrease of 46 ± 11% in weekend NO_x emissions ratios. Eliminating data from Saturdays and Mondays, commonly considered transitional or build-up days, does not significantly change the observed emissions ratios or the WD-to-WE ratios. Since the airborne data set has a limited sampling of weekdays and weekends, comparison to the CalNex ground-based measurements provides supporting evidence for the airborne results. NO_y/CO and NO_y/CO_2 emissions ratios from ground-based measurements at the CalNex-Pasadena site yield slightly smaller WD-to-WE ratios of 1.38 ± 0.11 and 1.59 ± 0.09, respectively, and correspond to an average decrease of 34 ± 4% in weekend NO_x emissions ratios. The CalNex airborne and ground-based ratios for NO_y/CO and NO_y/CO_2 agree within their propagated 1σ uncertainties, although differences in the inferred emissions ratios likely reflect basin-wide integration over all emissions sources by the aircraft compared to more localized sampling at the CalNex-Pasadena ground site.

[23] Large WD-to-WE differences observed in NO_y/CO and NO_y/CO_2 emissions ratios are supported by large WD-to-WE differences in measured abundances of NO_y. WD-to-WE ratios of 1.80 ± 0.36 and 1.52 ± 0.19 (Table 2) were determined from the ratio of mean weekday and weekend abundances of ΣNO_y from the CalNex airborne data and NO_y measurements from the ground-based data, respectively. WD-to-WE ratios of NO_y abundances are consistent with WD-to-WE ratios determined from NO_y/CO emissions ratios (Table 3). WD-to-WE ratios of abundances were also determined for the AQMD-SoCAB and AQMD-Pasadena data sets using mean weekday and weekend mixing ratios of NO_2. The respective data sets reveal WD-to-WE ratios of 1.41 ± 0.17 and 1.82 ± 0.27 (Table 2), and are consistent with the CalNex observations despite a known sensitivity of the network NO_2 measurements to organic nitrates and HNO_3, which is related to inlet configuration and thermal operation range of a molybdenum converter [*Fitz*, 2002; *Murphy et al.*, 2007; *Winer et al.*, 1974].

Table 3. The Slope, x-Intercept, and R^2 From Each Fit and Propagated Total Uncertainties for Weekdays and Weekends Using CalNex Data From the Aircraft, Pasadena Ground Site, and Mt. Wilson Observatory (MWO) Measurement Platforms[a]

		Weekday			Weekend			
	Platform	Slope	x-int[b]	R^2	Slope	x-int[b]	R^2	WD-to-WERatio[c]
$\Sigma NO_y/CO$[d]	Aircraft	0.13 ± 0.02	128 ± 6	0.91	0.07 ± 0.01	118 ± 6	0.66	1.72 ± 0.32
NO_y/CO[d]	Pasadena	0.11 ± 0.01	107 ± 4	0.87	0.08 ± 0.01	95 ± 4	0.88	1.38 ± 0.11
$\Sigma NO_y/CO_2$[e]	Aircraft	1.27 ± 0.15	392 ± 4	0.84	0.64 ± 0.08	389 ± 4	0.84	1.97 ± 0.34
NO_y/CO_2[e]	Pasadena	1.16 ± 0.05	391 ± 4	0.79	0.73 ± 0.03	388 ± 4	0.71	1.59 ± 0.09
BC/CO[f]	Aircraft	1.65 ± 0.67	124 ± 5	0.79	0.94 ± 0.38	112 ± 6	0.65	1.76 ± 1.01
BC/CO_2[g]	Aircraft	16.3 ± 6.5	392 ± 5	0.69	7.1 ± 2.9	387 ± 5	0.77	2.29 ± 1.30
CO/CO_2[e]	Aircraft	9.8 ± 0.5		0.79	8.2 ± 0.4		0.71	1.20 ± 0.09
CO/CO_2[e]	Pasadena	11.5 ± 0.5		0.83	11.8 ± 0.5		0.78	0.98 ± 0.06
CO/CO_2[e]	MWO	12.0 ± 0.2		0.82	11.1 ± 0.2		0.66	1.09 ± 0.02
benzene/CO[h]	Aircraft	0.93 ± 0.10		0.95	0.86 ± 0.10		0.92	1.07 ± 0.17
benzene/CO[h]	Pasadena	1.22 ± 0.26		0.93	1.25 ± 0.27		0.98	0.98 ± 0.29
acetylene/CO[h]	Aircraft	5.02 ± 0.56		0.95	4.15 ± 0.46		0.94	1.21 ± 0.19
acetylene/CO[h]	Pasadena	6.99 ± 1.46		0.84	6.07 ± 1.30		0.95	1.15 ± 0.34
o-xylene/NO_x[h]	Aircraft	2.96 ± 0.33		0.87	4.10 ± 0.49		0.74	0.72 ± 0.12
o-xylene/NO_x[h]	Pasadena	7.2 ± 1.5		0.57	10.2 ± 2.1		0.66	0.71 ± 0.21
ethene/NO_x[h]	Aircraft	49.1 ± 5.5		0.88	80.3 ± 9.0		0.72	0.61 ± 0.10
ethene/NO_x[h]	Pasadena	110.1 ± 22.8		0.76	160.0 ± 33.2		0.49	0.69 ± 0.20
ethylbenzene/NO_x[h]	Aircraft	3.8 ± 0.4		0.86	5.4 ± 0.7		0.65	0.70 ± 0.11
n-heptane/NO_x[h]	Aircraft	4.0 ± 0.4		0.82	6.5 ± 0.7		0.78	0.61 ± 0.10
n-octane/NO_x[h]	Aircraft	1.6 ± 0.2		0.81	2.3 ± 0.1		0.74	0.68 ± 0.11
toluene/NO_x[h]	Aircraft	28.1 ± 3.1		0.86	38.1 ± 4.3		0.73	0.74 ± 0.12
toluene/NO_x[h]	Pasadena	40.8 ± 8.4		0.76	58.4 ± 12.1		0.49	0.70 ± 0.21
$O_x/(PAN+HNO_3)$[d]	Aircraft	5.26 ± 0.68		0.22	7.93 ± 1.03		0.76	0.66 ± 0.12
$O_x/(NO_y-NO_x)$[d]	Pasadena	3.85 ± 0.43		0.59	4.71 ± 0.53		0.65	0.82 ± 0.21

