Airborne and ground-based observations of the weekend ozone effect and precursor emissions in the California South Coast Air Basin

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Weekend ozone effect = more ozone on weekends compared to weekdays

Well-documented for South Coast Air Basin (SoCAB):
Blanchard (2003), Chinkin (2003), Fujita (2003), Marr (2002), Murphy (2007), Qin (2004), Yarwood (2003)

- WE NO_x reductions considered to be dominant cause of higher WE O_3
- Affects O_3 in two ways:
  1) Reduced loss by titration; leaves higher mixing ratios of O_3 on WE

$$O_3 + NO \rightarrow NO_2 + O_2$$

  2) Enhanced WE O_3 production; due to relative increase in VOC/NO_x ratio

$$OH + RH + O_2 \rightarrow RO_2 + H_2O$$
$$RO_2 + NO \rightarrow NO_2 + RO$$
$$NO_2 + h\nu + O_2 \rightarrow NO + O_3$$

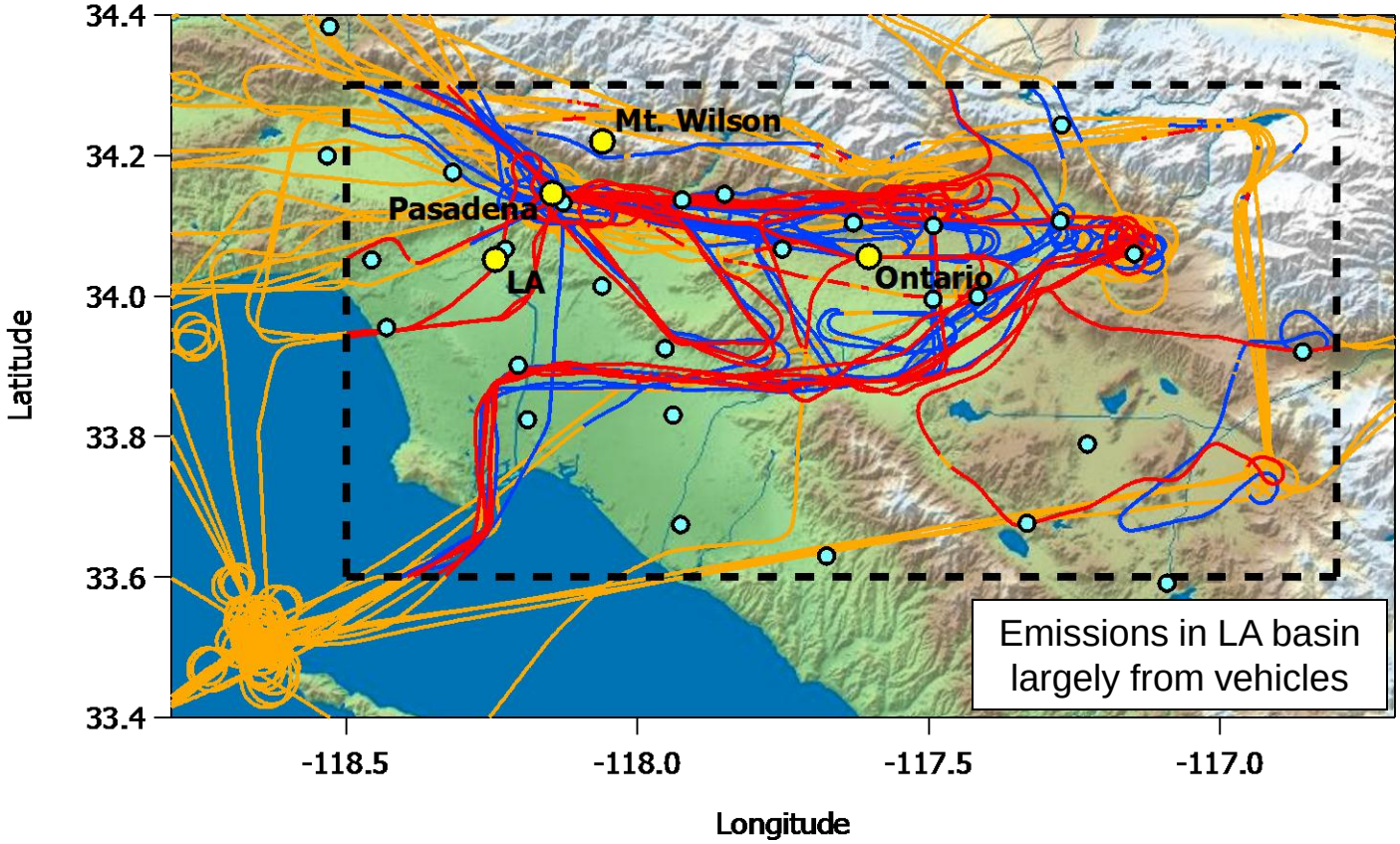
Outline

Part 1: WD-to-WE differences in O_3 and precursors (NO_x, VOCs) in SoCAB using 2010 CalNex and CARB data

Photochemical production contributes to observed WE O_3 levels

Part 2: Changes in ozone and precursors in SoCAB over time

Part 1: 2010 data sets and data selection



All P-3 Flights
Weekday
Weekend
CARB sites

CalNex P-3 Airborne data:
- 14 daytime flights
- Limited to mixed BL of LA basin, 0.2-1 km AGL, 12:00 – 18:00 PDT

7 Weekdays

May 4 (T)
May 7 (F)
May11 (T)
May 14 (F)
May 19 (W)
May 24 (M)
June 16 (W)

3 Weekends

May 8 (Sat)
May 16 (Sun)
June 20 (Sun)

