

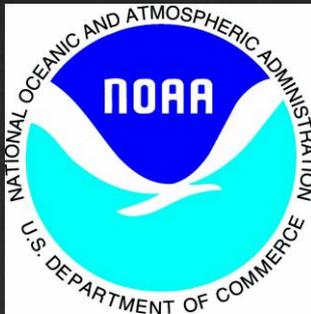
Airborne measurements of volatile organic compounds in the Los Angeles Basin, California

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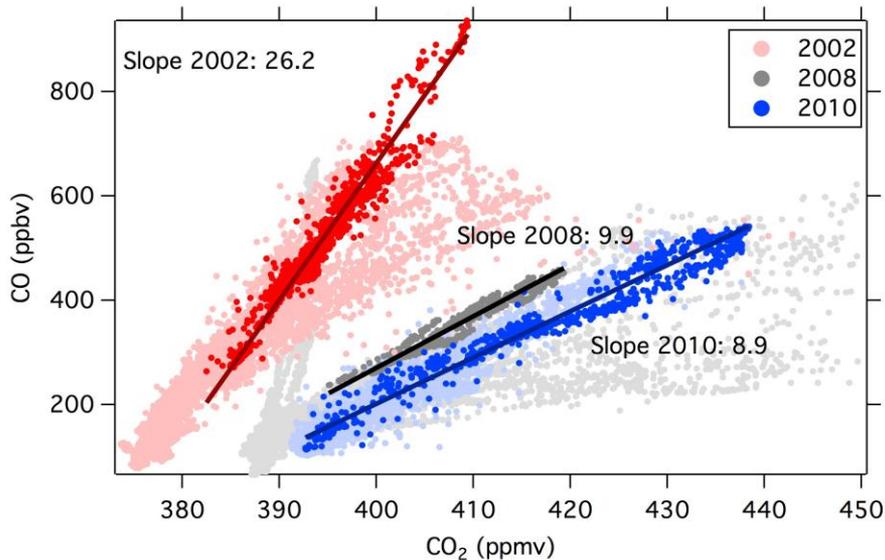
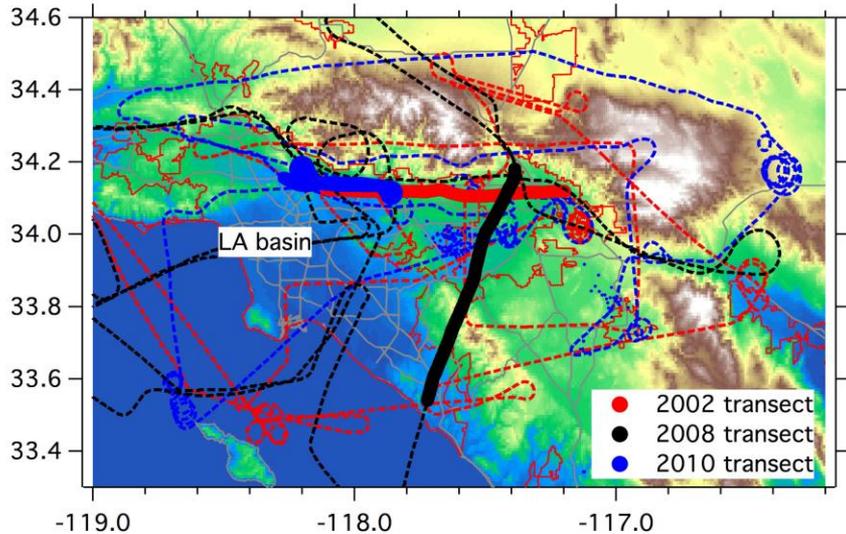
CalNex 2010

Research at the Nexus of Air Quality and Climate Change



- VOCs from CalNex 2010 compared to historical data from LA
- VOCs weekend effect
- VOCs indicate mixing with older pollution from LA

Comparison with 2002



LA flights:

May 2002: NOAA ITCT

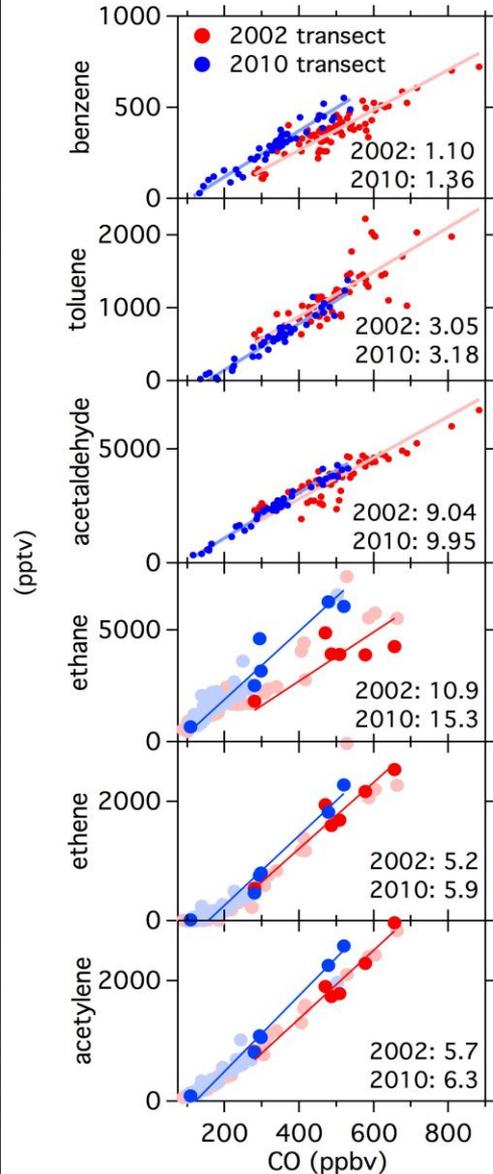
June 2008: NASA ARCTAS

May 2010: NOAA CalNex

Enhancement ratios to look at relative changes and to remove influence from atmospheric backgrounds

- CO₂ (fuel use) enhancement similar
- CO combustion marker
- CO/CO₂ reduced by over a factor of 2 (see Bishop and Stedman 2008)
- Cars are getting cleaner

Comparison with 2002



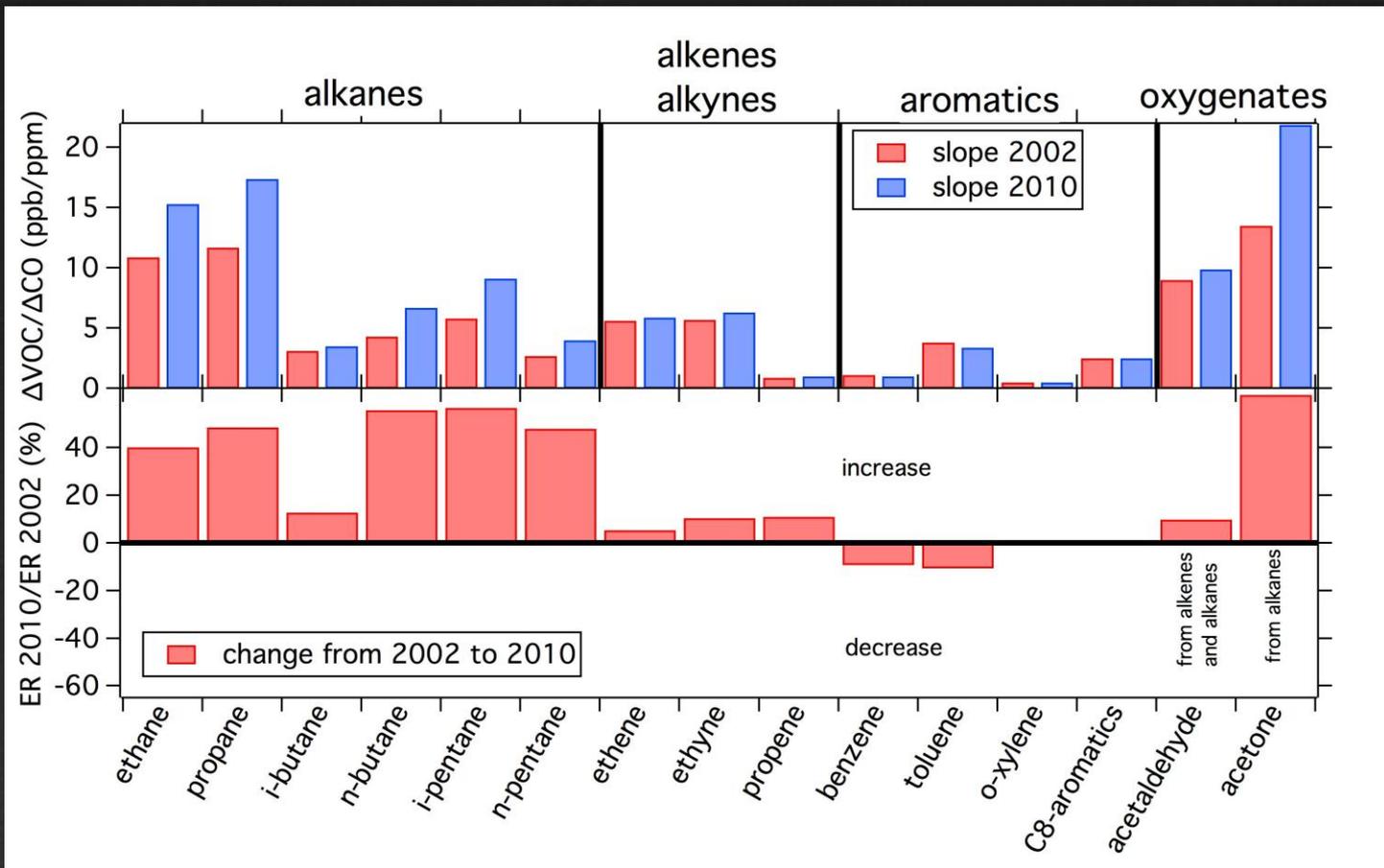
LA basin flights in May 2002 and 2010:

$\Delta\text{VOC}/\Delta\text{CO}$ basically ratios constant



most VOCs reduced by factor of two compared to CO_2

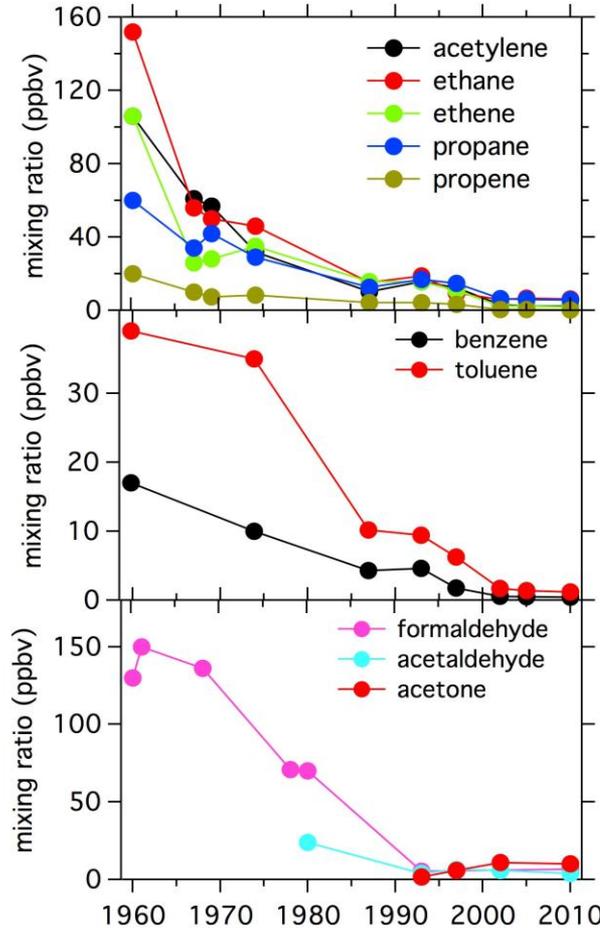
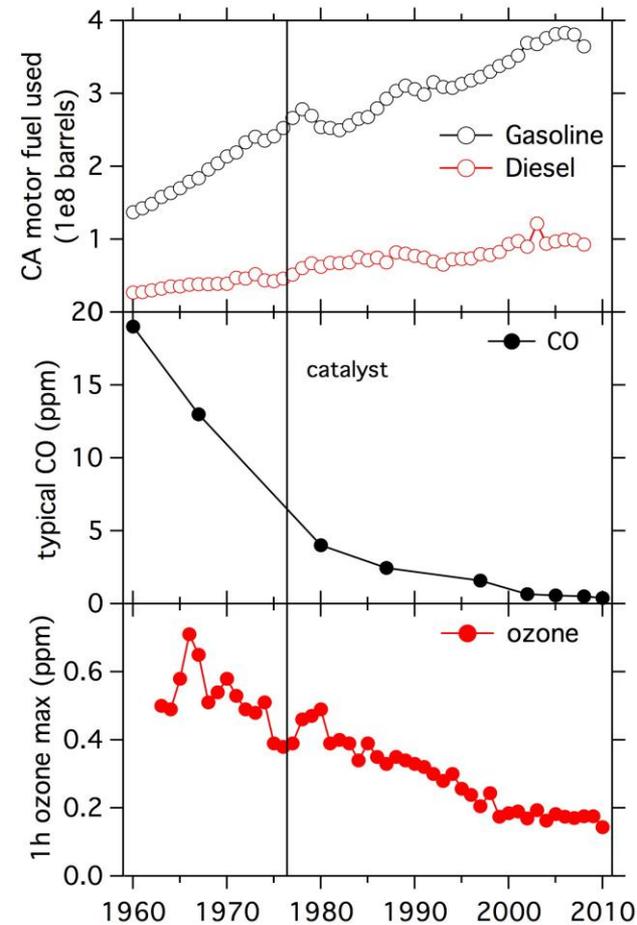
Comparison with 2002



- Alkenes and aromatics decrease with CO: main source is traffic related
- Small alkanes from area sources decrease slower
- Oxygenates mainly from secondary production are consistent

Reactivity determined by alkenes, aromatics and aldehydes

Looking back to the 60s in downtown LA



References:

1960: Neligan et al 1962
 1967: Gordon et al 1968
 1969: Mayrsohn et al 1972
 1974: ARB data set
 1980: Grosjean 1982
 1987: Lawson et al 1990
 1993: Fraser et al 1996, 1997
 1997: SCOS97 ARB data set
 2002: Warneke et al 2007
 2005: Baker et al 2008
 2008: NASA ARCTAS data
 2010: NOAA CalNex data

Ozone:

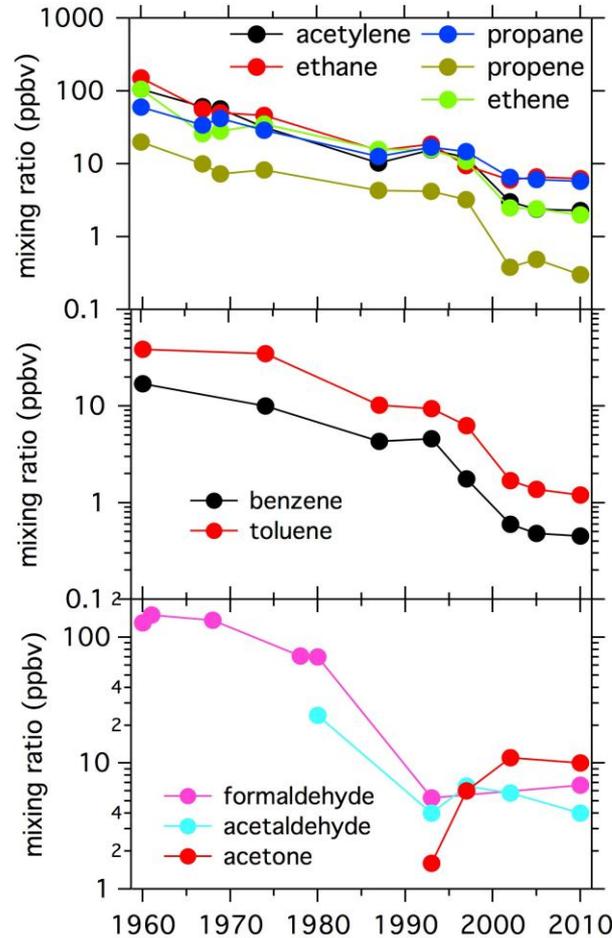
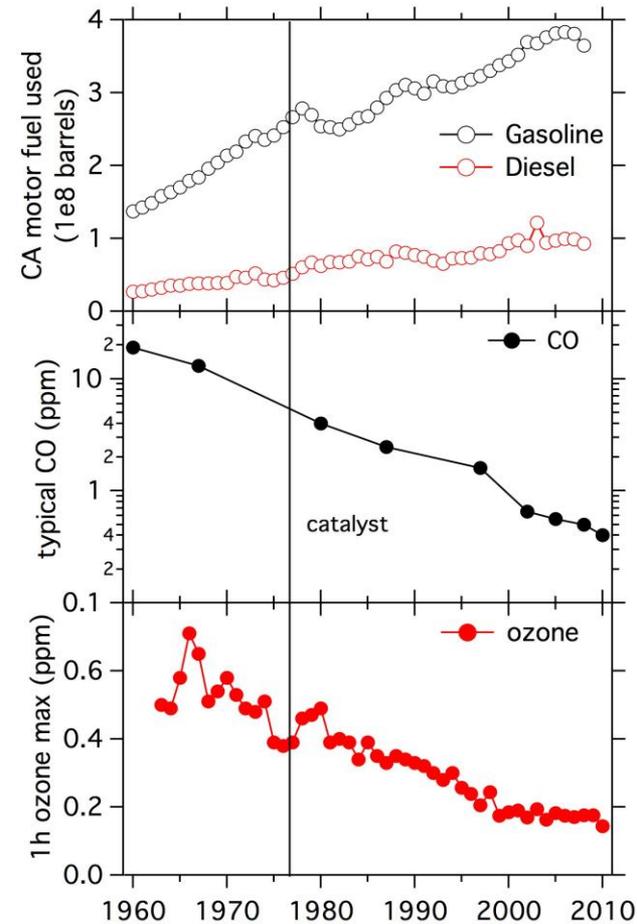
www.arb.ca.gov/adam/index.html