[a]Weekday-to-weekend (WD-to-WE) ratios are determined from the weekday and weekend slopes of each enhancement ratio.
[b]Here, x-intercepts represent background mixing ratios for CO (in units of ppbv) and CO_2 (in units of ppmv) determined from each LLS ODR fit.
[c]WD-to-WE ratios >1 demonstrate weekday enhancements; ratios <1 reflect weekend enhancements. WD-to-WE ratios are unitless.
[d]Units in (ppbv/ppbv).
[e]Units in (ppbv/ppmv).
[f]Units in (ng kg^{-1}/ppbv).
[g]Units in (ng kg^{-1}/ppmv).
[h]Units in (pptv/ppbv).

[24] Correlations of airborne measurements of BC to CO and to CO_2 (Figure 4) also show large WD-to-WE differences in emissions ratios (Table 3). A WD-to-WE comparison reveals an average decrease in BC of 50 ± 36% on weekends. Since diesel-fueled vehicles dominate both NO_x and BC emissions [*Ban-Weiss et al.*, 2008b; *Kirchstetter et al.*, 1999], simultaneous observation of reduced enhancement ratios of BC/CO and BC/CO_2 on weekends (Table 3) supports the conclusion that weekend decreases in NO_x emissions ratios are related to reduced diesel-fueled vehicle activity. In contrast, gasoline-fueled vehicles dominate CO and CO_2 emissions [*Ban-Weiss et al.*, 2008a; *Sullivan et al.*, 2004]. Emissions ratios of CO/CO_2 (Figure 5) from CalNex airborne and flask data show small differences between weekdays and weekends, while CalNex ground-based data show no significant difference between weekdays and weekends (Table 3). Background levels of CO (126 ± 5 ppbv on weekdays and 115 ± 6 ppbv on weekends) and CO_2 (392 ± 5 ppmv on weekdays and 388 ± 5 ppmv on weekends), determined from the x-intercepts of the LLS fits of the airborne NO_y/CO and NO_y/CO_2 emissions ratios, further demonstrate no significant WD-to-WE difference in background CO and CO_2. Further, average mixing ratios of CO and CO_2 from the CalNex-Pasadena site, the Mt. Wilson flask samples, and CO measurements from the AQMD network reveal no significant WD-to-WE differences in average CO and CO_2 abundances during the 15 May to 15 June time period (Table 2). Minimal WD-to-WE differences in observed CO/CO_2 enhancement ratios, their respective background levels