CalNex Ground Site: Caltech campus, Pasadena

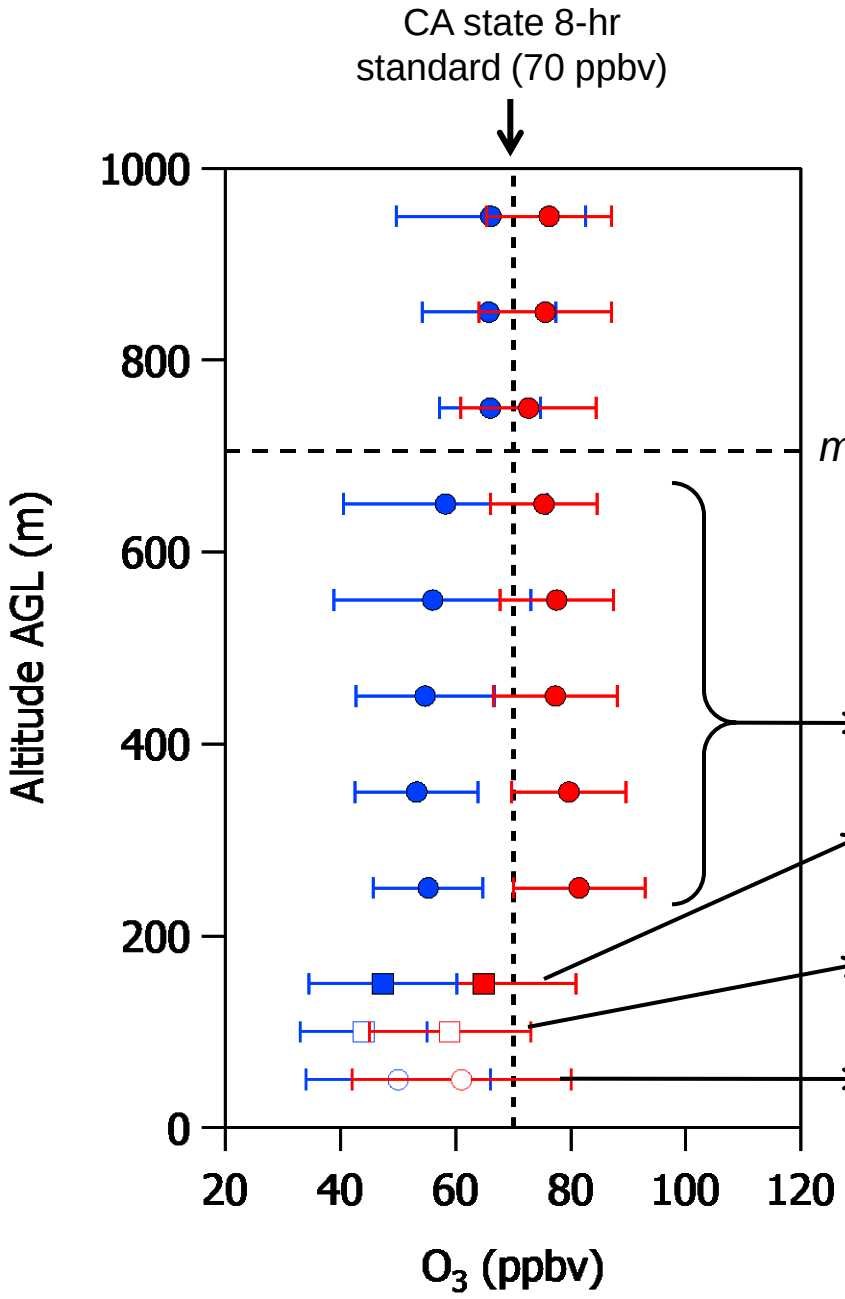
Flask samples: Mt. Wilson Observatory

CARB Network: 28 locations in SoCAB

15 May – 15 June
12:00 – 18:00 PDT

21 WD and **9 WE**
(excluding holidays)

Weekend ozone effect observed in airborne and ground-based measurements

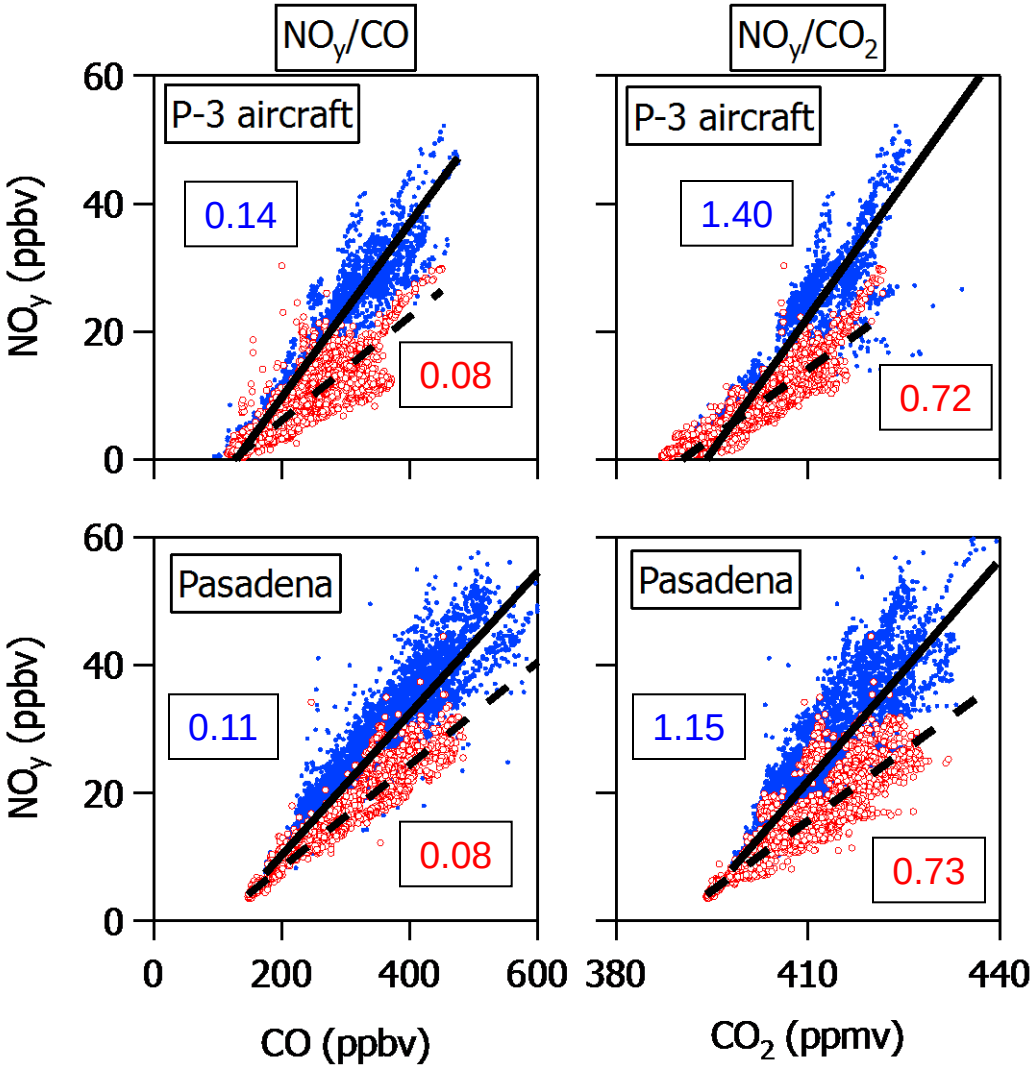


Aircraft data: average of 7 WDs and 3 WEs
Ground data: average of 21 WDs and 9 WEs

	Average O_3 (ppbv)			
	WD	WE	Δ(WE-WD)	↑ (WE)
CalNex, P-3 aircraft	55	78	23	42%
CalNex, Pasadena	47	65	17	36%
CARB, Pasadena	43	59	15	35%
CARB, SoCAB	50	61	11	22%

Weekend ozone effect observed in all 2010 data sets

Large WD-to-WE differences in NO_x



NO_y used as a conserved measure of NO_x

Aircraft: 2-sec data avg
7 WDs and 3 WEs

WD-to-WE ratios

NO_y/CO: 1.68 ± 0.21

NO_y/CO_2: 1.95 ± 0.22

Ground: 1-min data avg
21 WDs and 9 WEs

WD-to-WE ratios

NO_y/CO : 1.39 ± 0.08

NO_y/CO_2 : 1.58 ± 0.07

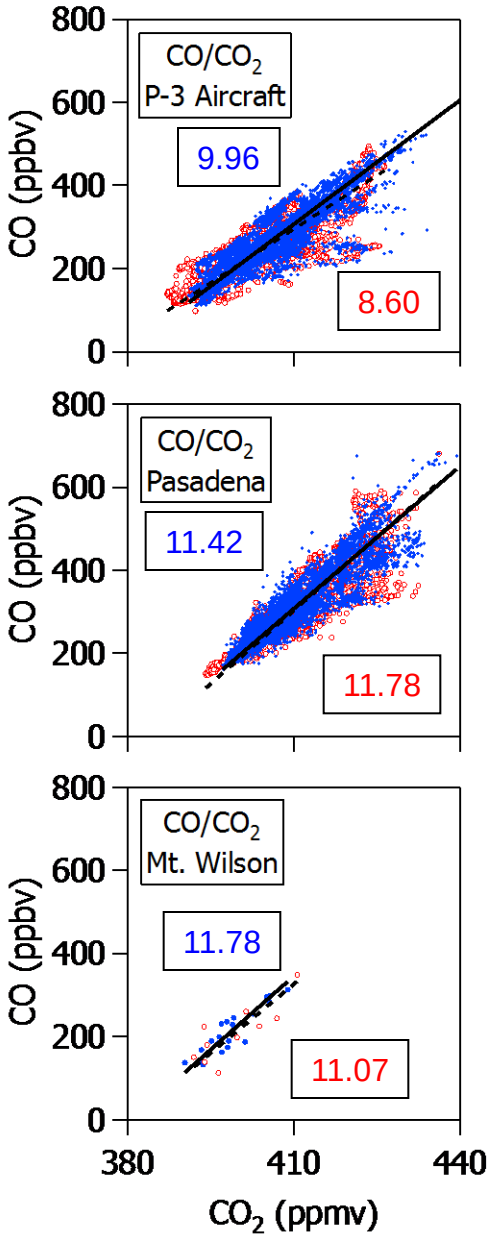
$0.71 < R^2 < 0.88$

average decrease of 40% on weekends

- Diesel-fueled vehicles tend to dominate NO_x and BC emissions
- Similar modulation observed in airborne BC/CO and BC/CO_2 enhancement ratios
- Attribute ↓ WE NO_x ratios to ↓ WE activity of diesel vehicles (*Harley et al.*, 2005)

