VOCs in the Greater Los Angeles Basin:

Characterizing the gas-phase chemical evolution of air masses via multi-platform measurements during CalNEX

Jessica B. Gilman

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CIRES at Univ. of Colorado

J. de Gouw, W. Kuster, D. Bon, C. Warneke, J. Holloway, E. Williams, B. Lerner, I. Pollack, T. Ryerson, E. Atlas, D. Blake, A. Vlasenko, S-M. Li, S. Alvarez, J. Flynn S. Herndon, M. Zahniser, B. Rappengluck, B. Lefer

CALNEX LOS ANGELES

NOAA | University of Colorado 1876 | CIRES | University of Miami | UC Irvine University of California, Irvine | Environment Canada | University of Houston | Aerodyne Research Inc.

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CALNEX LOS ANGELES

1. Comparison of VOC ratios
   - *RV Atlantis, NOAA WP-3, and ground site*
2. Diurnal variability
   - *VOC sources and boundary layer dynamics*
3. Chemical evolution
   - *Carbon mass, OH reactivity, and SOA potential*

VOC datasets: Instrumentation and speciation

RV Atlantis

- GC-FID: C2 – C5 hydrocarbons, benzene, toluene
- PTR-TOF-MS: Isoprene, C8-C9 aromatics, OVOCs, DMS
- QCL-TILDAS: Formaldehyde

NOAA WP-3D

- WAS: C2 – C5 hydrocarbons, C6-C9 aromatics, Isoprene, DMS
- PTR-MS: OVOCs

Ground site in Pasadena, CA

- GC-MS: C2 – C5 hydrocarbons, C6-C9 aromatics, OVOCS, DMS
- Hantzsch FR: Formaldehyde

Instrumentation and VOCs used in this presentation.

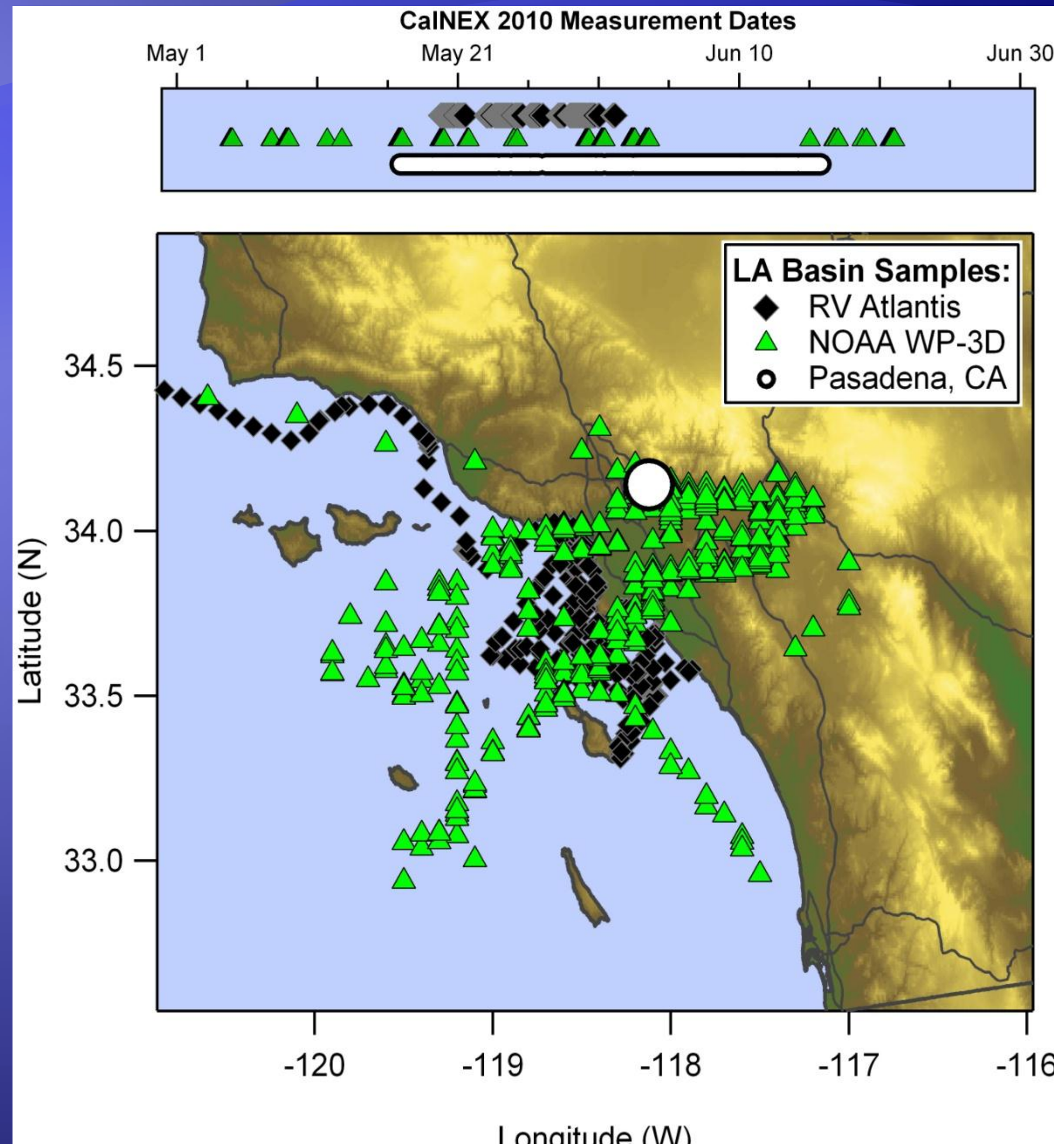
For a detailed list of all gas-phase measurements and principle investigators go to:
http://www.esrl.noaa.gov/csd/calnex/

VOC datasets: Temporal and spatial distribution

RV Atlantis:
- 300 samples
- Continuous sampling
- Onshore/offshore flow

NOAA WP-3D:
- 400 samples <1200m Alt
- Mostly daytime flights
- Spatial variability