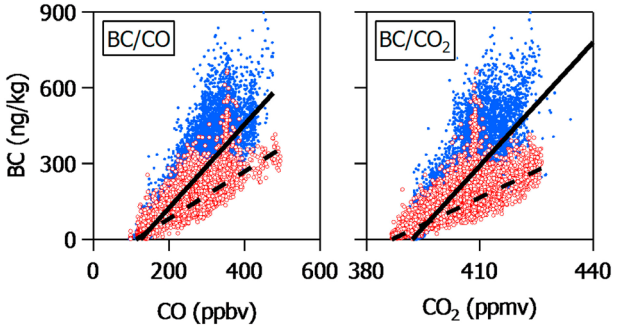

Figure 4. Plots of airborne measurements of BC versus (left) CO and (right) CO_2 on weekdays (blue dots, solid lines) and weekends (red circles, dashed lines).

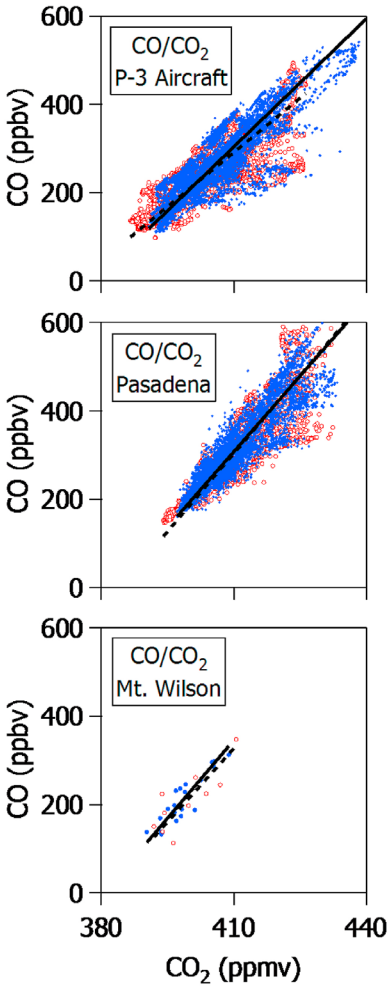

Figure 5. Plots of CO versus CO_2 from (top) CalNex airborne data, (middle) CalNex ground site measurements at Pasadena, and (bottom) flask samples from Mt. Wilson Observatory. No significant differences in the CO/CO_2 emissions ratios (Table 3) are observed on weekdays (blue dots, solid lines) compared to weekends (red circles, dashed lines).

(Table 3), and WD-to-WE similarities in average abundances determined from all data sets (Table 2) confirm two key observations about the primary emissions. First, total emissions from gasoline-fueled vehicles are similar on weekdays and weekends, as previously observed in roadside/tunnel studies of fuel-based emissions measurements [*Harley et al.*, 2005] and from traffic counts [*Marr et al.*, 2002; *Marr and Harley*, 2002b]. Second, large WD-to-WE differences in enhancement ratios of NO_y and BC to CO and CO_2 are predominantly a result of reductions in NO_x and BC emissions during weekends due to substantially less diesel-fueled vehicle activity.

[25] The 2010 CalNex airborne and ground-based data confirm and extend previous measurements of WD-to-WE differences observed in NO_x emissions. Figure 6 illustrates WD-to-WE ratios of NO_x emissions over the past two decades using a variety of measurement techniques; WD-to-WE ratios >1 are consistently observed. Fuel-based measurements of NO_x emissions from roadside/tunnel studies [*Harley et al.*, 2005] showed a 27% decrease in weekend NO_x emissions in 1990 and a 43% decrease in 2000 corresponding to WD-to-WE ratios of 1.37 and 1.75, respectively. Analyses of ground-based network data in the SoCAB in 2000 by *Chinkin et al.* [2003] resulted in similar decreases in NO_x emissions on Saturdays and Sundays, with WD-to-WE ratios ranging from 1.54 to 1.69. Airborne measurements of NO_y to CO and to CO_2 from one weekday flight and one weekend flight over the LA basin during the CARB phase of ARCTAS (Arctic Research of the Composition of the Troposphere from Aircraft and Satellites) [*Jacob et al.*, 2010] aboard the NASA DC-8 in 2008 suggest a WD-to-WE ratio of 1.66 ± 0.25, consistent with that reported here. NO_2 vertical column measurements from satellite-borne instrumentation, despite representing the net influence of emissions and oxidation chemistry, provide further supporting evidence of a weekend effect in precursor emissions. Measurements from GOME [*Beirle et al.*, 2003], SCIAMACHY [*Kim et al.*, 2009], and OMI [*Kim et al.*, 2009; *Russell et al.*, 2010] show large WD-to-WE differences in NO_x emissions with WD-to-WE ratios ranging from 1.66 to 1.90 in the LA basin since 1996 that are quantitatively consistent with the analysis presented here.