Gasoline use:

www.eia.gov/emeu/states/_seds.html

- Before catalyst: O₃ max around 700 ppbv, average CO around 20 ppm
- Rapid and steady decline since
- Fuel use increases

Looking back to the 60s in downtown LA



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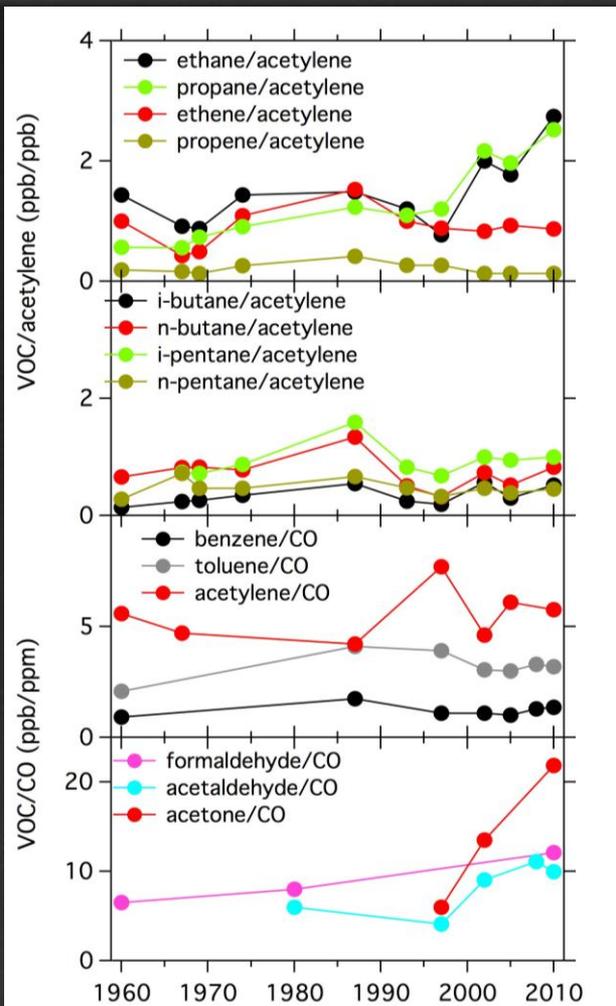
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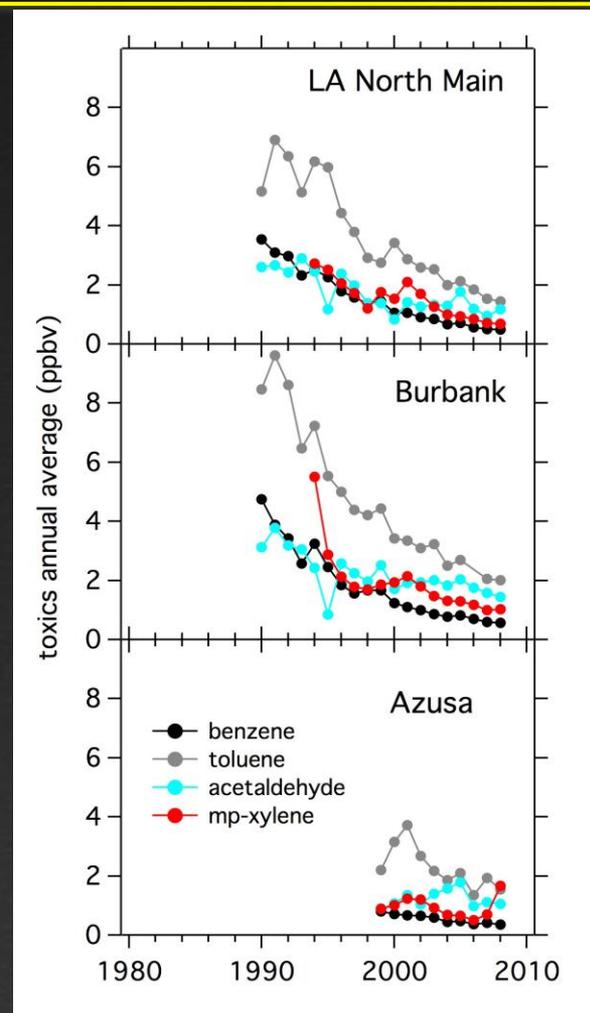
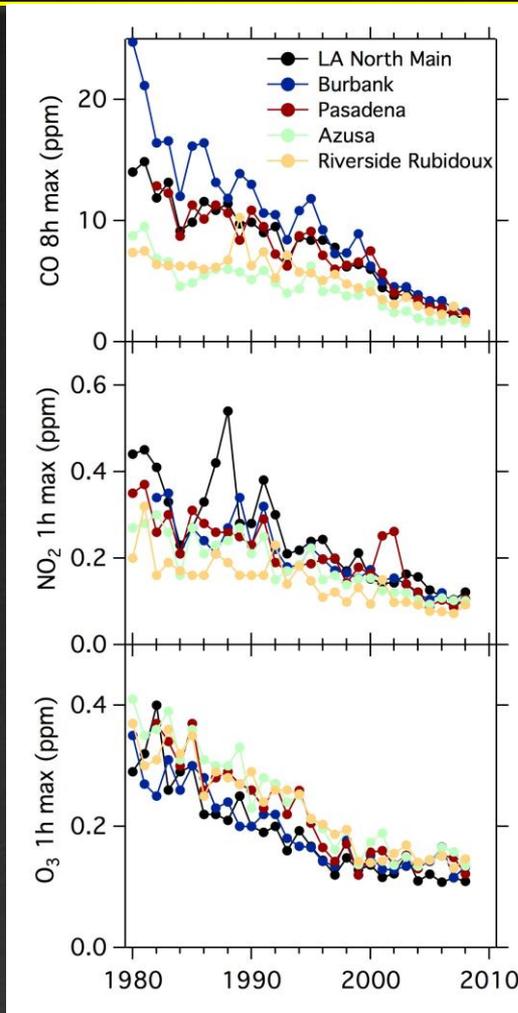
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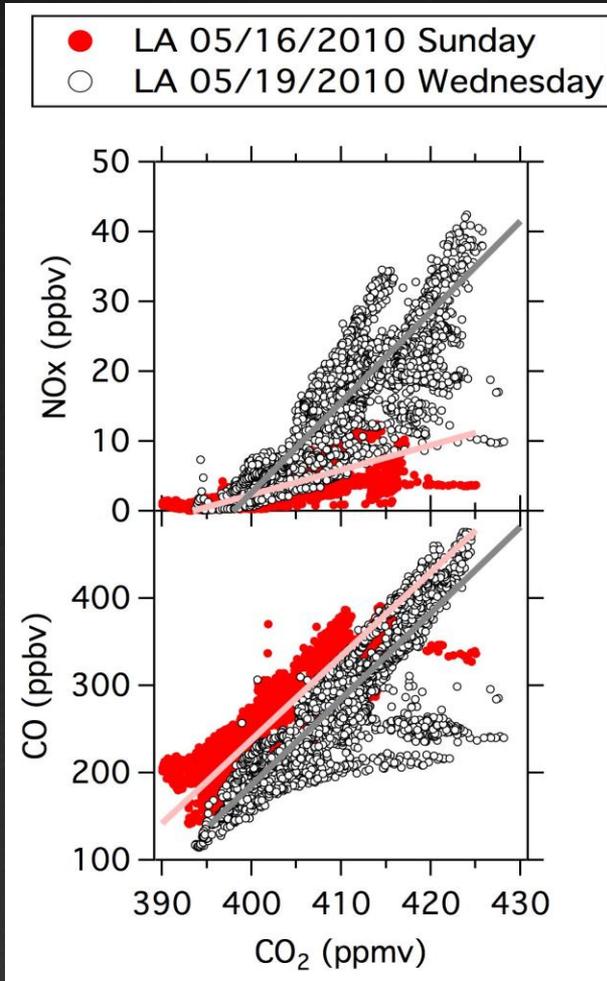
- Most $\Delta\text{VOC}/\Delta\text{CO}$ or $\Delta\text{VOC}/\Delta\text{acetylene}$ ratios constant over the years
- Common source from traffic
- Alkanes and ketones decrease slower

ARB monitoring network



SoCAB extensive monitoring network: CO, NO₂, ozone and toxics
Same declining trend for all stations
Canister sampling network: VOC trends consistent

NO_x emission decrease in weekends



In the weekends:

- Less truck traffic
- Reduction in NO_x emissions
- VOC emissions constant

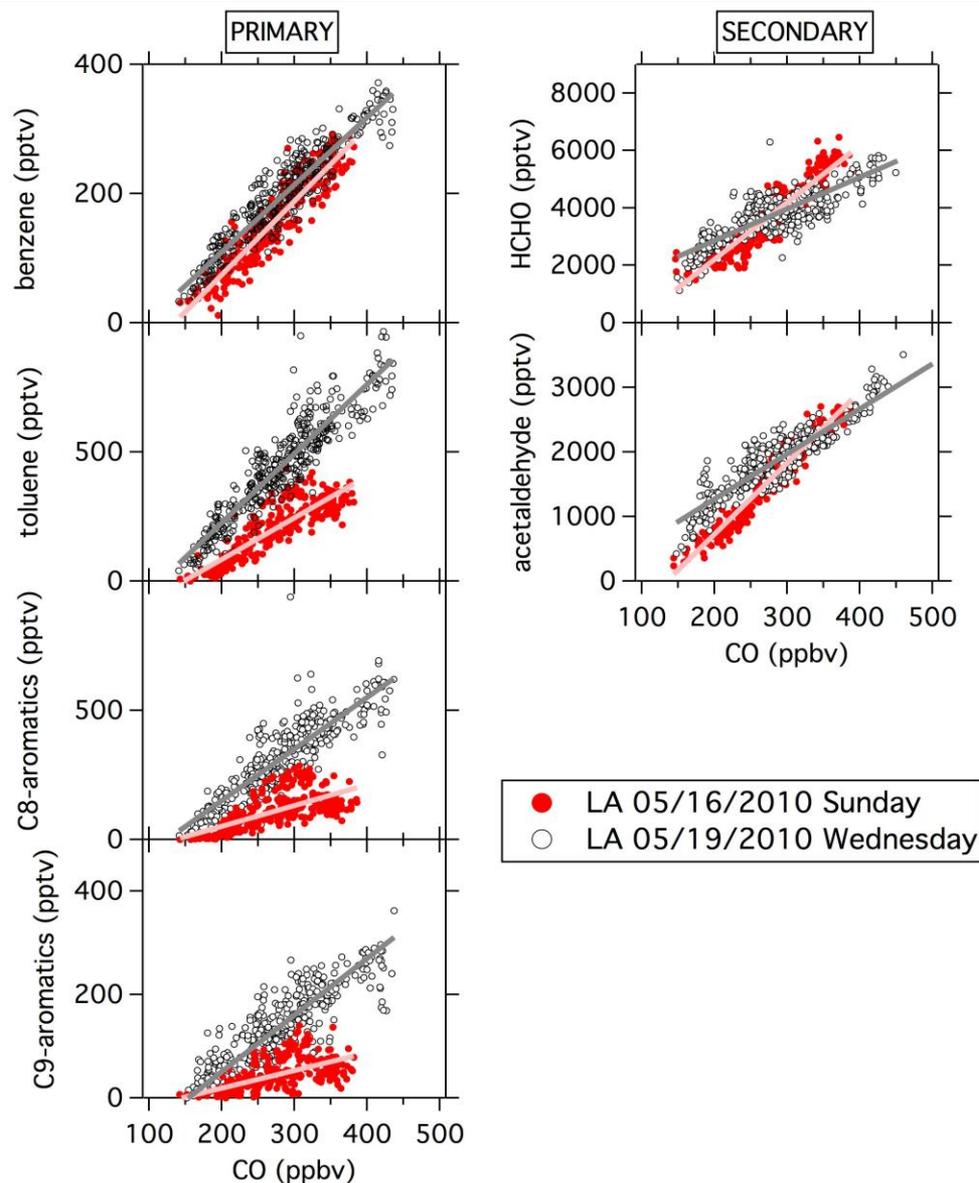
→ faster chemistry

see Ilana Pollack talk
and Harley et al 2005
Tonse et al 2008

Future selective NO_x reduction likely
Urea-based selective catalytic reduction (SCR)

Data from two flights in the South Coast Air Basin (boundary layer only)

NO_x emission decrease in weekends



In the weekends:

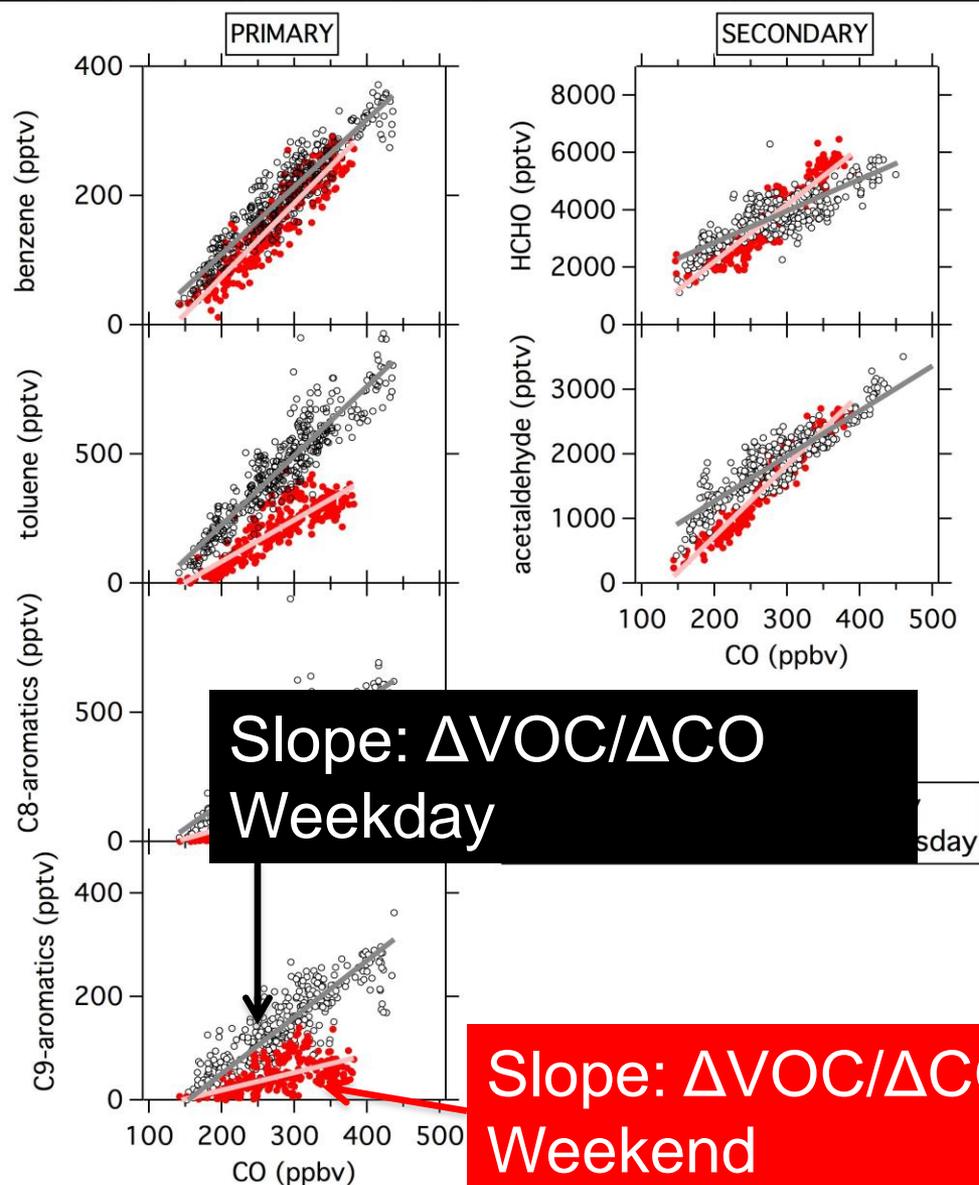
Primary VOCs

- Shorter lived compounds have lower enhancement ratios

Secondary compounds

- Larger enhancement ratios

NO_x emission decrease in weekends



In the weekends:

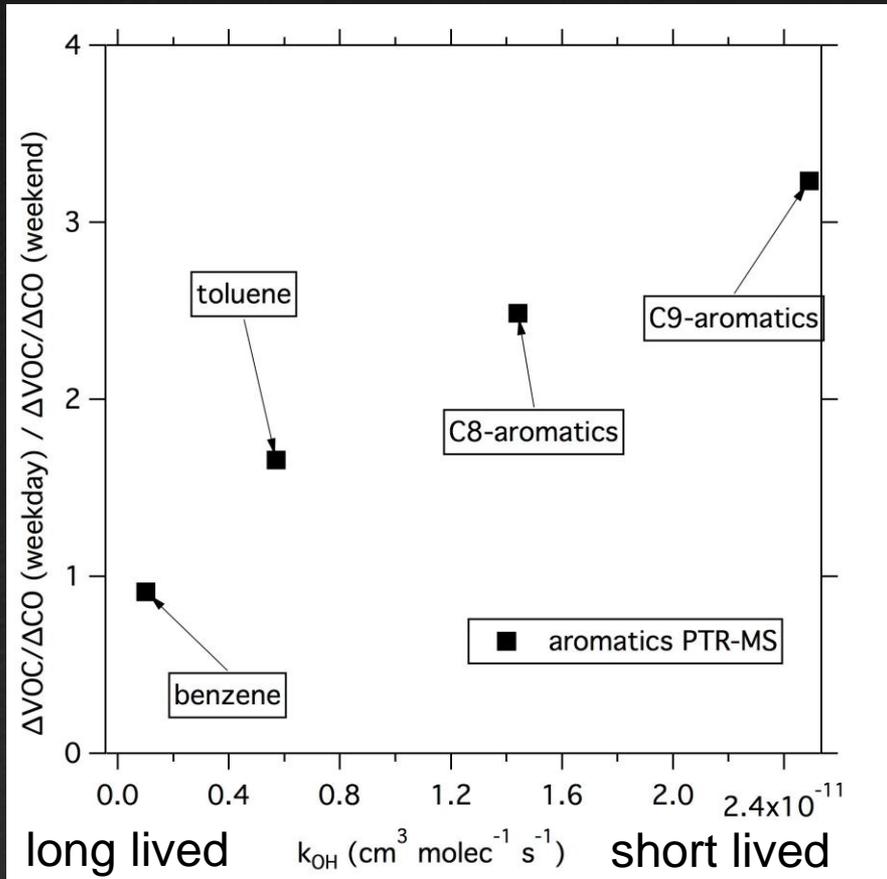
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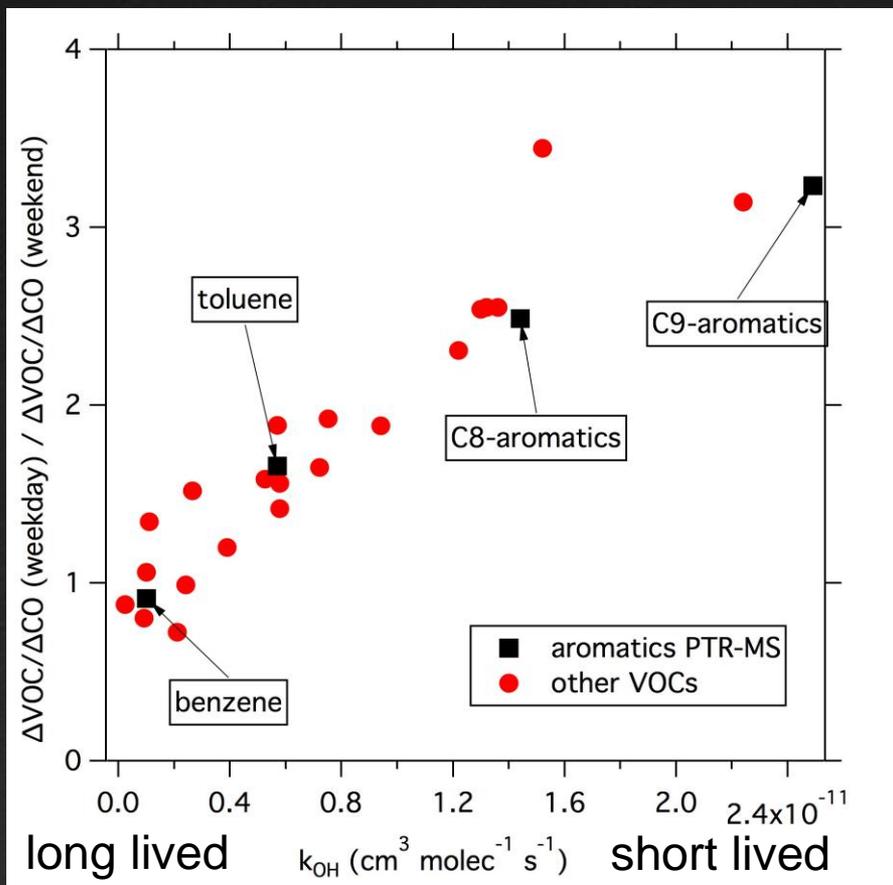


In the weekends:

$\Delta\text{VOC}/\Delta\text{CO}$ enhancement ratios strongly dependent on lifetime

→ faster chemistry

NO_x emission decrease in weekends



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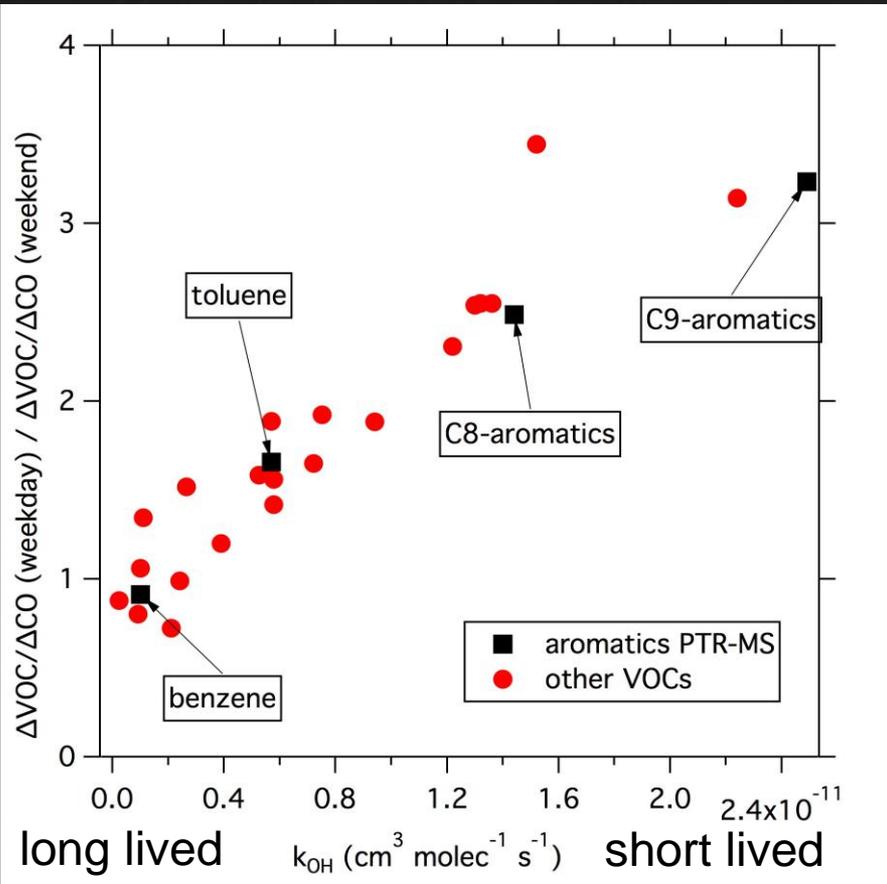
$\Delta\text{VOC}/\Delta\text{CO}$ enhancement ratios strongly dependent on lifetime

→ faster chemistry

→ VOC composition looks more aged

Caveat: meteorology influence, but effect was consistently observed

NO_x emission decrease in weekends



In the weekends:

$\Delta\text{VOC}/\Delta\text{CO}$ enhancement ratios strongly dependent on lifetime

→ faster chemistry

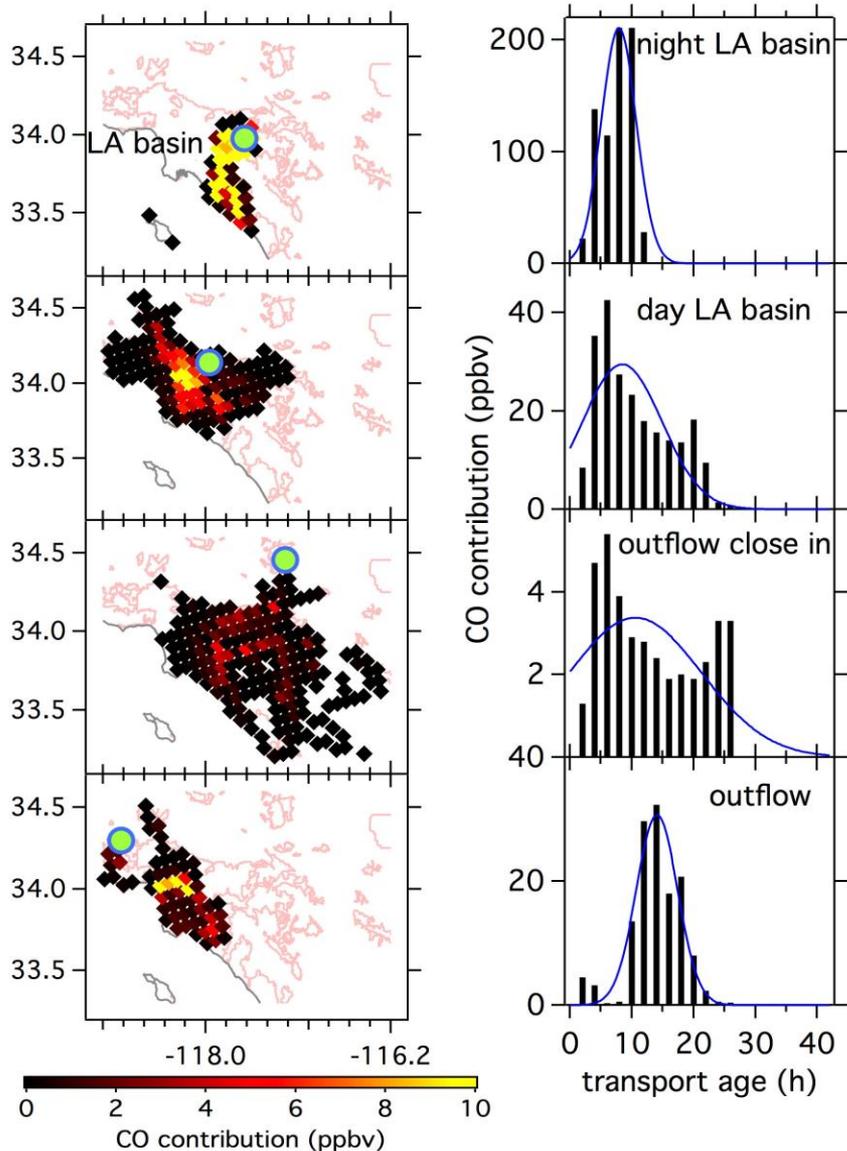
→ VOC composition looks more aged

Future selective NO_x reduction likely
Urea-based selective catalytic reduction (SCR)