Ground site:
- 1000+ samples
- Continuous sampling
- Diurnal variability



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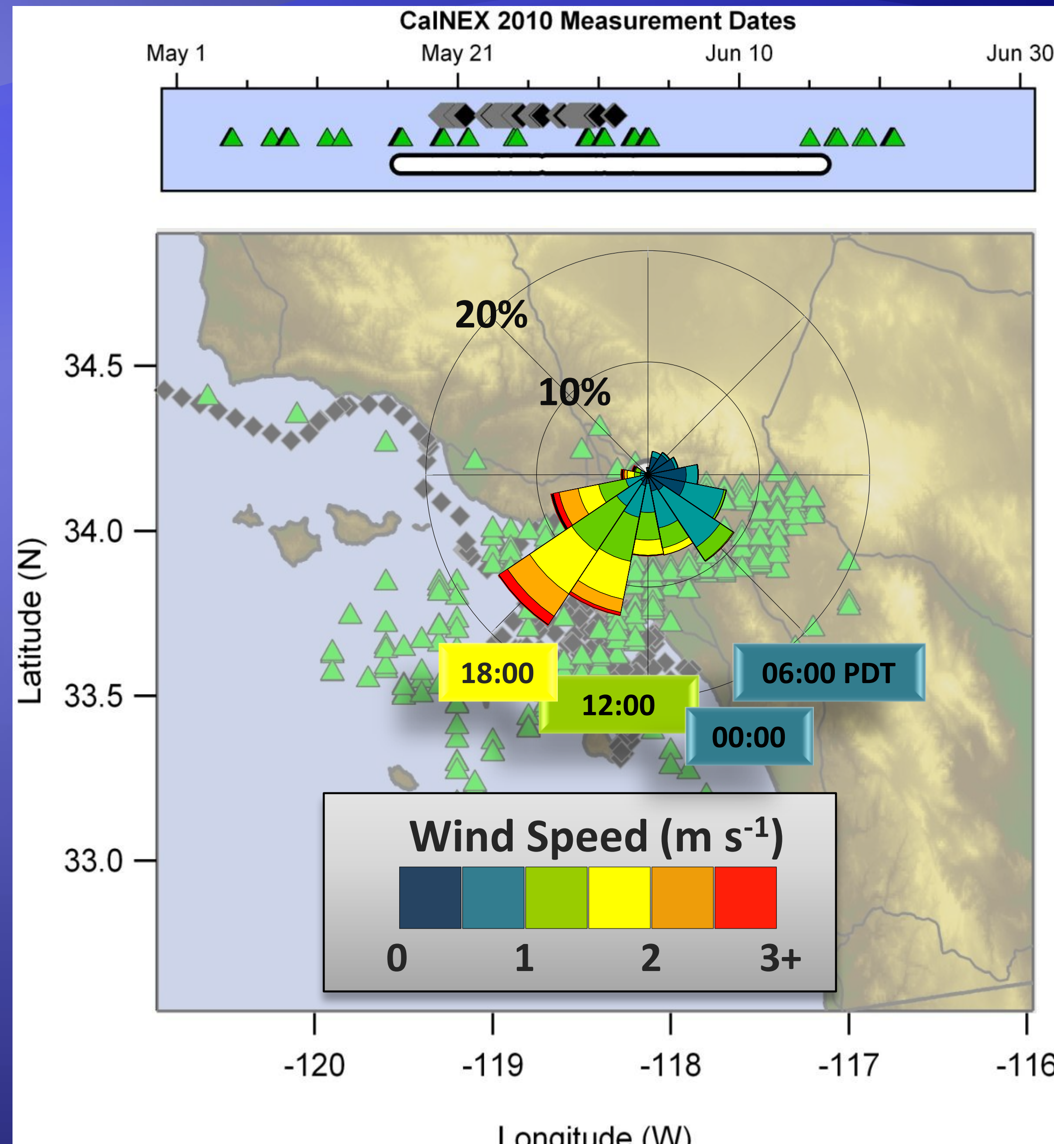
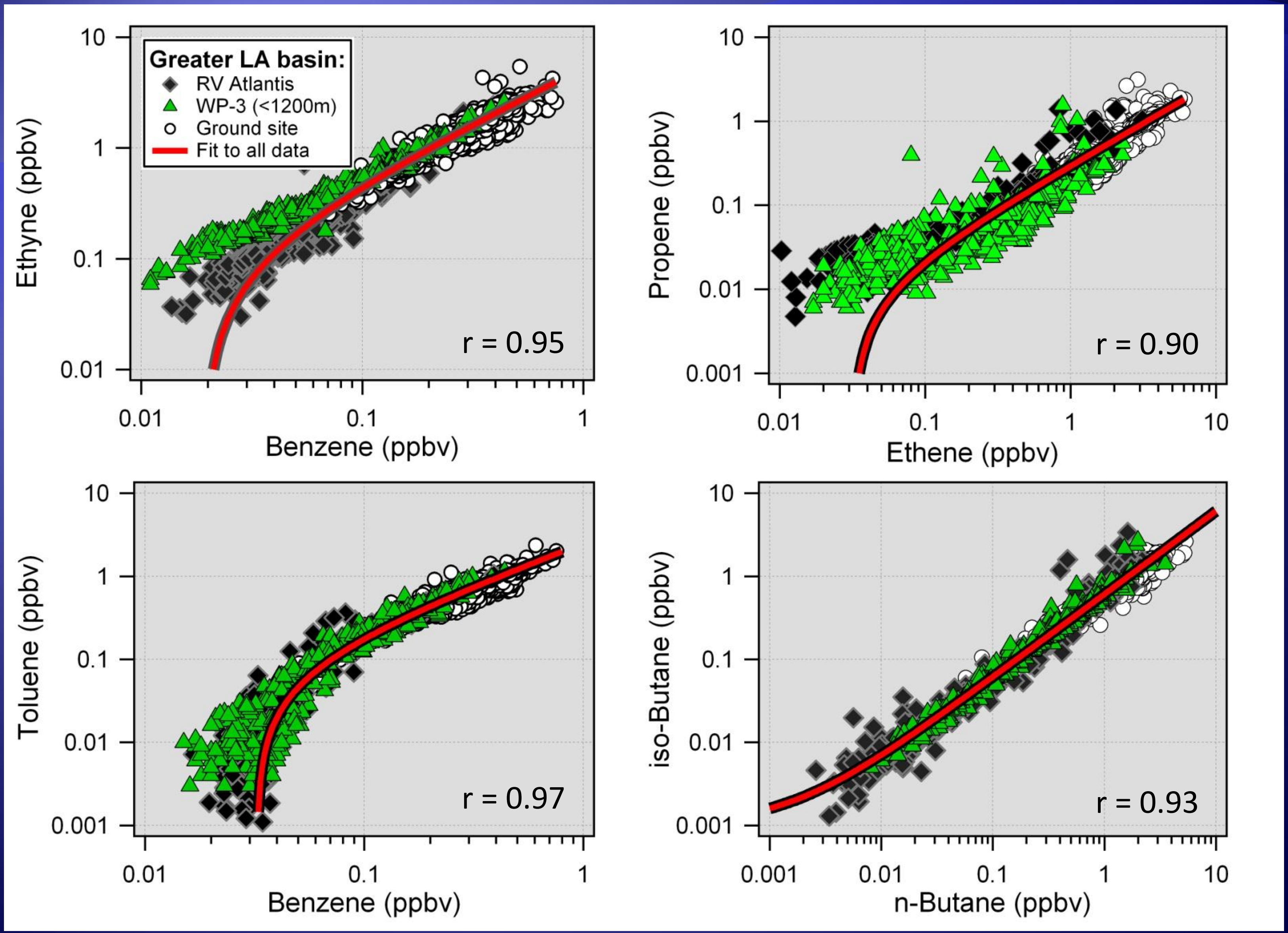