3.2.2. VOC/NO_x Ratio

[26] Certain non-methane VOCs, including benzene, acetylene, o-xylene, ethene, n-octane, ethylbenzene, n-heptane, and toluene, are characteristic of vehicle exhaust [*Fujita et al.*, 2003; *Kirchstetter et al.*, 1996; *Rubin et al.*, 2006]. These species, measured using the WAS and PTR-MS

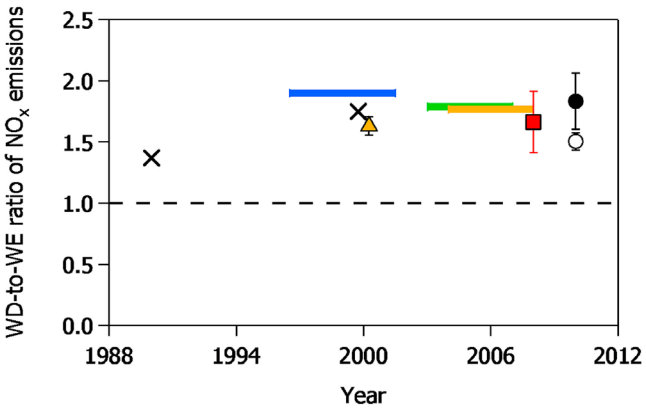

Figure 6. WD-to-WE ratios of NO_x emissions >1 (dashed line) are consistently observed in the LA basin over time. CalNex airborne (solid black circle) and ground-based (open circle) measurements confirm and extend previous airborne studies in 2008 during the CARB phase of ARCTAS (red square), roadside/tunnel studies in 1990 and 2000 by *Harley et al.* [2005] (crosses), and analyses of ground-based network measurements from 2000 by *Chinkin et al.* [2003] (orange triangle). Symbols representing the CalNex and ARCTAS measurements reflect the average WD-to-WE ratio of the NO_y/CO and NO_y/CO_2 emissions ratios; error bars represent the total propagated uncertainties. NO_2 vertical column measurements from GOME [*Beirle et al.*, 2003] (blue bar), SCIAMACHY [*Kim et al.*, 2009] (orange bar), and OMI [*Kim et al.*, 2009; *Russell et al.*, 2010] (green bar) satellite-borne instruments also show WD-to-WE differences >1. The width of each horizontal bar reflects the range of years over which the satellite data were averaged.

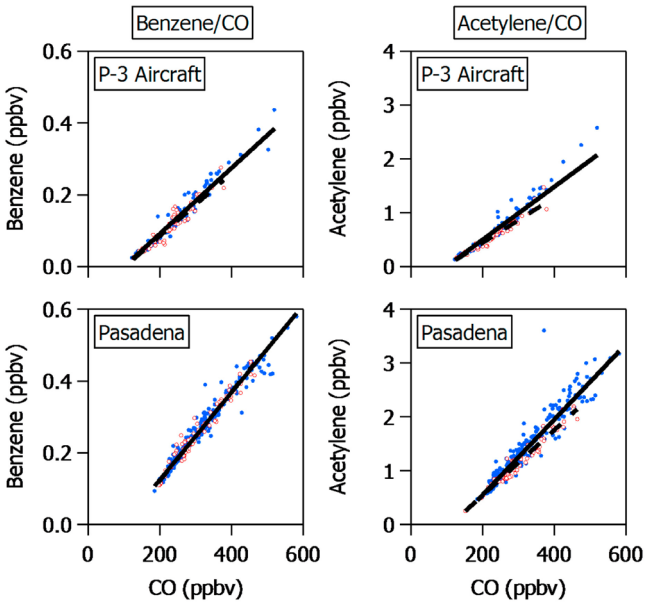

Figure 7. Plots of (top) airborne (WAS) and (bottom) ground-based (GC-MS) measurements of (left) benzene and (right) acetylene versus CO for weekdays (blue dots, solid lines) and weekends (red circles, dashed lines).