Weekend NO_x reductions drive observed changes – confirmed by no change in CO/CO_2

CO/CO_2 enhancement ratios



CalNex P-3

WD-to-WE ratio = 1.16

CalNex ground site

WD-to-WE ratio = 0.97

Flasks at Mt. Wilson

WD-to-WE ratio = 1.06

No WD-to-WE difference in CO/CO_2 ratio

CO and CO_2 abundance

CARB – SoCAB

CO WD-to-WE ratio = 1.04

CARB – Pasadena

CO WD-to-WE ratio = 1.05

CalNex ground site

CO WD-to-WE ratio = 1.03

CO_2 WD-to-WE ratio = 1.00

Mt. Wilson Flasks

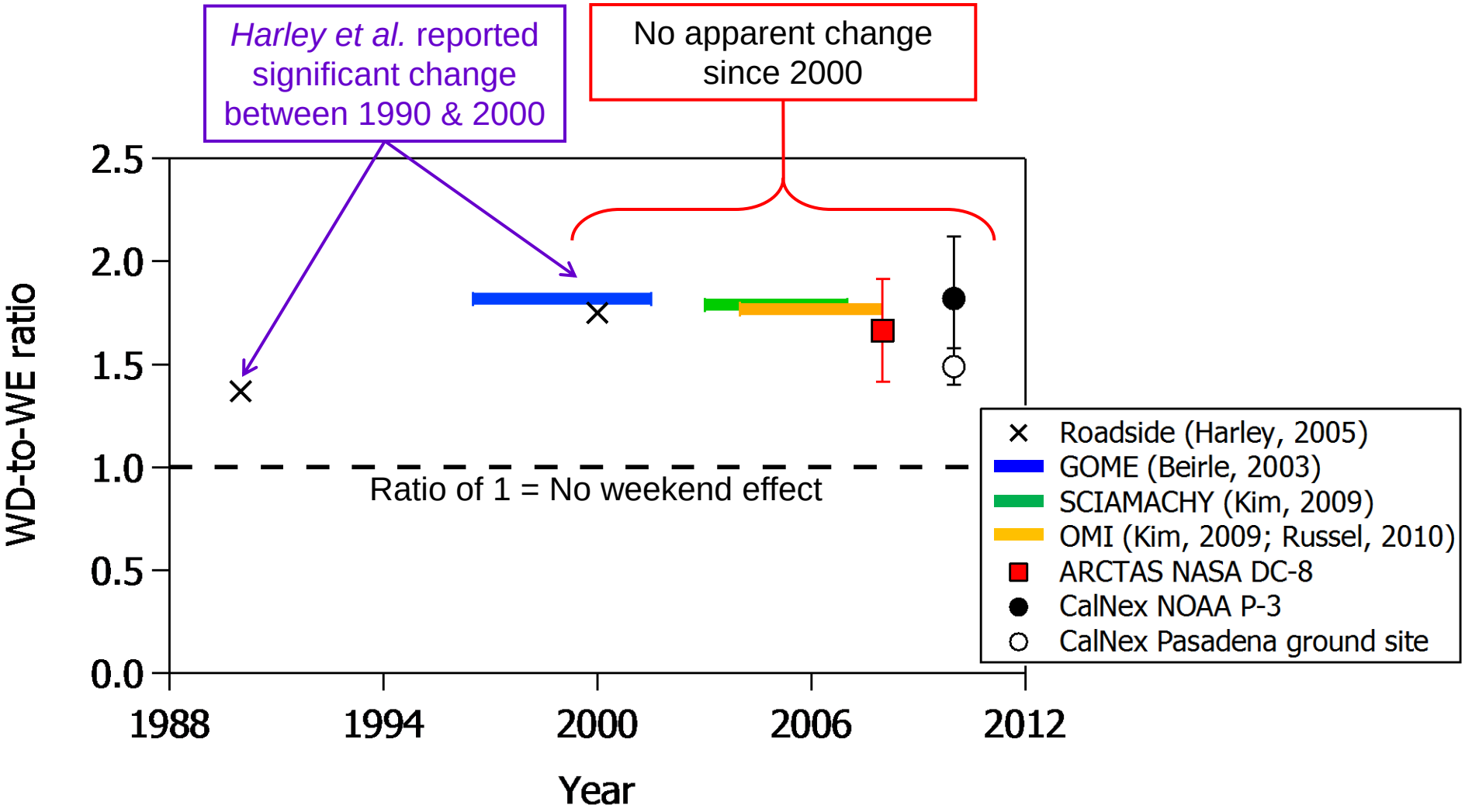
CO WD-to-WE ratio = 1.00

CO_2 WD-to-WE ratio = 1.00

No WD-to-WE difference in average CO and CO_2 abundance

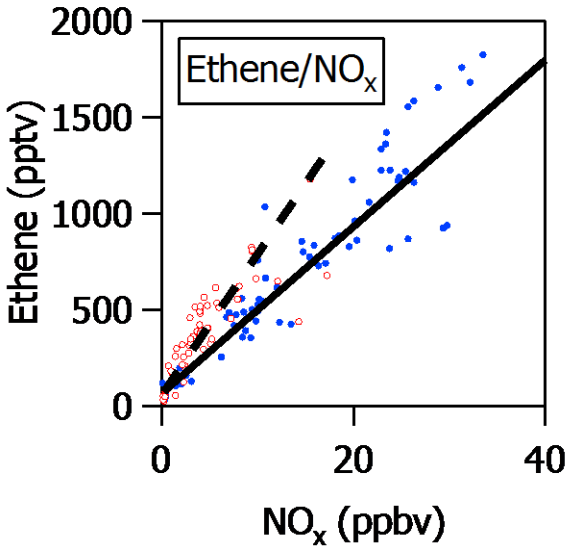
Consistent with observations by *Harley et al. (2005)* which suggest similar emissions on WDs and WEs from gasoline-fueled vehicles (main emitters of CO and CO_2)

Large WD-to-WE differences in NO_x are consistently observed over time



WD-to-WE ratios expected to decrease in the future with implementation of diesel control strategies

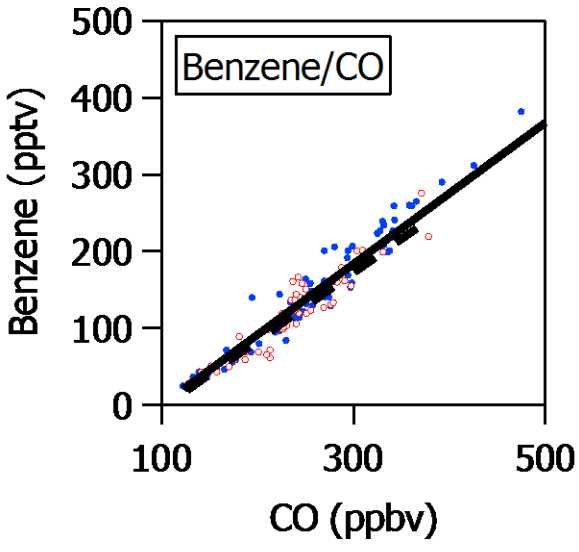
Weekend NO_x reductions lead to increased weekend VOC/NO_x ratios