How well do the VOC ratios compare?



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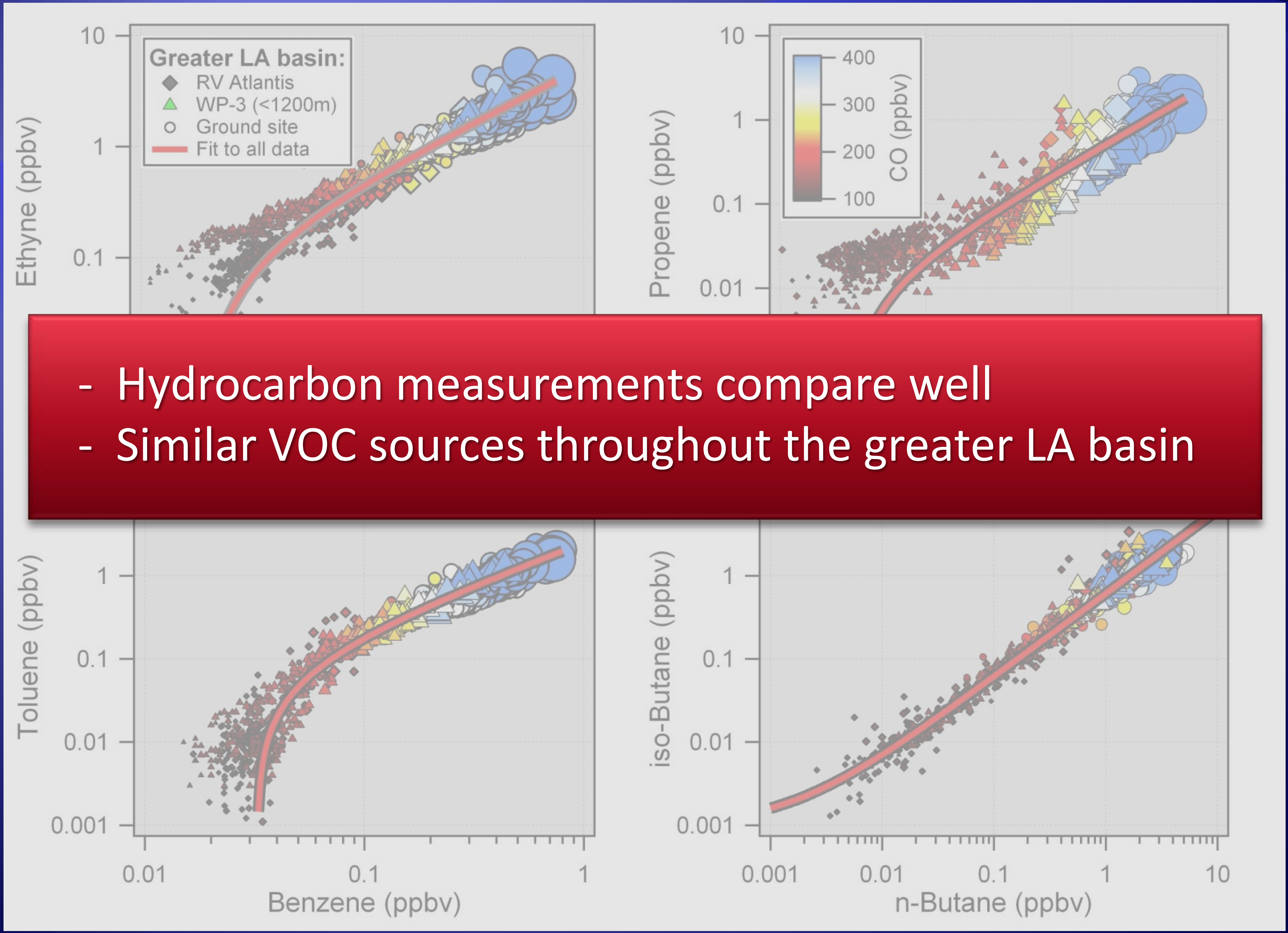
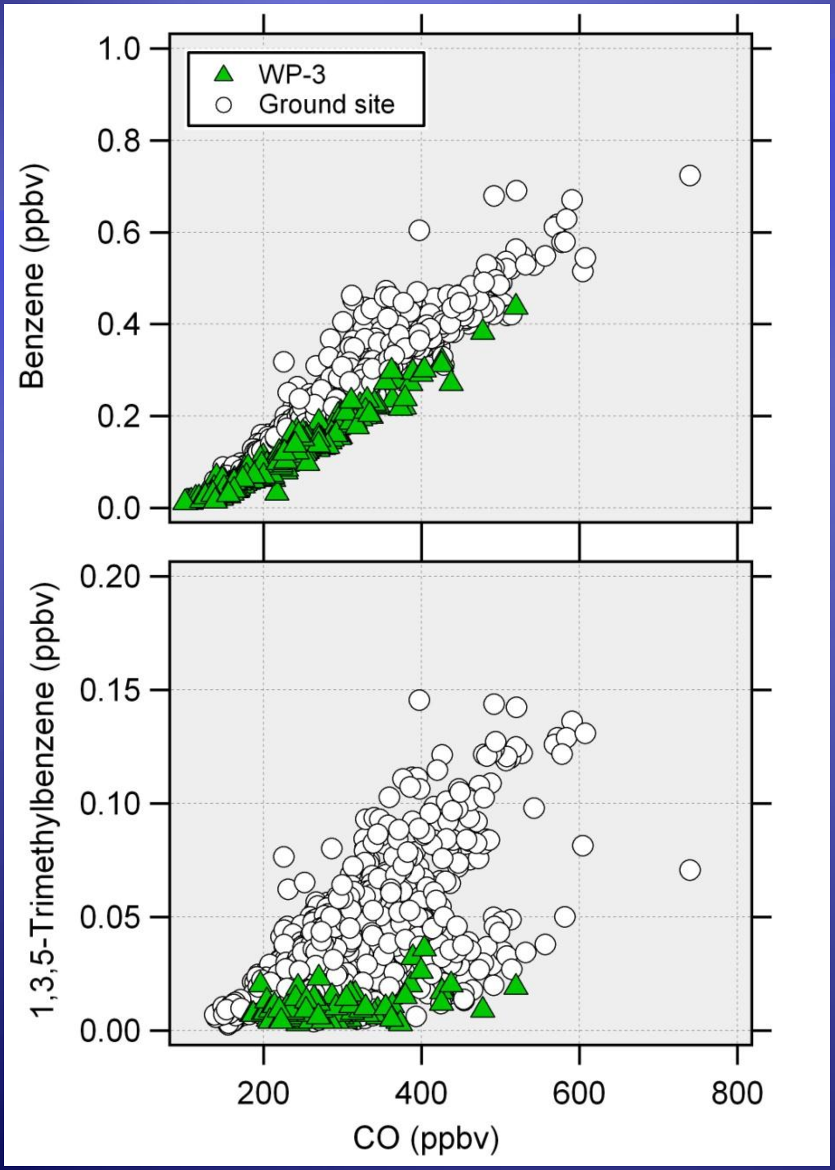