from the P-3 aircraft and using the GC-MS at the CalNex-Pasadena site, were positively correlated with corresponding measurements of CO (Figure 7) and NO_x (Figure 8). Emissions ratios to CO show no significant WD-to-WE increases in VOC emissions, while correlations to NO_x demonstrate increased VOC/NO_x ratios on weekends (Table 3). Ratios to long-lived species that react relatively slowly with OH compared to times for transport of air out of the LA basin, such as benzene (k_{298} = 1.3×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}) and acetylene (k_{298} = 7.8×10^{-13} cm^3 $molecules^{-1}$ sec^{-1}) [*Atkinson*, 1986], reveal information about emissions independent of chemistry on the time scales considered here. A WD-to-WE ratio determined for benzene to CO using airborne measurements of benzene from the PTR-MS are in agreement with those determined from the WAS canisters given the propagated 1σ uncertainties. Additionally, surface observations of benzene and acetylene emissions ratios to CO (Figure 7) at the CalNex-Pasadena site result in similar WD-to-WE ratios for VOC/CO (Table 3). From the weekday and weekend slopes from LLS fits to CO of airborne measurements of benzene and acetylene using the WAS canisters, we determine an average WD-to-WE ratio of 1.14 ± 0.25 for VOC/CO.

[27] Combining the observed WD-to-WE ratio for VOC/CO with a WD-to-WE ratio of 1.72 ± 0.32 for NO_y/CO from the airborne measurements, a WD-to-WE ratio of 0.66 ± 0.19 for VOC/NO_x is expected for VOCs with OH reaction rates similar to that of NO_2 (2nd order rate coefficient for OH+NO_2 reaction, k_{298} = 1.24×10^{-11} cm^3 $molecules^{-1}$ sec^{-1}) [*Sander et al.*, 2006]. WD-to-WE ratios for VOC/NO_x ranging from 0.61 to 0.74 were observed for o-xylene (k_{298} = 1.5×10^{-11} cm^3 $molecules^{-1}$ sec^{-1}), ethene (k_{298} = 8.5×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}), n-octane (k_{298} = 8.1×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}), ethylbenzene (k_{298} = 7.5×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}), n-heptane (k_{298} = 6.8×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}), and toluene (k_{298} = 6.2×10^{-12} cm^3 $molecules^{-1}$ sec^{-1}) [*Atkinson*, 1986, 2003]. The observed WD-to-WE ratios range from 0.61 to 0.74 and correspond to an average increase in VOC/NO_x ratio of 48 ± 8% on weekends, which is in agreement with the expected WD-to-WE ratio for VOC/NO_x. Enhancement ratios of o-xylene, ethene, and toluene to NO_x determined from the CalNex-Pasadena data result in similar WD-to-WE ratios for VOC/NO_x (Table 3) and correspond to a weekend increase in VOC/NO_x ratio of 43 ± 22%, further supporting the conclusions reached from analysis of the airborne data. From these observations, we confirm weekend enhancements in VOC/NO_x ratios are primarily due to significant reductions in weekend NO_x emissions rather than increased weekend VOC emissions.

3.3. Causes of the Weekend Ozone Effect

[28] In addition to differences in emissions and photochemical production, the weekend ozone effect in the SoCAB derived from any limited data set depends on day-to-day variability in meteorology and transport, and carryover of ozone and precursors from previous days. The CalNex airborne data set is spatially extensive but temporally limited due to the very few weekdays and weekends sampled. The CalNex surface data set is more temporally representative, while surface sampling outside of the CalNex-Pasadena site lacks ancillary chemical measurements useful in diagnosing the causes of the weekend effect in ozone. Accurate 3-D model simulations of the complex transport patterns in the LA basin are required to better quantify the influence of carryover of pollutants recirculated from the previous day. Despite these limitations, in this section we analyze the available CalNex data to better quantify