With faster chemistry secondary compounds such as ozone increase relative to CO₂ but

most VOCs (including secondary VOCs) have a strong decreasing trend in LA

Pollution trapped in SoCAB

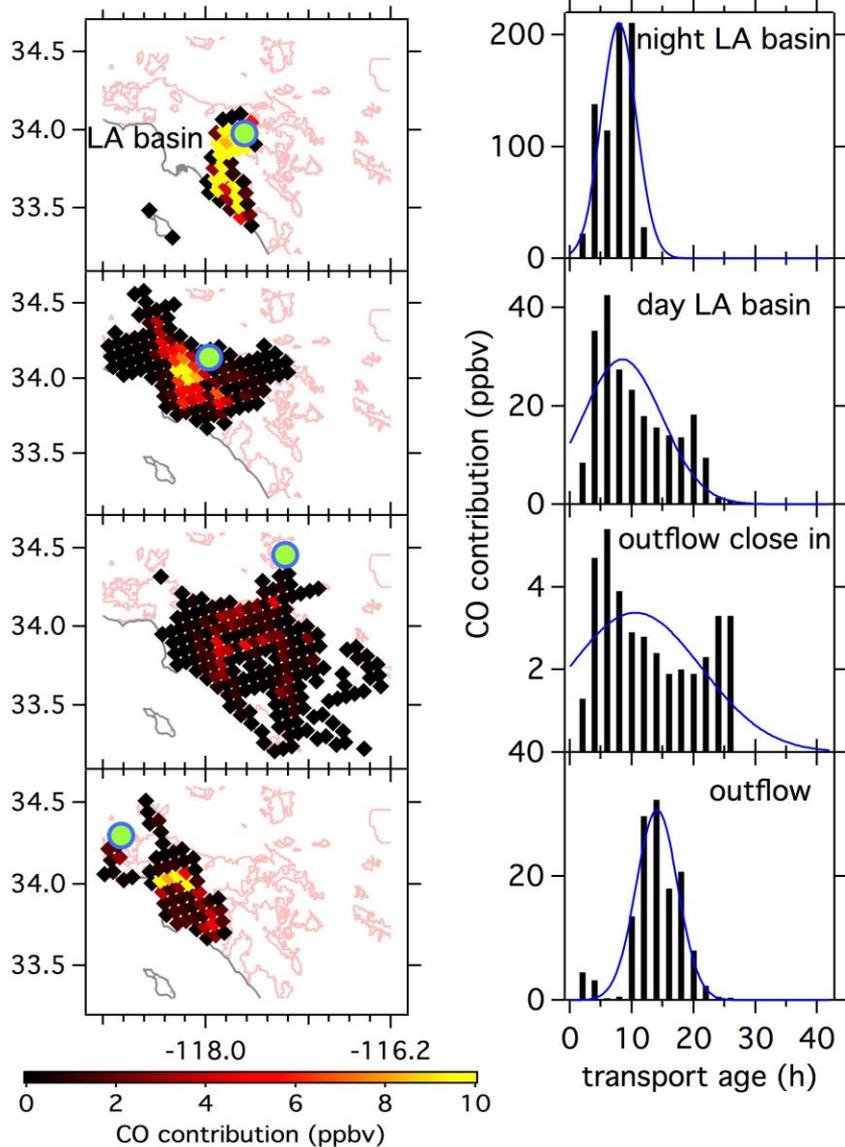


FLEXPART transport model:
20,000 trajectories released along the flight track

FLEXPART CO source contribution:
Shows where CO comes from at the aircraft

FLEXPART age distribution:
Shows how long CO was transported to the aircraft

Pollution trapped in SoCAB



Plume 1

Nighttime in the LA basin (below 200m)

Plume 2

Typical daytime LA basin

Plume 3

Just over the San Gabriel Mountains

Plume 4

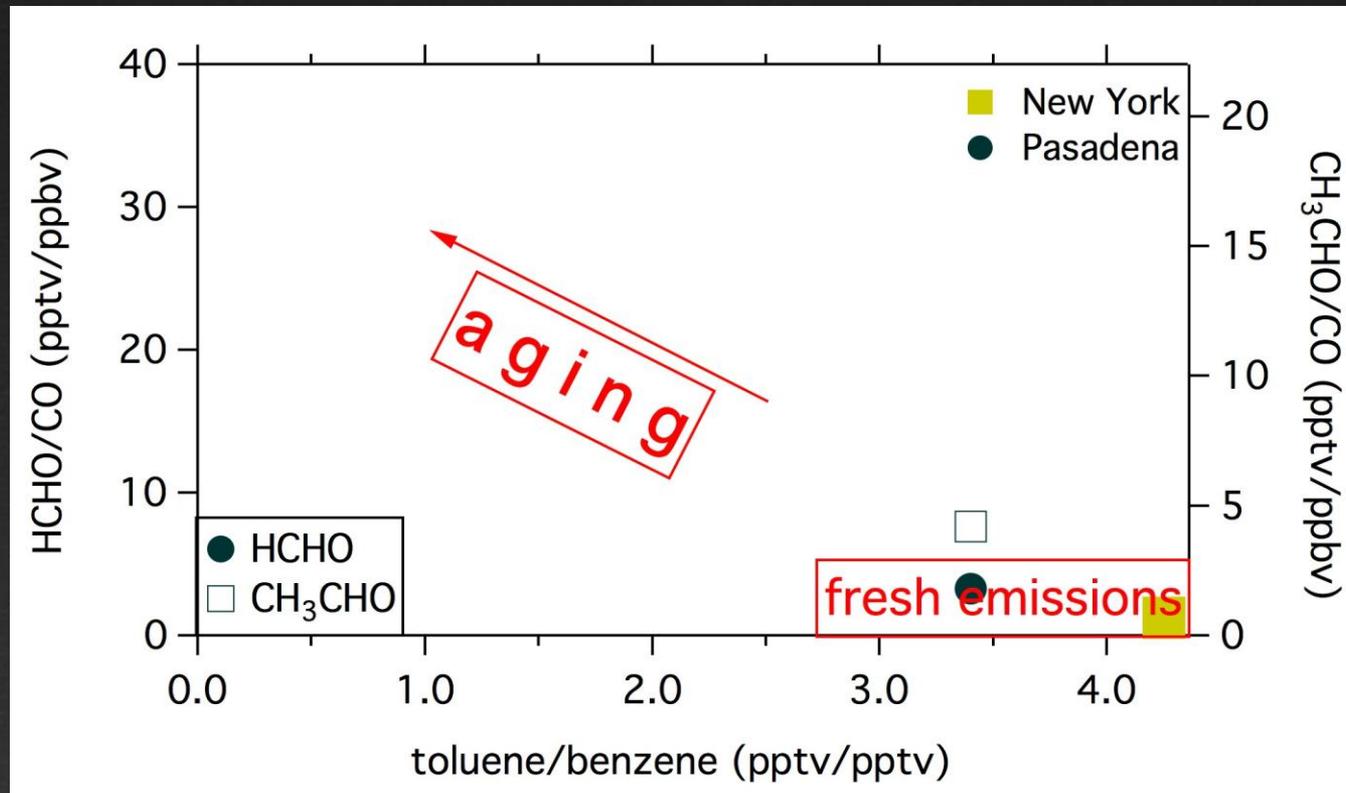
Close to Central Valley

Photochemical age of individual LA Plumes

VOC ratios as chemical clocks:

- toluene/benzene decrease with age
- HCHO/CO and CH₃COH/CO increase with age

Secondary production



Primary traffic emissions

Emissions ratios:

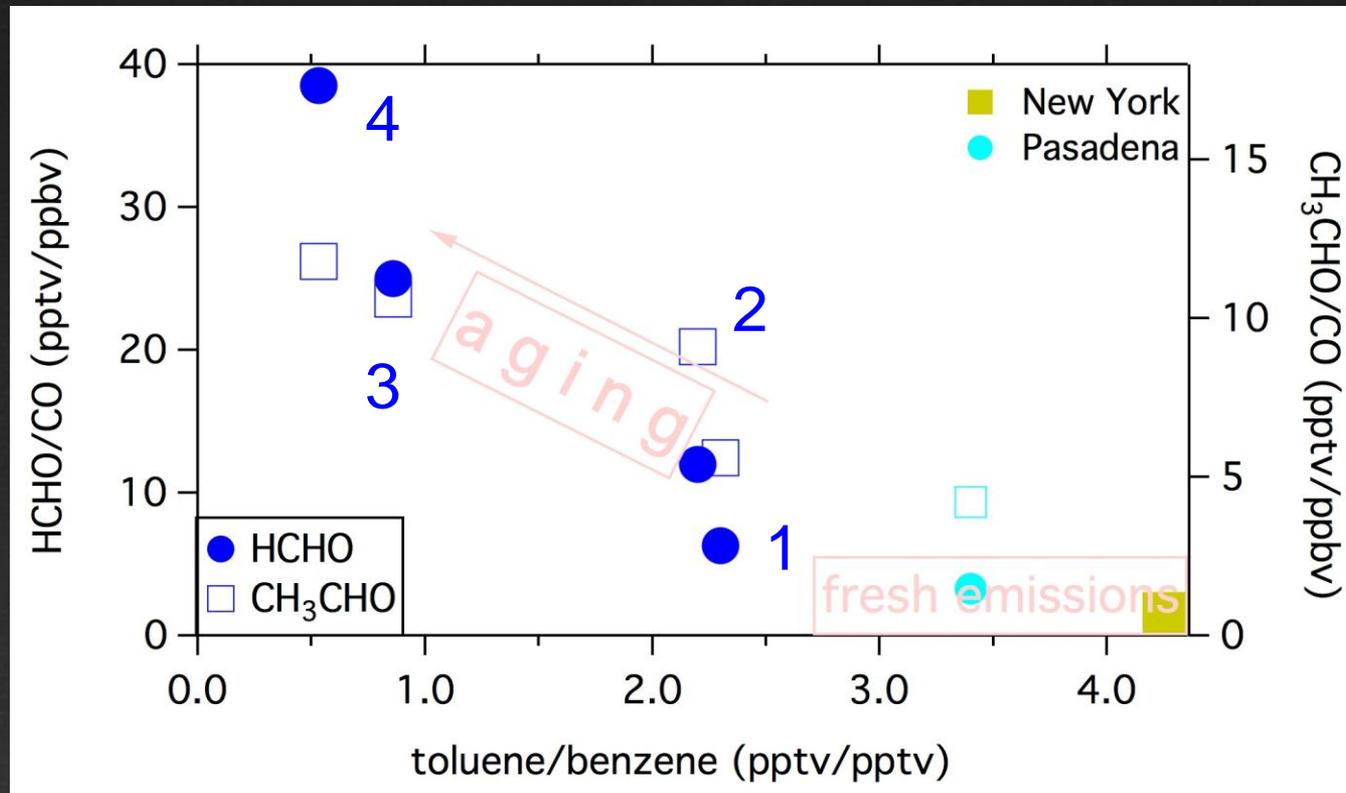
New York: Warneke et al 2007
Pasadena ground site: estimate

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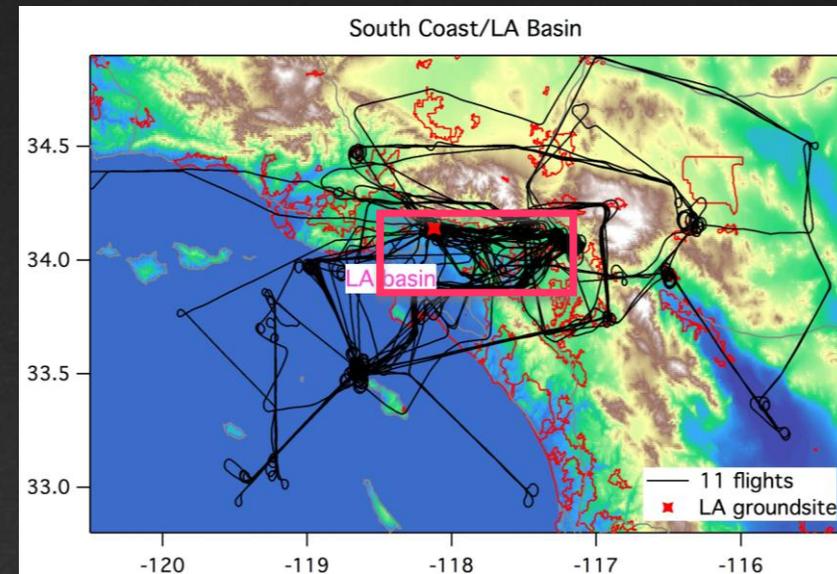
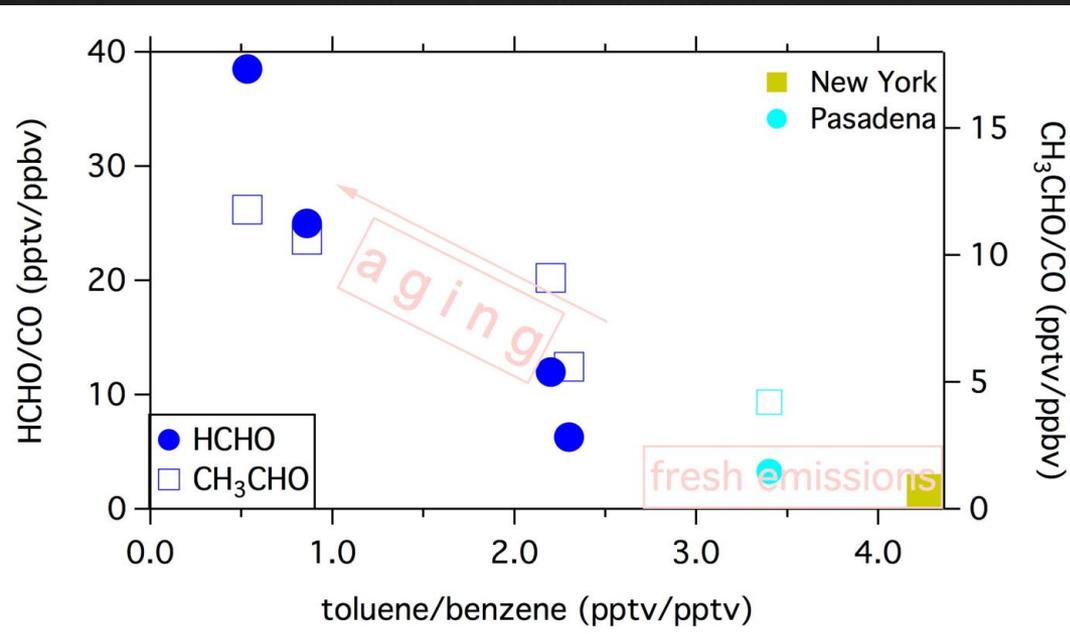
Primary traffic emissions

- LA basin plumes are processed (even at night)
- Mixture of fresh and previous day emissions