- Hydrocarbon measurements compare well
- Similar VOC sources throughout the greater LA basin

How well do the VOC to CO ratios compare?

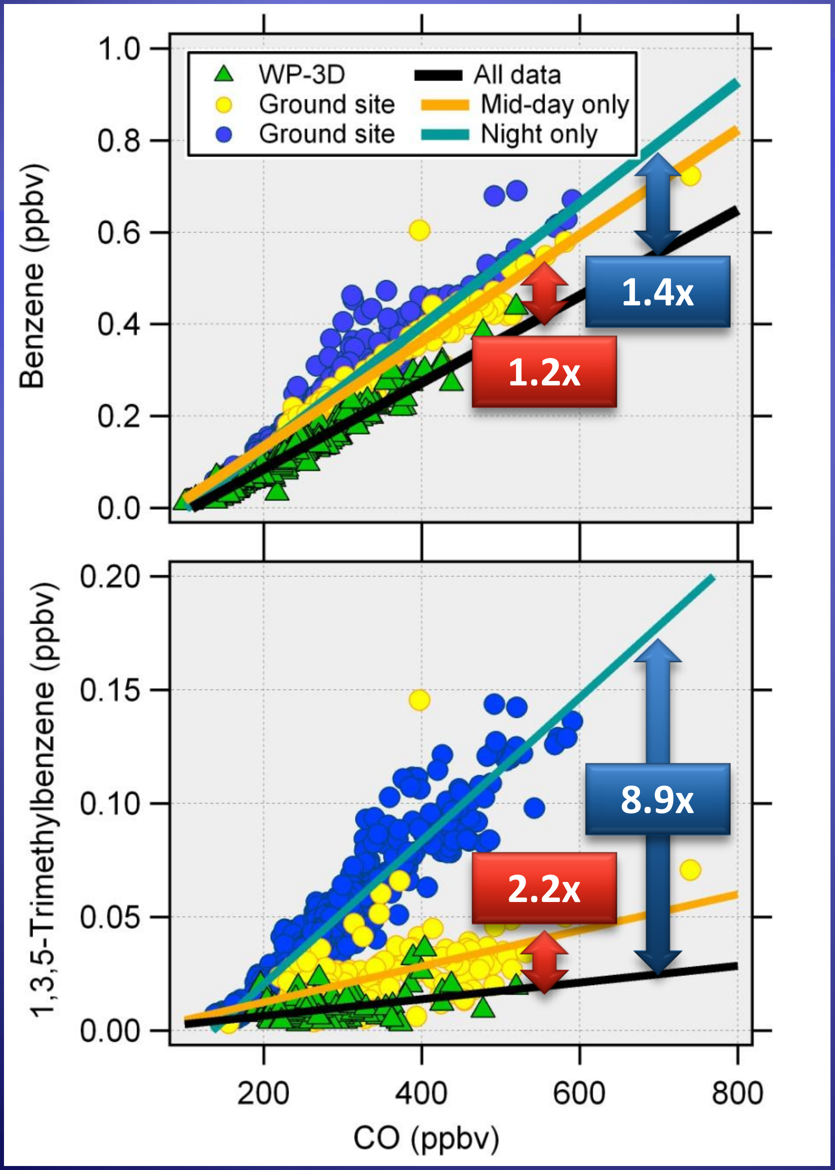


Benzene vs. CO

1,3,5-Trimethylbenzene vs. CO

See Agnes Borbon's talk for more on VOC emission ratios during CalNex

How well do the VOC to CO ratios compare?