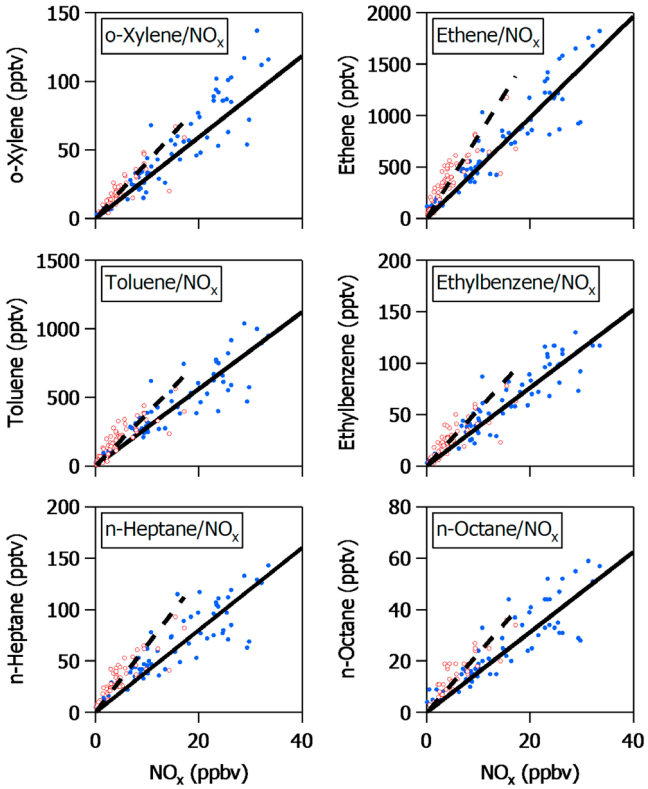

Figure 8. Plots of airborne (WAS) measurements of select VOCs versus NO_x for weekdays (blue dots, solid lines) and weekends (red circles, dashed lines).

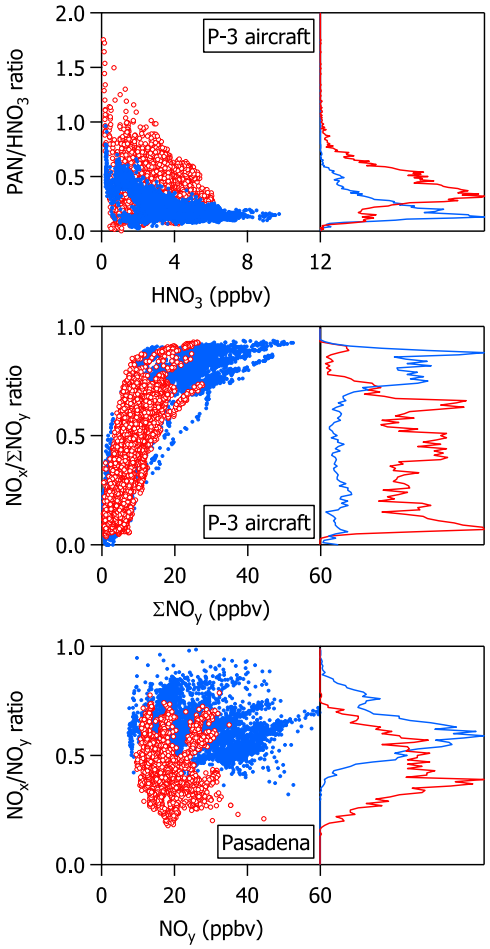

Figure 9. (left) Plots of (top) airborne measurements of the PAN/HNO_3 ratio versus HNO_3, (middle) airborne observations of $NO_x/\Sigma NO_y$ ratio versus ΣNO_y, and (bottom) ground-based measurements of NO_x/NO_y ratio versus NO_y for weekdays (blue dots) compared to weekends (red circles). (right) Histograms of the corresponding PAN/HNO_3 ratio, $NO_x/\Sigma NO_y$ ratio, and NO_x/NO_y ratio on weekdays (blue) and weekends (red). The *x*-axes of the histograms have been normalized to give an equal mode for each distribution.

the major causes of the weekend ozone effect observed in the SoCAB in 2010.