Photochemical age in LA/SoCAB

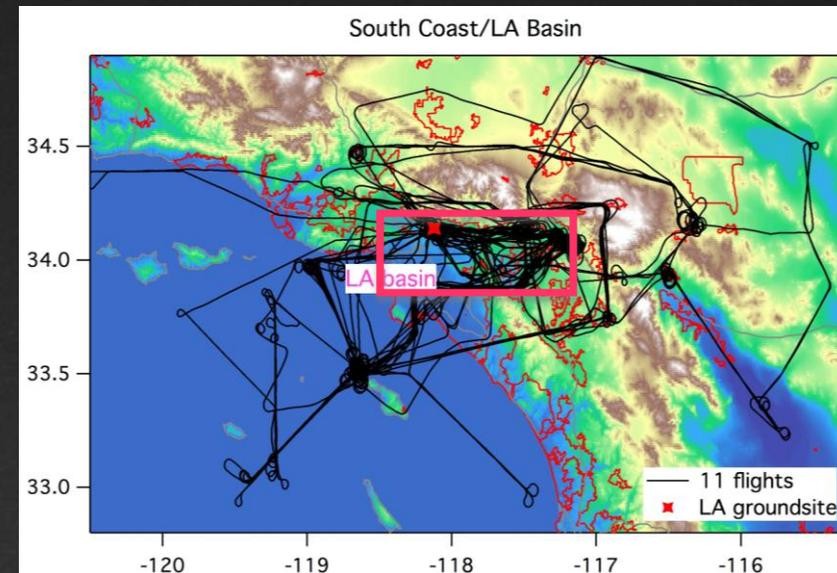
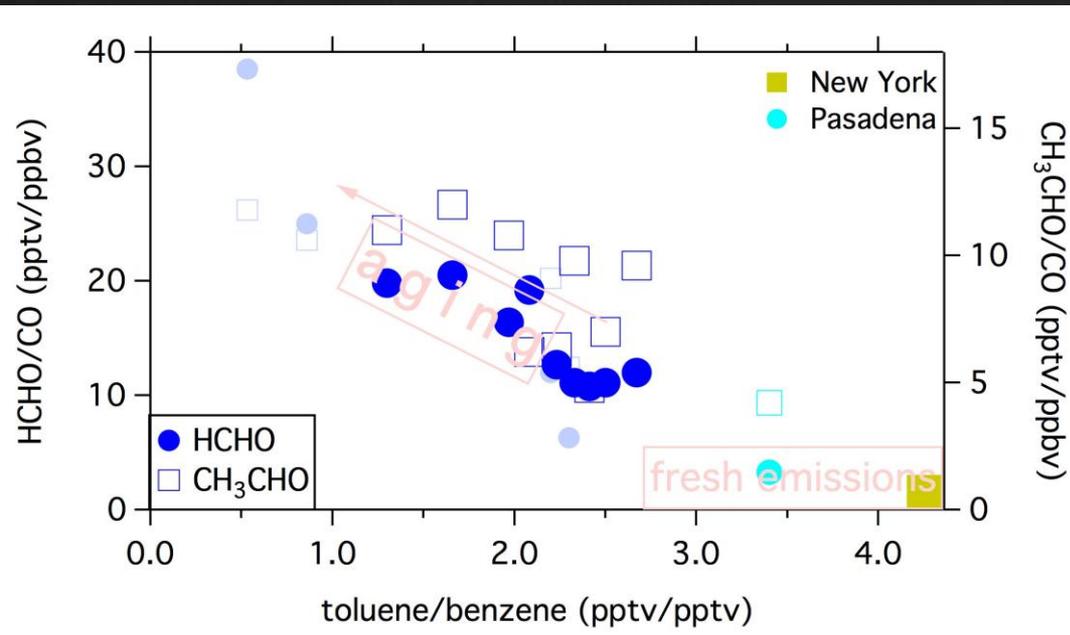
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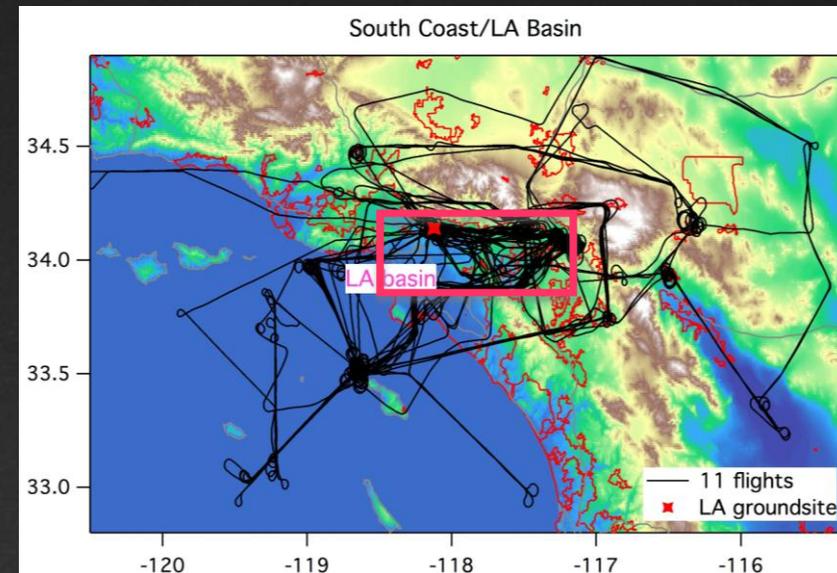
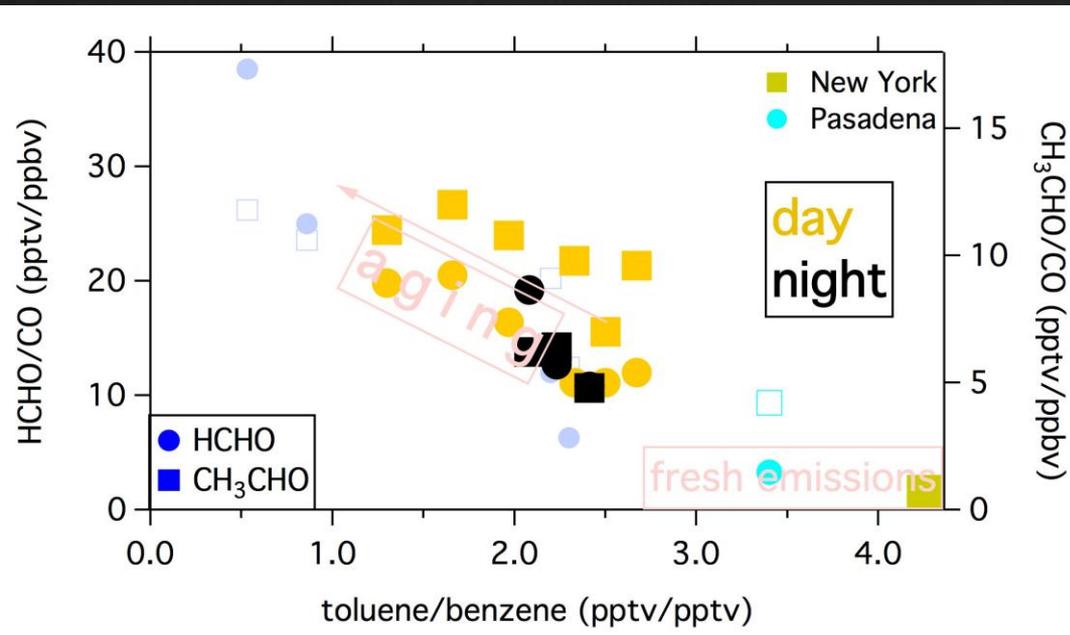
Each flight in the LA basin boundary layer is one data point



- all LA basin plumes are processed
- mixture of fresh and previous day emissions

Photochemical age in LA/SoCAB

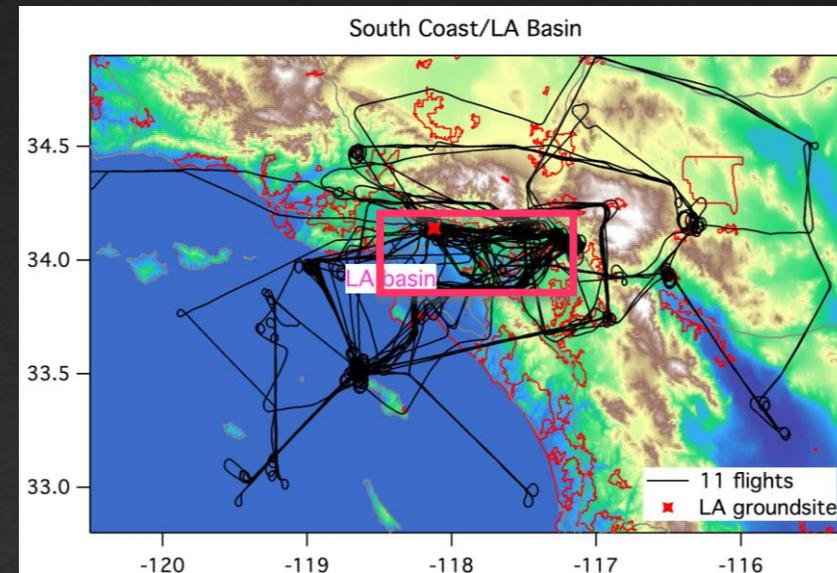
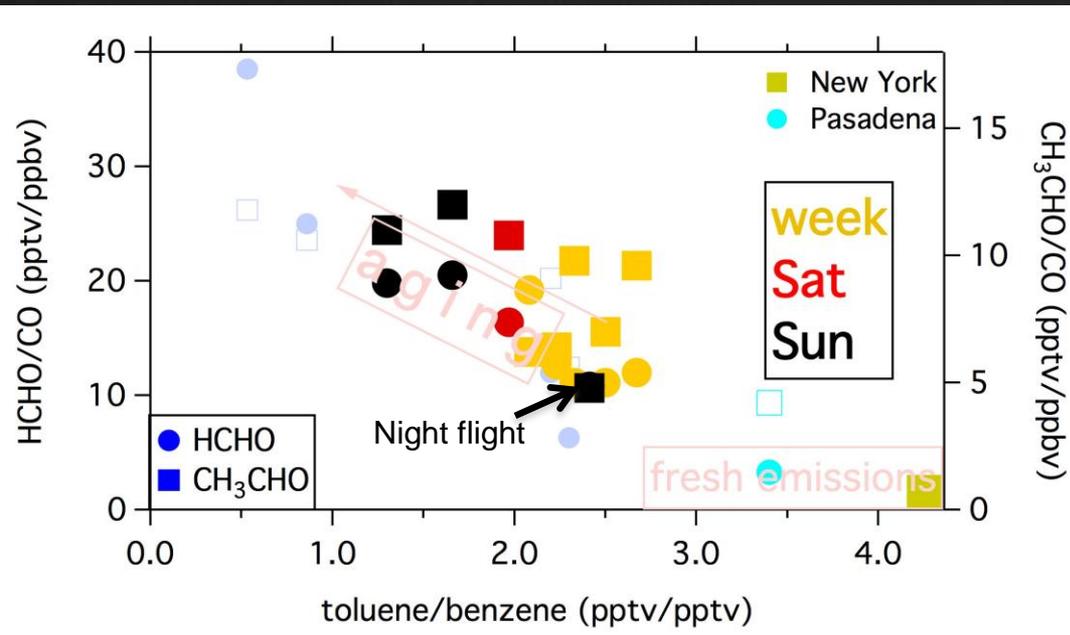
Every flight in the LA basin boundary layer is one data point
Color coded by **day/night**



- all LA basin plumes are processed
- mixture of fresh and previous day emissions
- nighttime flight somewhat less processed

Photochemical age in LA/SoCAB

Every flight in the LA basin boundary layer is one data point
Color coded by **weekday/weekend**



- all LA basin plumes are processed
- mixture of fresh and previous day emissions
- nighttime flight somewhat less processed
- weekend days more processed (faster chemistry due to lower NO_x?)

Conclusions

LA basin:

- CO and VOCs have decreased by about a factor of two since 2002
- and almost two orders of magnitude since 60s in downtown LA
- Emission ratios for most compounds constant since 60s: traffic main source
- Weekends: VOCs more processed than during the week due to faster NO_x chemistry
- Inside LA basin pollution often builds up for days

Thanks to:

CalNex Science team

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and David Parrish***