Benzene vs. CO

- Strong correlations (r > 0.96)
- Small differences
  - Mid-day vs. Night
  - Ground site vs. WP-3D aircraft

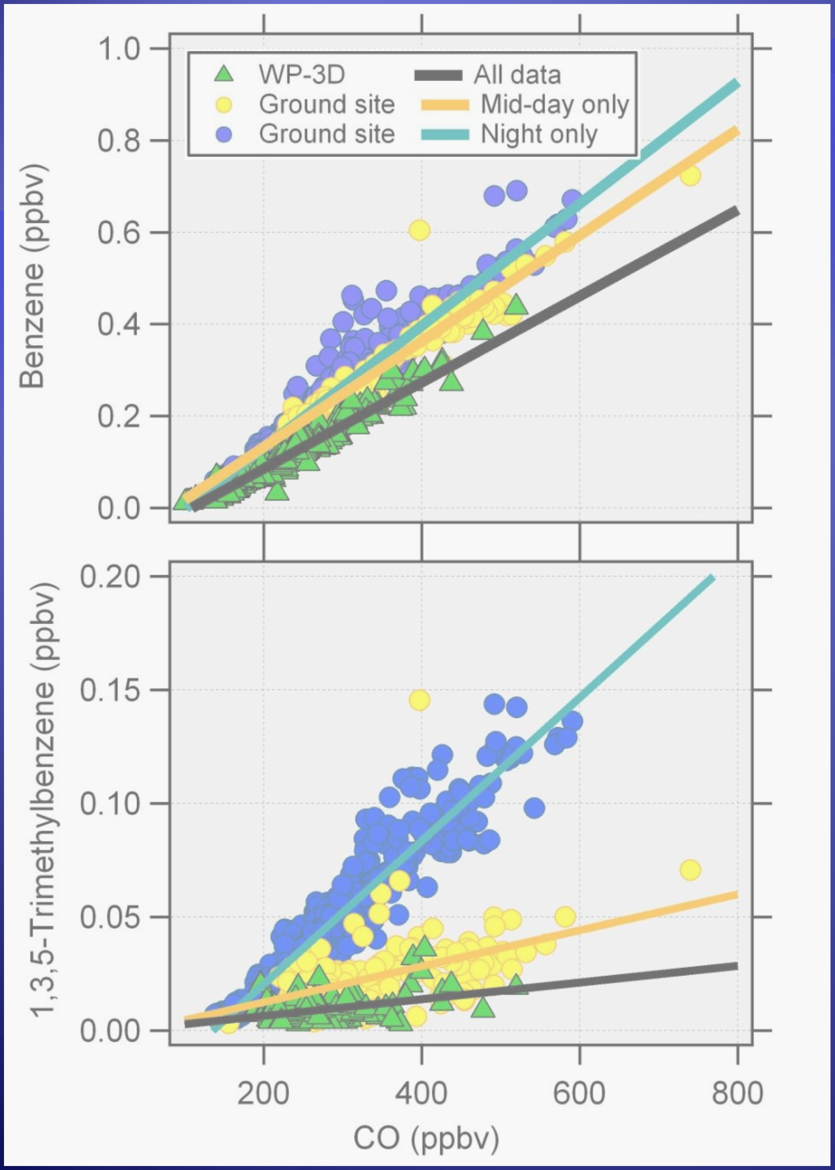
Benzene is well mixed throughout the boundary layer in the greater LA basin

1,3,5-Trimethylbenzene vs. CO

- Mid-day (1130 to 1430 PDT):
  - Weak correlations (r < 0.46)
  - Ground site 2.2x higher than WP-3
- Nighttime (2030 to 0530 PDT):
  - Strong correlations (r > 0.95)
  - Higher enhancement ratio

1,3,5-Trimethylbenzene has strong diurnal and vertical gradients

How well do the VOC to CO ratios compare?



Benzene is well mixed throughout the boundary layer in the greater LA basin

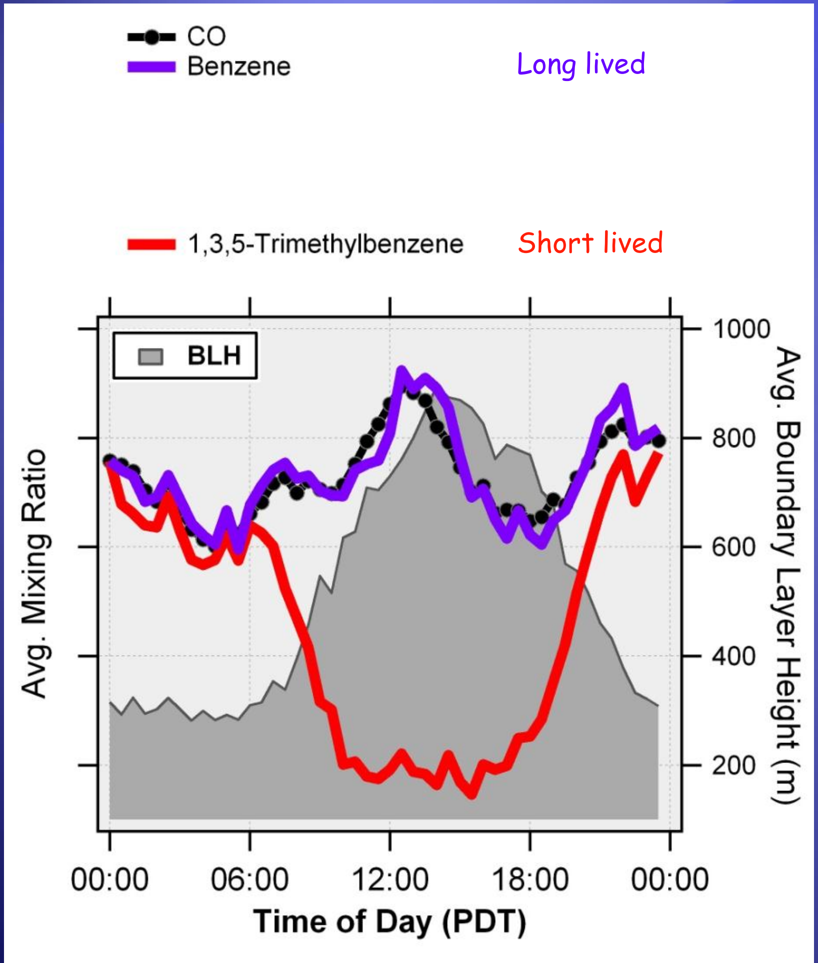
Reactivity with OH radical (kOH)