3.3.1. Enhanced Photochemistry on Weekends

[29] Increased weekend VOC/NO_x ratios are expected to decrease radical termination via (R8), which produces HNO_3, and favor radical production via (R3), which leads to PAN formation via (R9) and ozone formation via (R4 – R7). The relative amounts of PAN and HNO_3 therefore act as indicators for the contribution of ozone production to the observed WD-to-WE differences in ozone mixing ratios. Airborne observations of the ratio of PAN to HNO_3 versus HNO_3 and the corresponding histogram of the PAN/HNO_3 ratio (Figure 9, top) demonstrate that PAN production relative to HNO_3 is enhanced on weekends. Average weekday and weekend mixing ratios also demonstrate the WD-to-WE differences in PAN and HNO_3. From the airborne data set, average weekday and weekend mixing ratios of 0.7 ± 0.2 and 1.2 ± 0.3 ppbv, respectively, were observed for PAN while average mixing ratios of 3.0 ± 0.6 and 2.9 ± 0.2 ppbv were observed for HNO_3. Notably, similar total concentrations of the oxidized products of NO_x are observed on weekends, as shown below, despite lower NO_x emissions on weekends. The increased formation of PAN relative to HNO_3 on weekends indicates enhanced RO_2 formation, which is expected to lead to enhanced photochemical production of ozone on weekends. Increased RO_2 formation and enhanced photochemistry on weekends is further emphasized when the expected WD-to-WE differences in the primary sources of aldehydes, the precursors to PAN, are considered. Motor vehicle emissions measured during tunnel studies in 2006 [*Ban-Weiss et al.*, 2008a] report significantly greater emissions of aldehydes from heavy-duty diesel-fueled trucks compared to light-duty gasoline-fueled vehicles. Given the reduction in diesel-fueled vehicle activity on weekends, near-tailpipe aldehyde emissions are expected to be greater on weekdays compared to weekends. The observed enhancement in PAN on weekends, despite a likely reduction in PAN-specific precursors, emphasizes the significant increase in photochemistry of the emissions on weekends.

[30] Airborne observations of $NO_x/\Sigma NO_y$ versus ΣNO_y and the corresponding histogram of the $NO_x/\Sigma NO_y$ ratio (Figure 9, middle) and similar plots of ground-based measurements of NO_x/NO_y versus NO_y (Figure 9, bottom) indicate more extensive oxidation of NO_x to NO_y on weekends. The histograms illustrate differences in the extent to which NO_x has been oxidized on weekends at the CalNex-Pasadena site compared to an integrated representation of NO_x oxidation over the entire LA basin from the airborne data. A relatively narrow distribution is observed at the ground site compared to a broad distribution determined using the airborne data; the latter reflects a gradient in the extent of oxidation across the LA basin from coastal to inland areas.

[31] Differences in O_x also indicate enhanced photochemical production of ozone on the weekends. Since net production of ozone and O_x is only achieved by formation of NO_2 via (R2 – R5), negligible WD-to-WE differences in O_x would indicate that titration was the dominant process affecting ozone levels. Conversely, significant WD-to-WE differences in O_x would indicate enhanced photochemical production dominates titration as the cause of increased weekend ozone. Mean O_x mixing ratios of 65 ± 5 ppbv and 81 ± 3 ppbv (Table 2), determined by averaging over the four weekday and three weekend flights, respectively, result in a nonzero WE-to-WD difference of 16 ± 6 ppbv indicating enhanced peroxy radical oxidation of NO to NO_2 via (R2 – R5) on weekends. Nonzero WE-to-WD differences in average mixing ratios of O_x are also observed for CalNex-Pasadena, AQMD-Pasadena, and AQMD-SoCAB (Table 2). Similar to the ozone observations in Section 3.1, similarities and inconsistencies in WE-to-WD differences between the data sets reflect differences in the number of weekdays and weekends sampled, day-to-day variability over the sampling period, and coastal versus inland sampling coverage within the SoCAB.

3.3.2. Increased Ozone Production Efficiency and NO_x Oxidation Rate on Weekends

[32] Analysis of airborne observations of O_x versus PAN $+HNO_3$ (Figure 10, left) and ground-based measurements of O_x versus NO_y-NO_x (Figure 10, right) allows attribution of the enhanced weekend ozone production to increased ozone

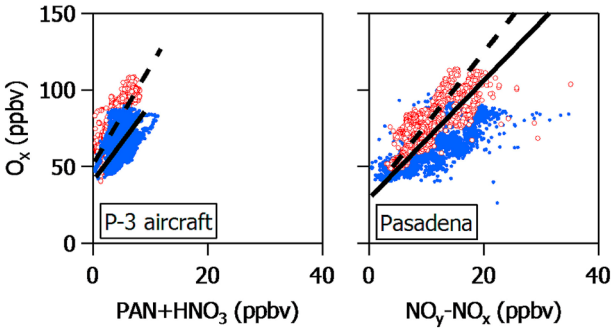

Figure 10. Plots of (left) airborne observations of O_x versus PAN + HNO_3 and (right) ground-based measurements of O_x versus NO_y-NO_x on weekdays (blue dots, solid lines) and weekends (red circles, dashed lines).