WD-to-WE ratio

ethene/NO_x = 0.64 ± 0.08

36% increase in weekend VOC/NO_x ratio



WD-to-WE ratio

benzene/CO = 1.07 ± 0.13

No significant WD-to-WE difference in VOC/CO

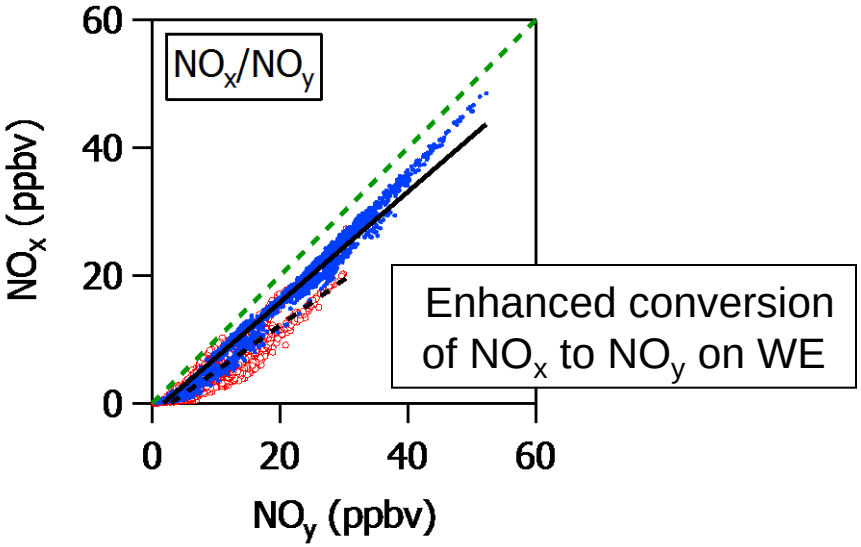
Increased WE VOC/NO_x ratio shifts chemistry toward RO_2 and O_3 production on WEs

Measurements provide evidence of O_3 production on weekends

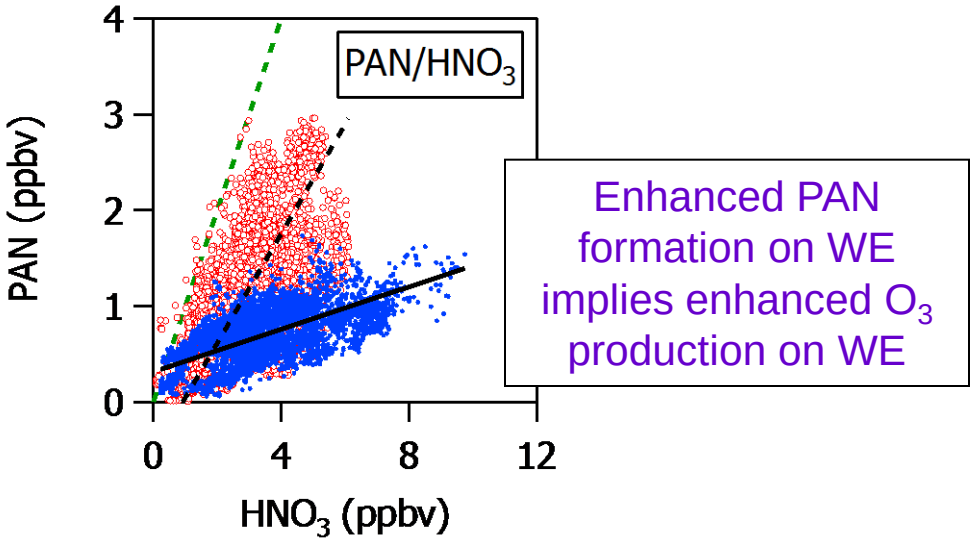
1) Weekend enhancements in O_x ($=O_3+NO_2$) indicate contribution from O_3 production → 24-29% ↑ in O_x on WEs observed in CalNex airborne and ground-based data

2) Weekend decrease in NO_x/NO_y ratio shows enhanced conversion of fresh emissions to mainly HNO_3 and PAN

Formation of HNO_3 indicates OH removal and termination of the O_3 reaction chain



Formation of PAN indicates production of RO_2 radicals that propagate O_3 production



Part 1 Summary: 2010 data

- Reduced NO_x and BC enhancement ratios on weekends are consistent with reduced diesel-fueled vehicle activity on weekends

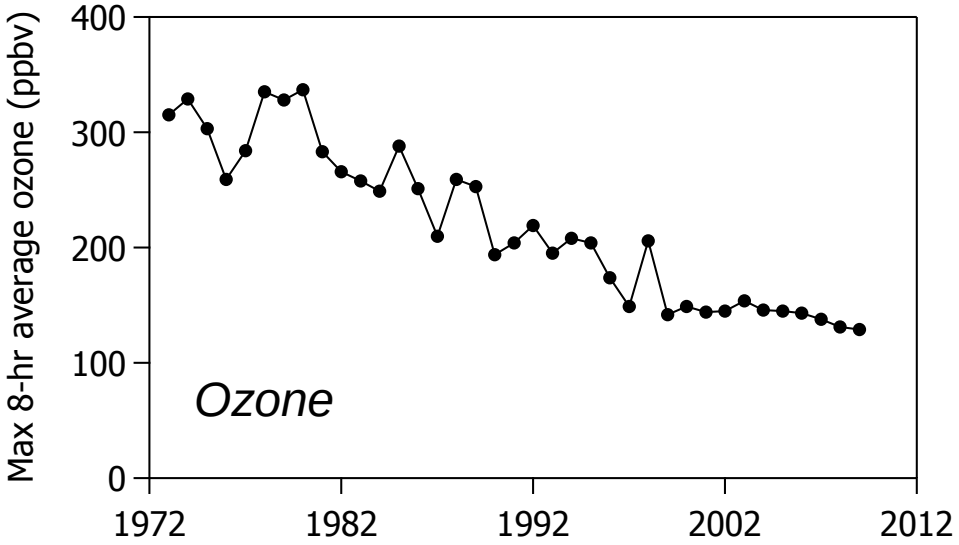
- WD-to-WE differences in NO_x and VOC/NO_x ratios drive differences in O_3

- Weekend enhancements in O_x indicate contribution from photochemical production to observed weekend O_3 levels

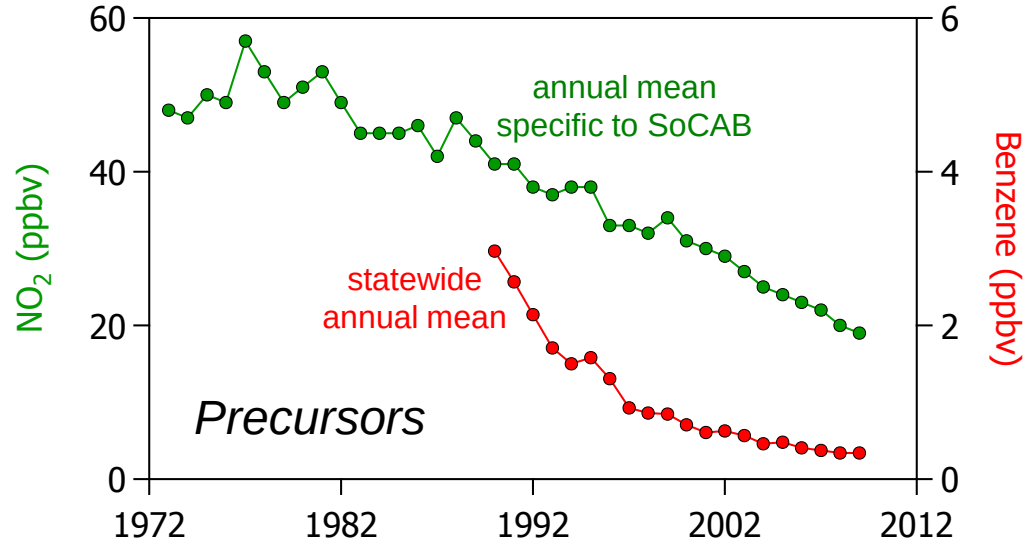
- Enhanced weekend formation of PAN compared to HNO_3 further show increased photochemical production of O_3 on weekends