Chemical lifetime

1,3,5-Trimethylbenzene has strong diurnal and vertical gradients

Diurnal profiles: VOC sources, transport, dilution, and reaction

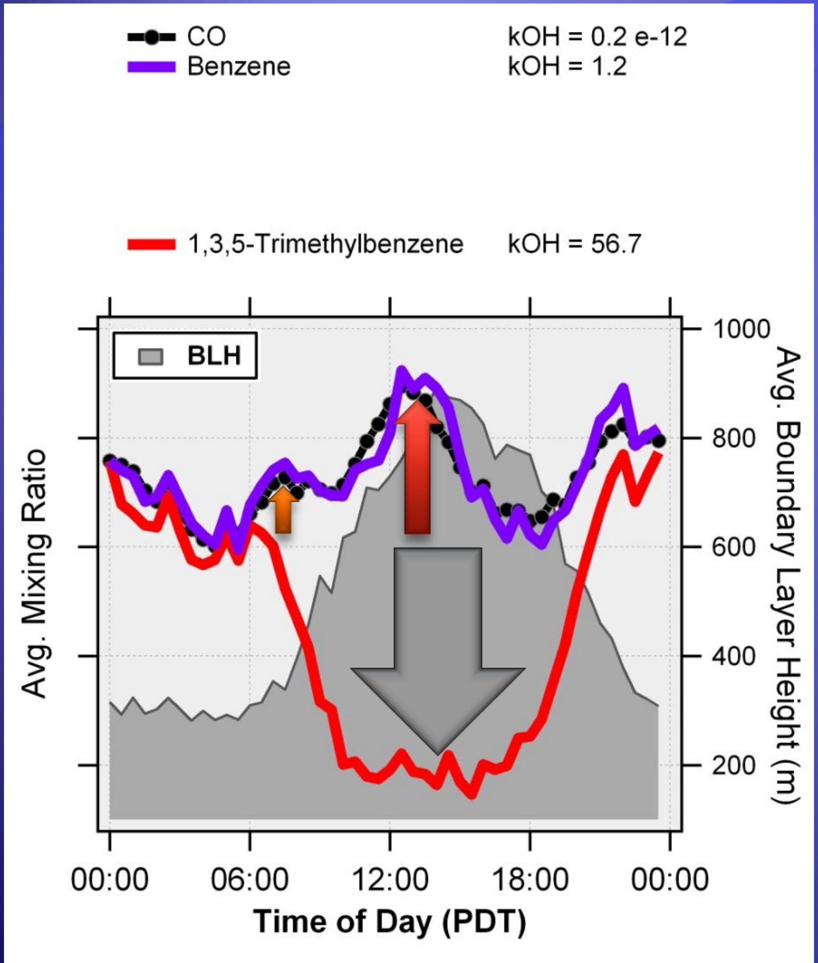
Primary anthropogenic VOCs



k_{OH+VOC} (cm^3 $molec^{-1}$ s^{-1}) at 298 K and 1013 mbar

Diurnal profiles: VOC sources, transport, dilution, and reaction

Primary anthropogenic VOCs



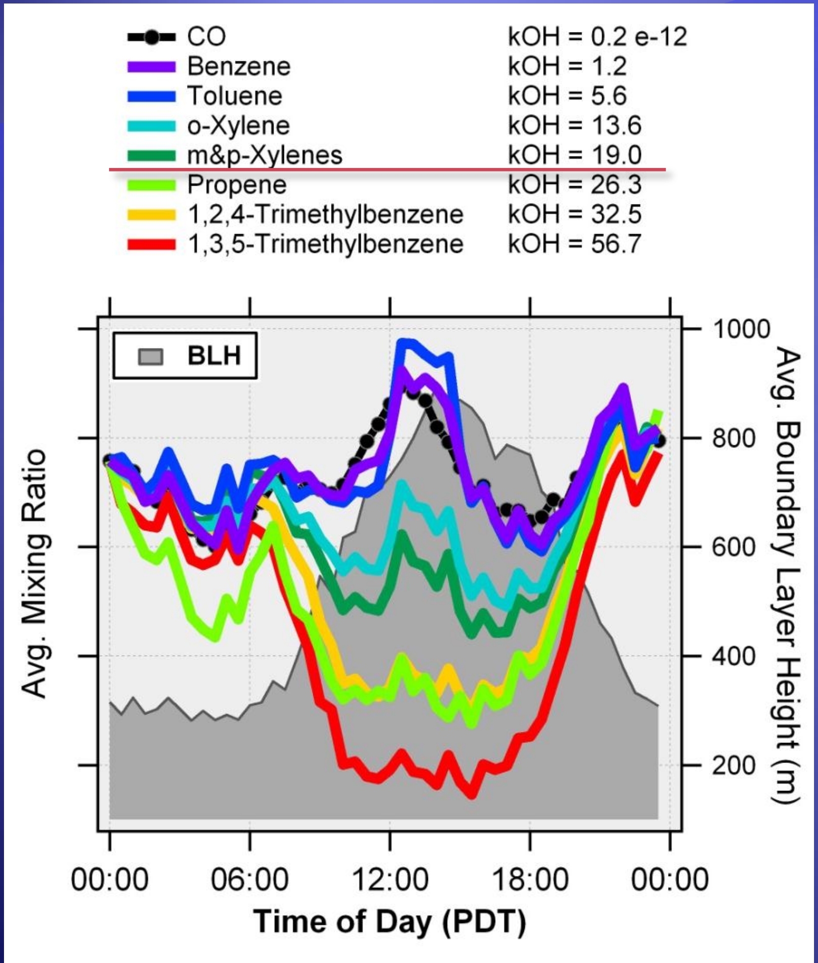
k_{OH+VOC} (cm^3 $molec^{-1}$ s^{-1}) at 298 K and 1013 mbar

Low reactivity, Longer lifetime:

- Transport of primary emissions
  - Local rush hour: 0700-0800 PDT
  - "LA plume": 1130-1300 PDT