production efficiency, enhanced photochemical processing rate, or both. First, WD-to-WE differences in the LLS ODR slopes give a measure of WD-to-WE differences in ozone production per NO_x oxidized. A larger LLS ODR slope is observed on weekends compared to weekdays (Table 3) in both the airborne and ground-based data. A consistently larger slope is observed on weekends in both data sets, although the relative difference between the slopes from the airborne data is greater than that of the ground-based data. The larger slope on weekends in the airborne data indicates 51 ± 14% greater ozone production per oxidized NO_x on weekends compared to weekdays, while the ground-based data suggest 22 ± 17% greater production efficiency of ozone. Second, WD-to-WE differences in the fraction of oxidized NO_x relative to NO_y indicate differences in the rate of photochemical processing. Average mixing ratios of (PAN + HNO_3)/ΣNO_y of 0.40 ± 0.03 ppbv on weekdays and 0.58 ± 0.05 ppbv on weekends from the airborne observations indicate a 45 ± 13% increase in the relative amount of oxidized NO_x on weekends compared to weekdays, while average mixing ratios of (NO_y-NO_x)/NO_y of 0.38 ± 0.02 ppbv on weekdays and 0.55 ± 0.04 ppbv on weekends from the ground-based observations indicate a 42 ± 12% increase on weekends. Enhancements in the fraction of oxidized NO_x on weekends demonstrate more extensive photochemical processing on weekends. Assuming basin air mass residence times are similar on average for weekends and weekdays, this indicates more rapid processing on weekends, consistent with the elevated VOC/NO_x ratios on weekends. The more rapid photochemical processing on weekends accounts for comparable concentrations of PAN + HNO_3 observed on weekends (3.7 ± 0.7 ppbv) and weekdays (4.1 ± 0.5 ppbv) in the airborne data, and concentrations of NO_y-NO_x on weekends (10.6 ± 1.2 ppbv) and weekdays (10.4 ± 1.1 ppbv) in the ground-based data, even though NO_x emissions are lower on weekends. From the above considerations, we conclude that higher weekend ozone mixing ratios observed in the SoCAB during CalNex can be attributed to increases in both ozone production efficiency and rate of photochemical processing on weekends.

4. Summary

[33] A significant weekend ozone effect was observed in airborne and ground-based measurements in the SoCAB during the CalNex 2010 field study and supported by measurements from the routine monitoring network. Previous studies show WD-to-WE differences in ozone are driven primarily by WD-to-WE differences in NO_x emissions. The 2010 CalNex study data confirm and extend observations of WD-to-WE differences in NO_x emissions compiled from roadside, ground-based, aircraft, and satellite studies since 1990. Correlations of CalNex 2010 airborne and ground-based observations of NO_y to CO and NO_y to CO_2 indicate an average decrease of 46 ± 11% and 34 ± 4%, respectively, in NO_x emissions on weekends in the LA basin, and are attributed primarily to decreased activity of diesel-fueled vehicles. A minimal weekend effect in CO and CO_2 abundances and in the CO/CO_2 emissions ratio confirms that large WD-to-WE differences in NO_y/CO and NO_y/CO_2 ratios primarily arise from the significant reduction in NO_x emissions due to decreased diesel-fueled vehicle activity on weekends. Enhancement ratios of long-lived non-methane VOCs, such as benzene and acetylene, to CO show small WD-to-WE differences in VOC emissions. Thus, average increases of 48 ± 8% and 43 ± 22% in weekend VOC/NO_x ratio determined from the airborne and ground-based measurements, respectively, are mainly due to the significant reduction in NO_x emissions on weekends, as confirmed by correlations of speciated VOCs to NO_x. As expected from the weekend increase in VOC/NO_x ratio, enhancement in the ratio of PAN to HNO_3 on weekends indicates increased RO_2 formation, which propagates the chain reactions for ozone production. Additional interpretation of the products of NO_x oxidation and correlations of O_x to NO_x oxidation products using the CalNex 2010 data shows 45 ± 13% and 42 ± 12% more extensive photochemical processing and 51 ± 14% and 22 ± 17% greater ozone production efficiency on weekends in the airborne and ground-based data, respectively, indicating that both contribute to higher weekend ozone levels in the SoCAB.

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