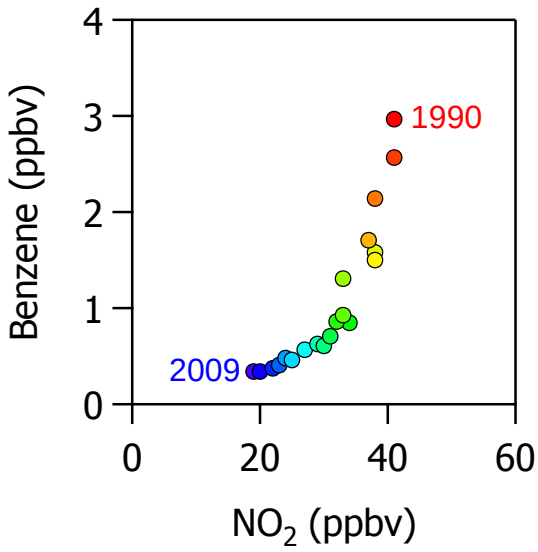
- Observations are consistent with enhanced photochemical aging of VOCs on weekends [C. Warneke, A. Borbon (next), R. Bahreini (Thurs, pm)]

Part 2: Changes in SoCAB over time



Data from CARB network
(http://www.arb.ca.gov/adam/index.html)





Ozone and precursor concentrations have decreased over time

Change in emissions relative to CO_2 over past decade

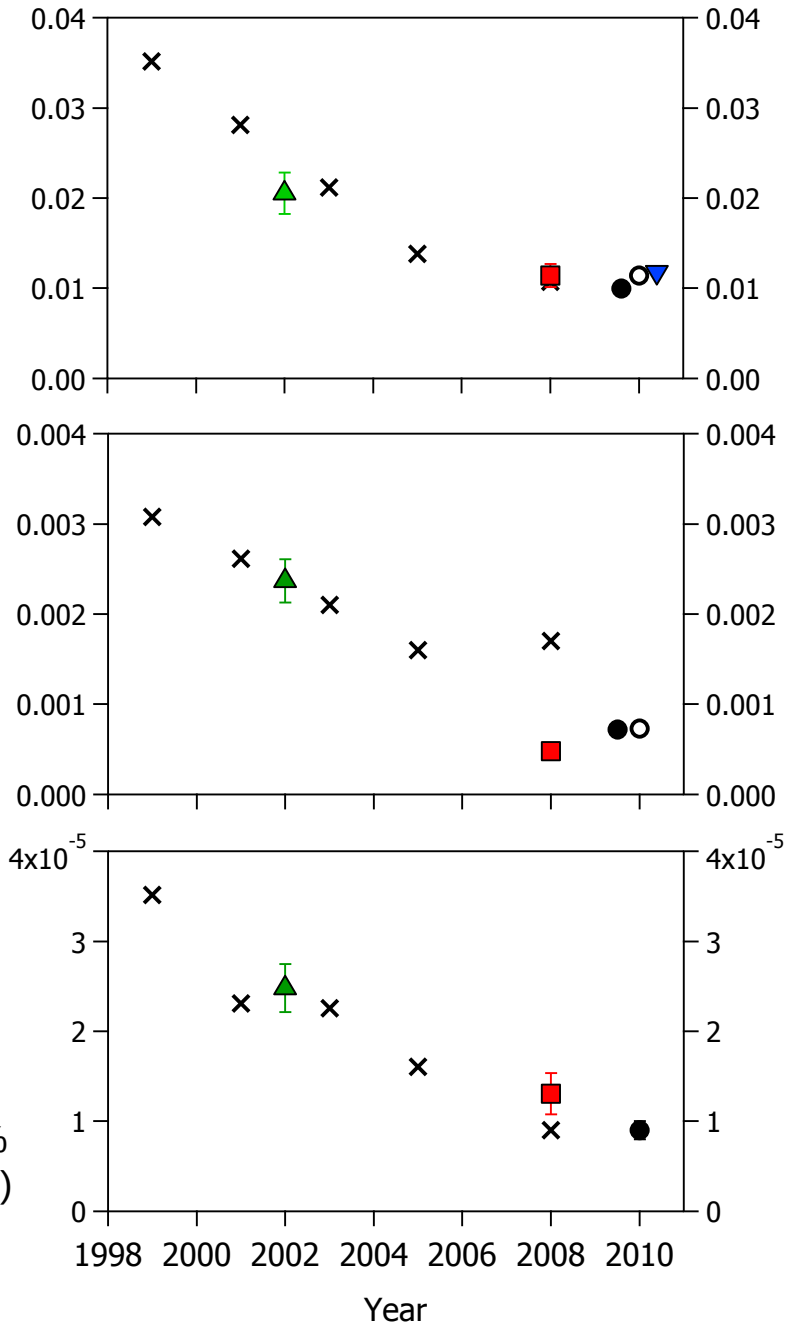
Roadside observations
(Bishop and Stedman, 2008)

CO/CO_2

NO/CO_2

$Benzene/CO_2$

(Determined from total HC measurements scaled by wt% of benzene in vehicle exhaust)



Airborne and ground-based observations

CO/CO_2

NO_y/CO_2

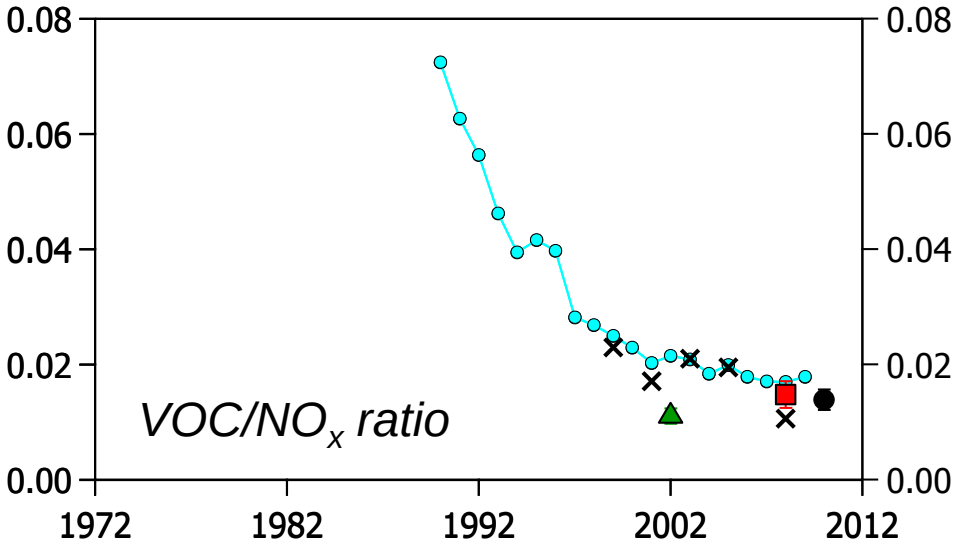
$Benzene/CO_2$

- Roadside Studies
- ITCT NOAA P-3
- ARCTAS NASA DC-8
- CalNex NOAA P-3
- CalNex ground site
- Mt. Wilson Flasks