Diurnal profiles: VOC sources, transport, dilution, and reaction

Primary anthropogenic VOCs



k_{OH+VOC} (cm^3 $molec^{-1}$ s^{-1}) at 298 K and 1013 mbar

Low reactivity, Longer lifetime:

- Transport of primary emissions
  - Local rush hour: 0700-0800 PDT
  - "LA plume": 1130-1300 PDT

Intermediate reactivity:

- Transport of primary emissions
- Dilution/mixing

Highly reactive, Shorter lifetime:

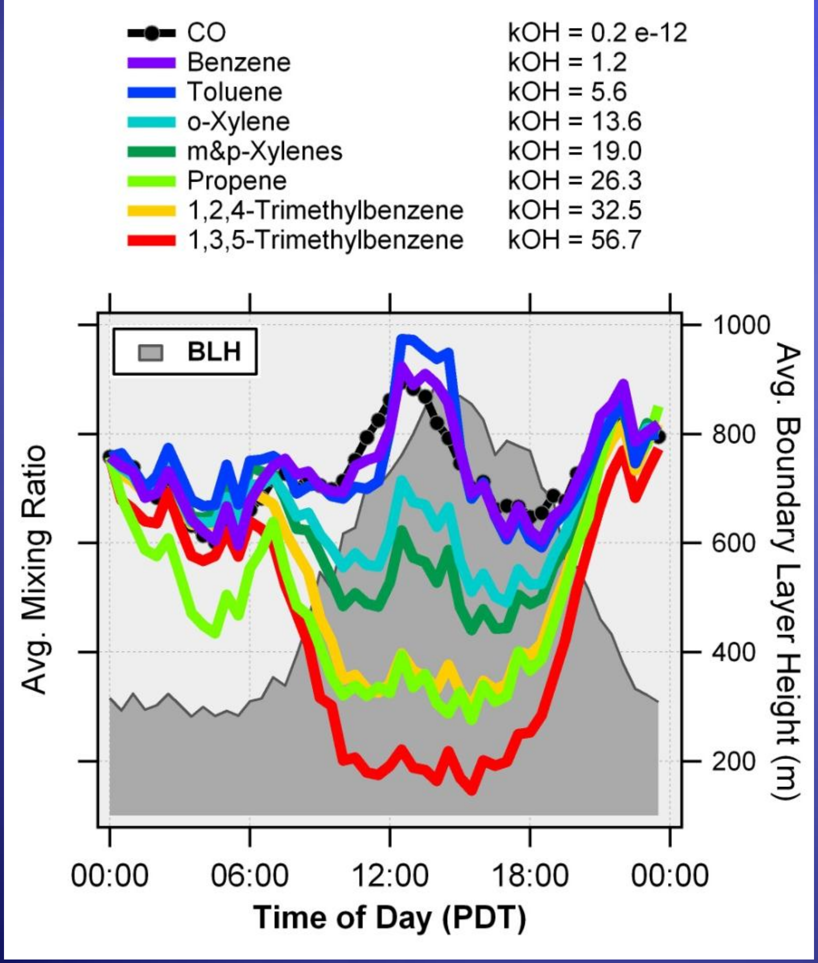
- Dilution/mixing: Air aloft is depleted
- Photochemical removal
  - Sunlight hours: 0600-2000 PDT

"LA plume" is not evident for VOCs with kOH ≥ 20 x 10^{-12} cm^3 s^{-1}

More on photochemical aging:
Carsten Warneke and Joost de Gouw

Diurnal profiles: VOC sources, transport, dilution, and reaction

Primary anthropogenic VOCs



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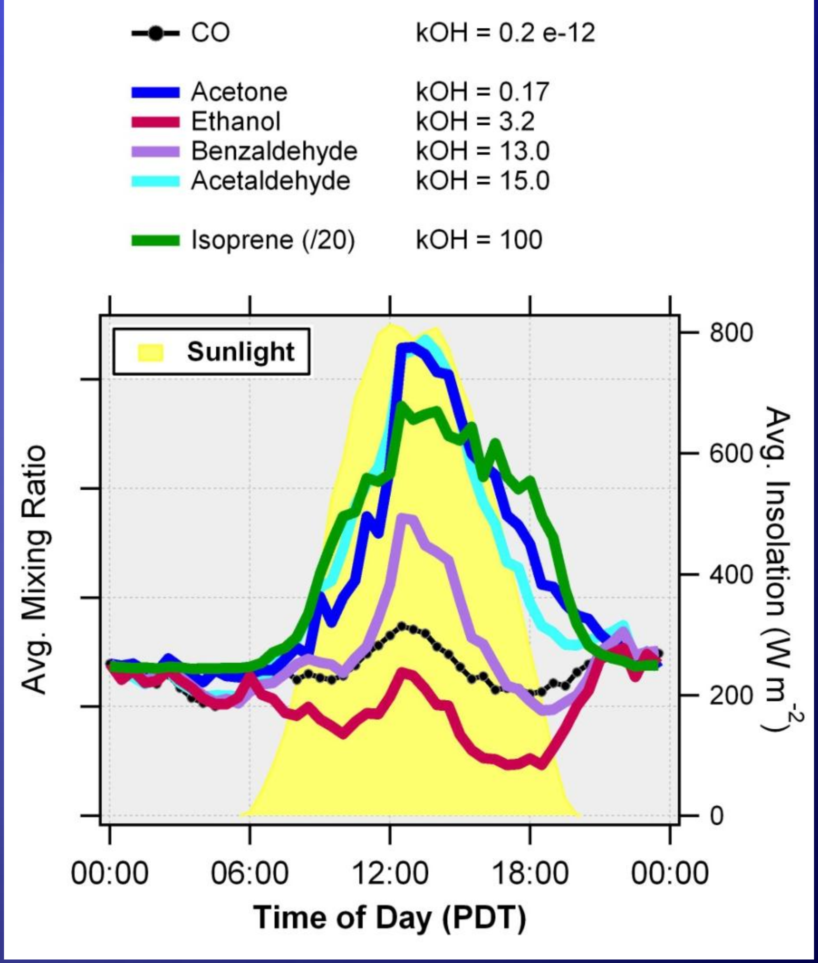
Oxygenated and Biogenic VOCs