General decrease in emissions ratios consistent with decreasing concentrations

Decrease in VOC/NO_x ratio over time

CARB - $Benzene/NO_2$



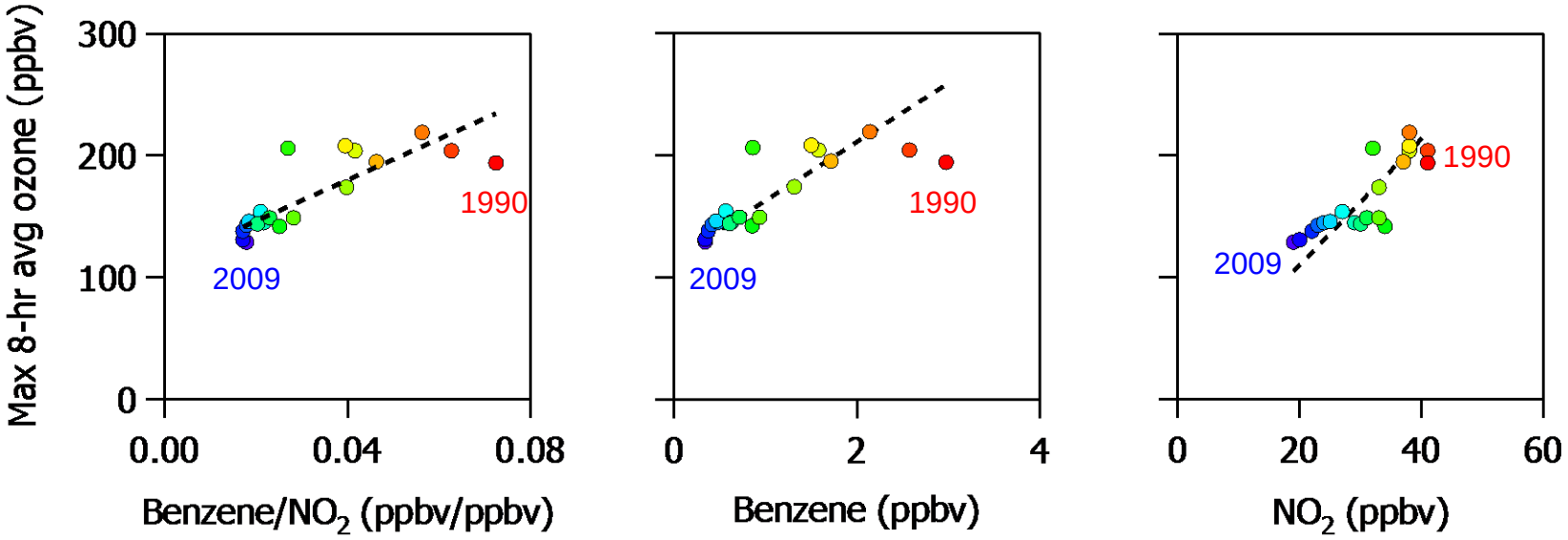
Roadside - Benzene/NO

Airborne - $Benzene/NO_y$

CARB data consistent with field observations

CARB data shows ↓ in O_3 over time is correlated with both:

↓ *VOC/NO_x ratio* *and* ↓ *VOC and NO_x concentrations*



Part 2 Summary: Changes in SoCAB over time

- CARB network data show distinct changes in O_3 and precursors in SoCAB over time

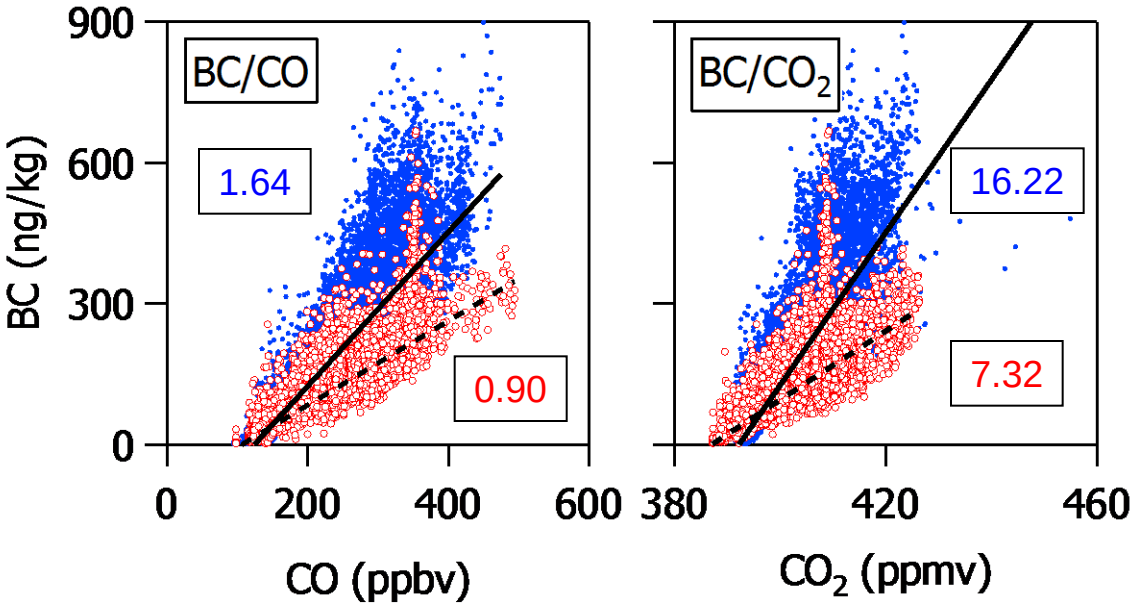
- Consistent trend between NO_x, CO, and benzene emissions ratios from roadside and airborne measurements and abundances from CARB data

- Decrease in O_3 over time are correlated with a decrease in VOC/NO_x ratio and decreases in VOC and NO_x abundances over time

Extra slides

Large weekend effect in BC enhancement ratios

Aircraft data: 2-sec average



Weekday-to-weekend ratios

BC/CO: **1.83 ± 1.04**

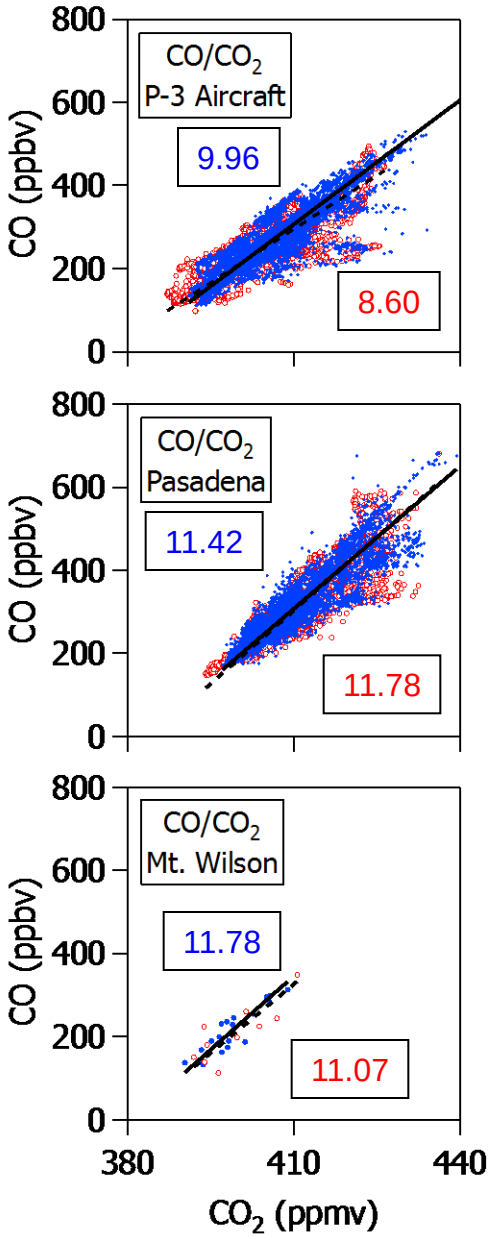
BC/CO_2: **2.21 ± 1.24**

NO_x and BC emissions dominated by diesel-fueled vehicles

Weekend effect in BC ratios support weekend decreases in NO_x ratios being from reduced diesel-fueled vehicle activity

Weekend NO_x reductions drive observed changes – confirmed by no change in CO/CO_2

CO/CO_2 enhancement ratios



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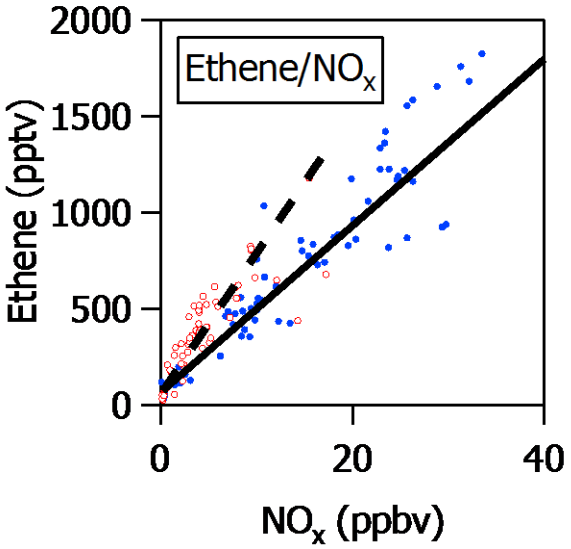
Consistent with observations by *Harley et al. (2005)* which suggest similar emissions on WDs and WEs from gasoline-fueled vehicles (main emitters of CO and CO_2)

Weekend NO_x reductions lead to increased weekend VOC/NO_x ratios



WD-to-WE ratio

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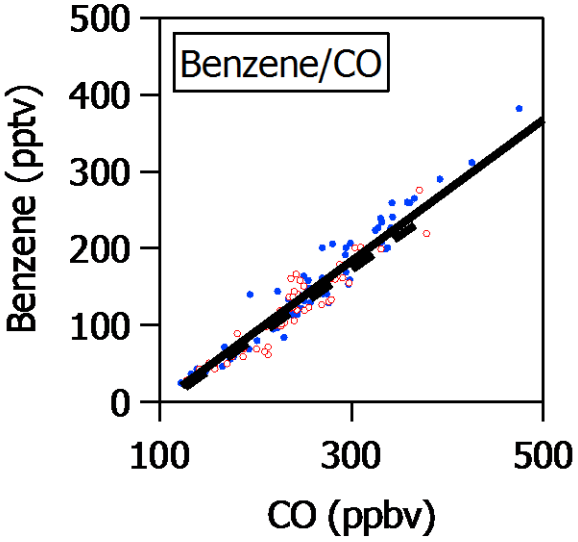
36% increase in weekend VOC/NO_x ratio



WD-to-WE ratio

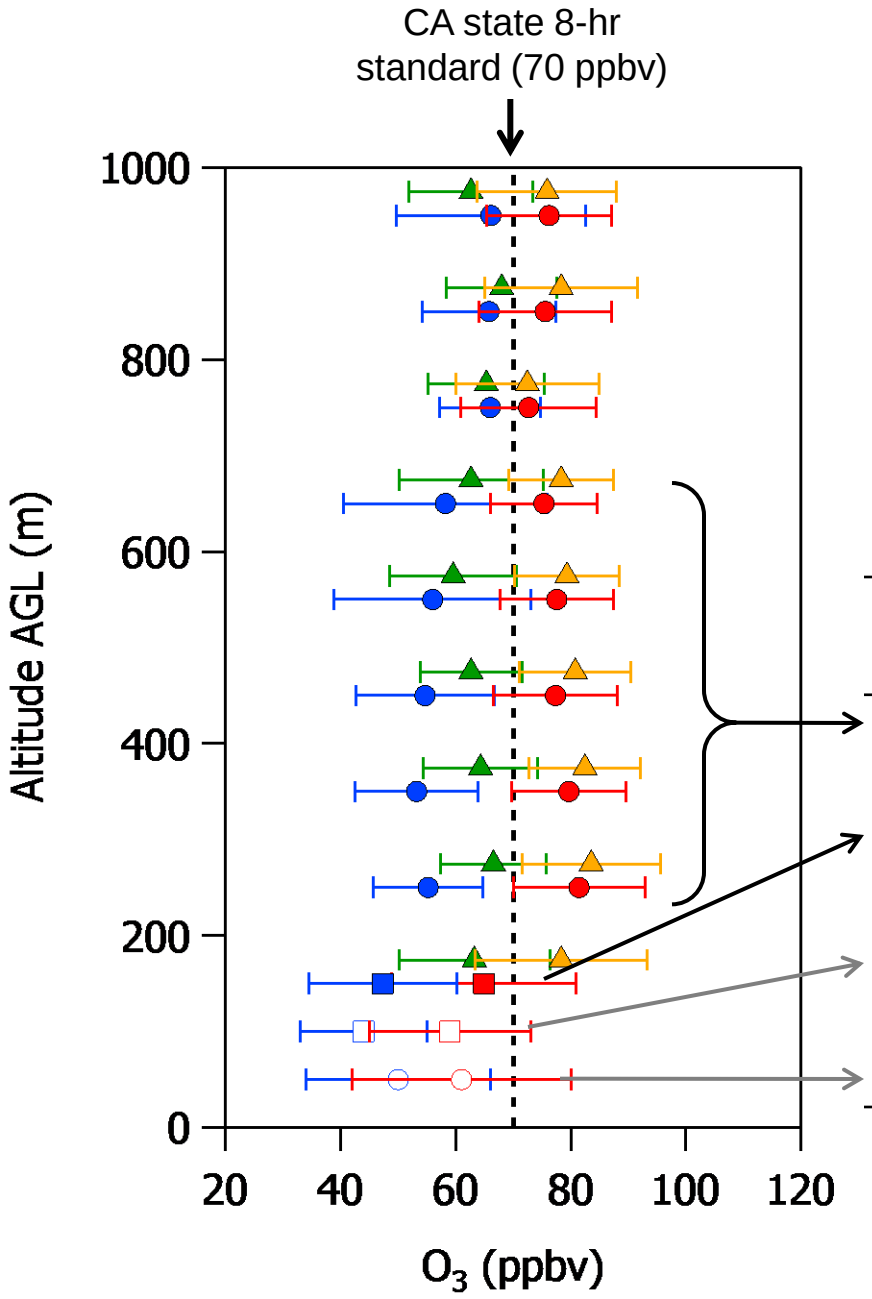
benzene/CO = 1.07 ± 0.13

No significant change in VOC

$$\text{Calculated VOC/NO}_x\text{ ratio} = \frac{\text{VOC/CO}}{\text{NO}_y\text{/CO}} = \frac{1.07}{1.68} = 0.64$$

WE increase in VOC/NO_x primarily due to reductions in NO_x rather than increased weekend VOC emissions

O_x (=O_3+NO_2) acts as indicator for O_3 titration/production



Use O_x (=O_3+NO_2) to signify contributions from:

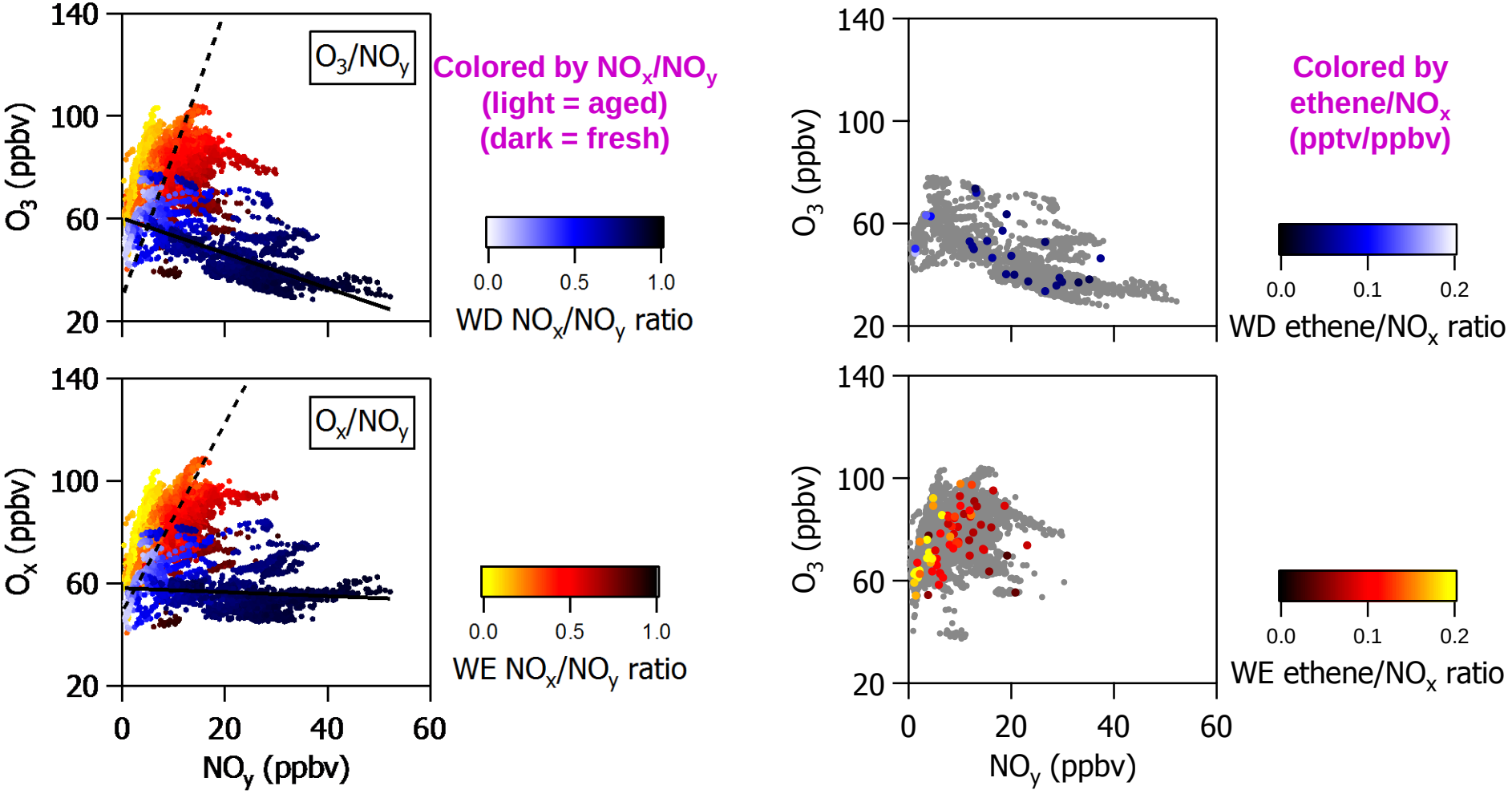
O_3 titration	***O_3 production***
$O_3 + NO \rightarrow NO_2 + O_2$	$OH + RH + O_2 \rightarrow RO_2 + H_2O$
$NO_2 + h\nu + O_2 \rightarrow NO + O_3$	$RO_2 + NO \rightarrow NO_2 + RO$
No net O_3 production	$NO_2 + h\nu + O_2 \rightarrow NO + O_3$
ΔO_x (WE-WD) = 0	*ΔO_x (WE-WD) ≠ 0*

	Average O_3 mixing ratios (ppbv)			
	WD	WE	Δ(WE-WD)	↑ on WE
CalNex, P-3 aircraft	55	78	23	42%
O_x	63	81	18	29%
CalNex, Pasadena	47	65	17	36%
O_x	63	78	15	24%
CARB, Pasadena	43	59	15	35%
CARB, SoCAB	50	61	11	22%

ΔO_x (WE-WD) ≠ 0
indicates contribution from
photochemical production of O_3 on weekends

WD-to-WE differences in ozone couple to differences in precursors

P-3 aircraft data shown; similar observations using ground site data



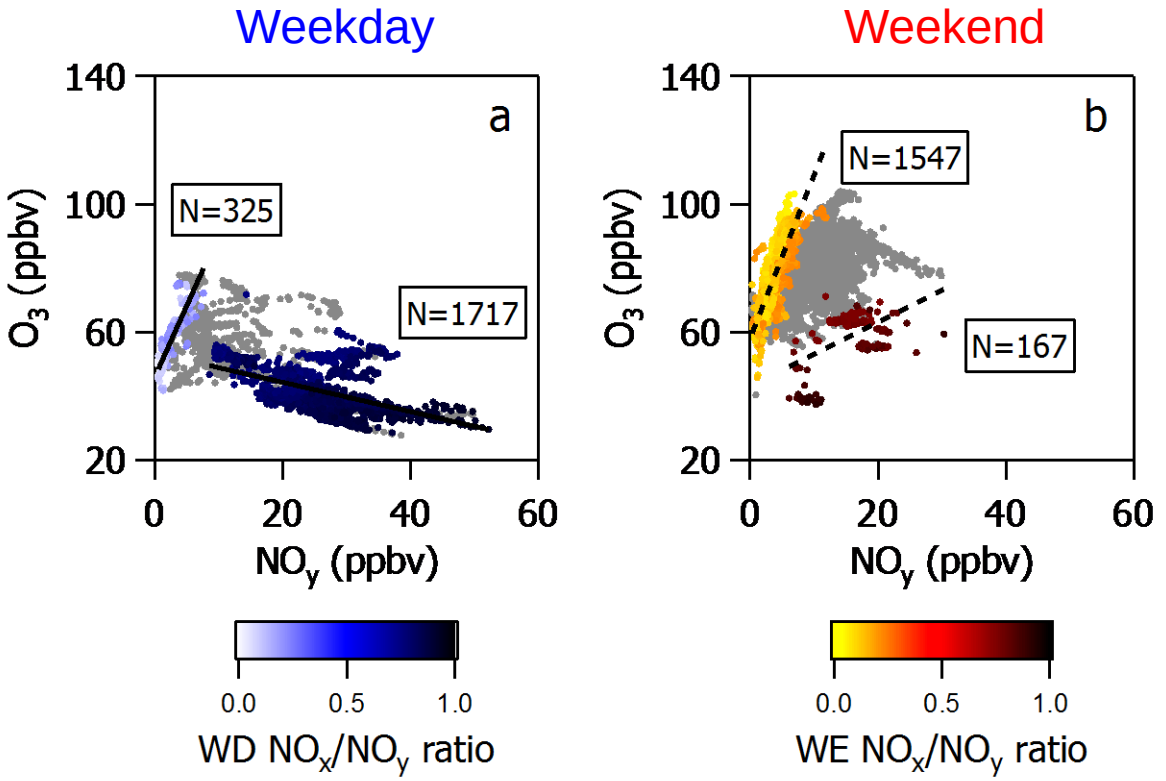
Negative or flat slopes indicate titration on WD
(↑ in fresh NO emissions leads to ↓ O_3 and $\Delta O_x = 0$)

Positive slopes indicate production on WE
(↑ NO_x leads to ↑ O_3 and ↑ O_x)

Majority of WD points with lower O_3 have
ethene/NO_x < 0.1 (dark colors)

Majority of WE points with higher O_3 have
ethene/NO_x > 0.1 (light colors)

WD-to-WE differences in titration and photoproduction: NO_x/NO_y ratio



P-3 aircraft data

Data separated by NO_x/NO_y ratio:

Ratios > 0.75 refer to fresh NO_x emissions (dark colors)

Ratios < 0.25 refer to chemically aged emissions (light colors)

Weekdays:

Increased number of data points associated with fresh emissions along negative-going slope

titration

Weekends:

Increased number of data points associated with aged emissions along positive-going slope

production