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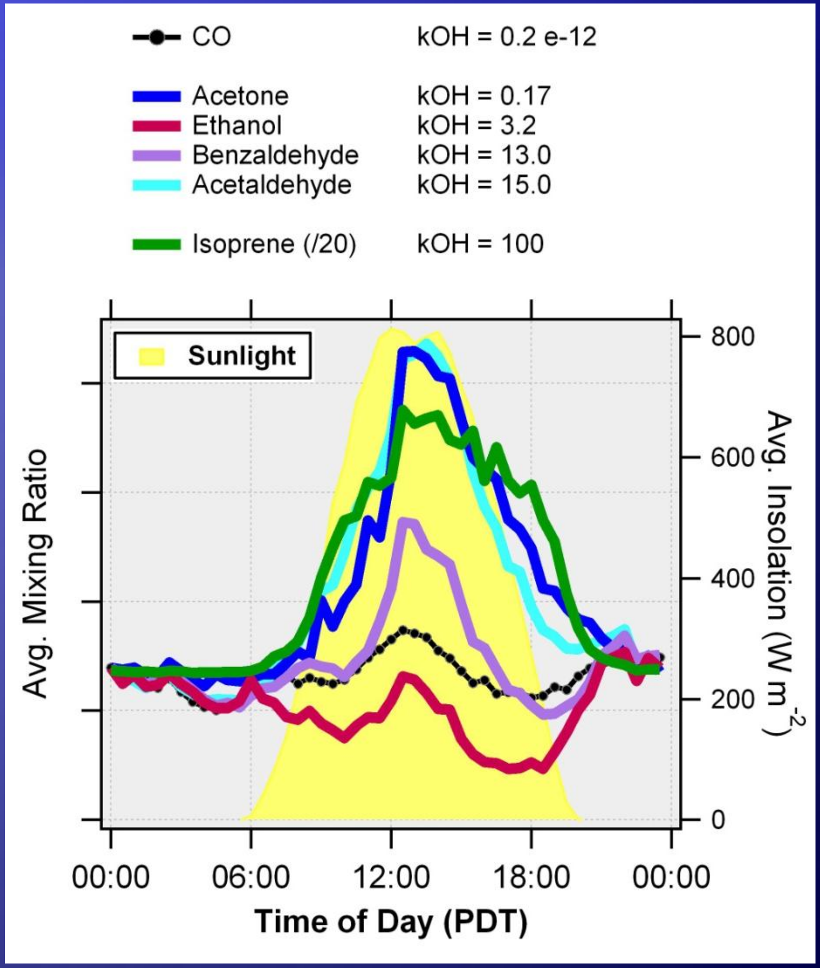
Diurnal profiles: VOC sources, transport, dilution, and reaction

Primary oxygenated VOCs:

- Transport of primary emissions
  - Mid-day peak assoc. w/ "LA plume"
- Alcohols and benzaldehyde
  - Avg. Ethanol = 9 ppb
  - Avg. Benzaldehyde = 0.20 ppb

Oxygenated and Biogenic VOCs



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Diurnal profiles: VOC sources, transport, dilution, and reaction

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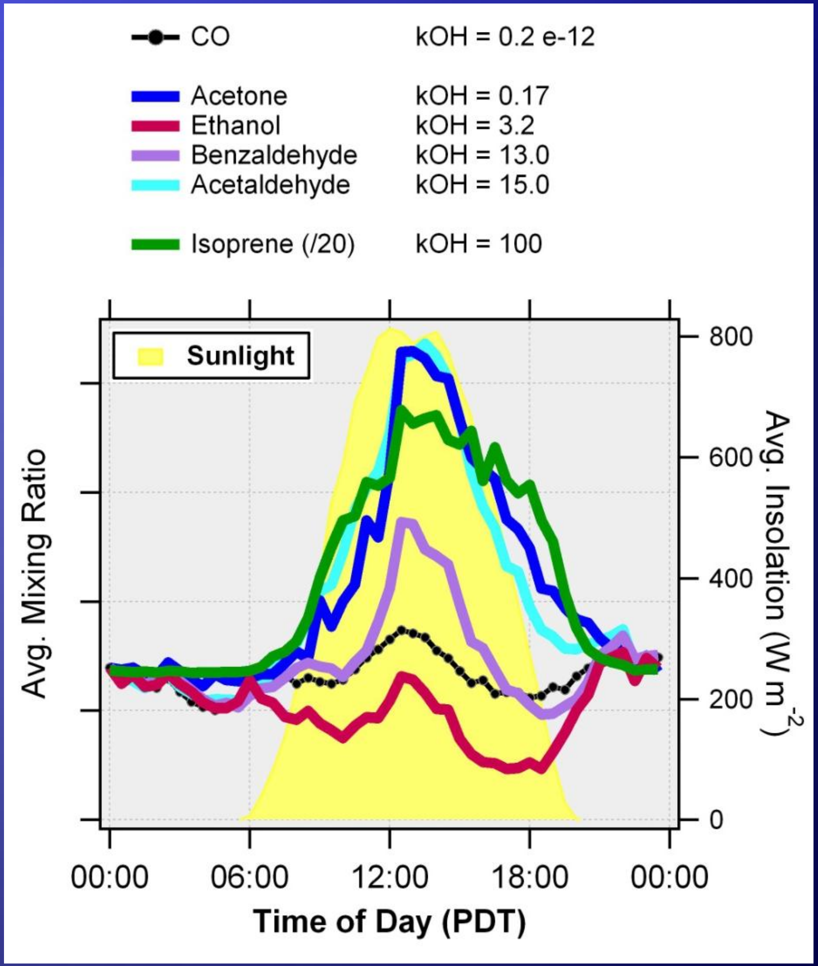

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Secondary oxygenated VOCs:

- Photochemical production
  - Mid-day peak w/ solar noon
- Aldehydes and ketones

Diurnal profiles: VOC sources, transport, dilution, and reaction

Primary oxygenated VOCs:

- Transport of primary emissions
  - Mid-day peak assoc. w/ "LA plume"
- Alcohols and benzaldehyde
  - Avg. Ethanol = 9 ppb
  - Avg. Benzaldehyde = 0.20 ppb

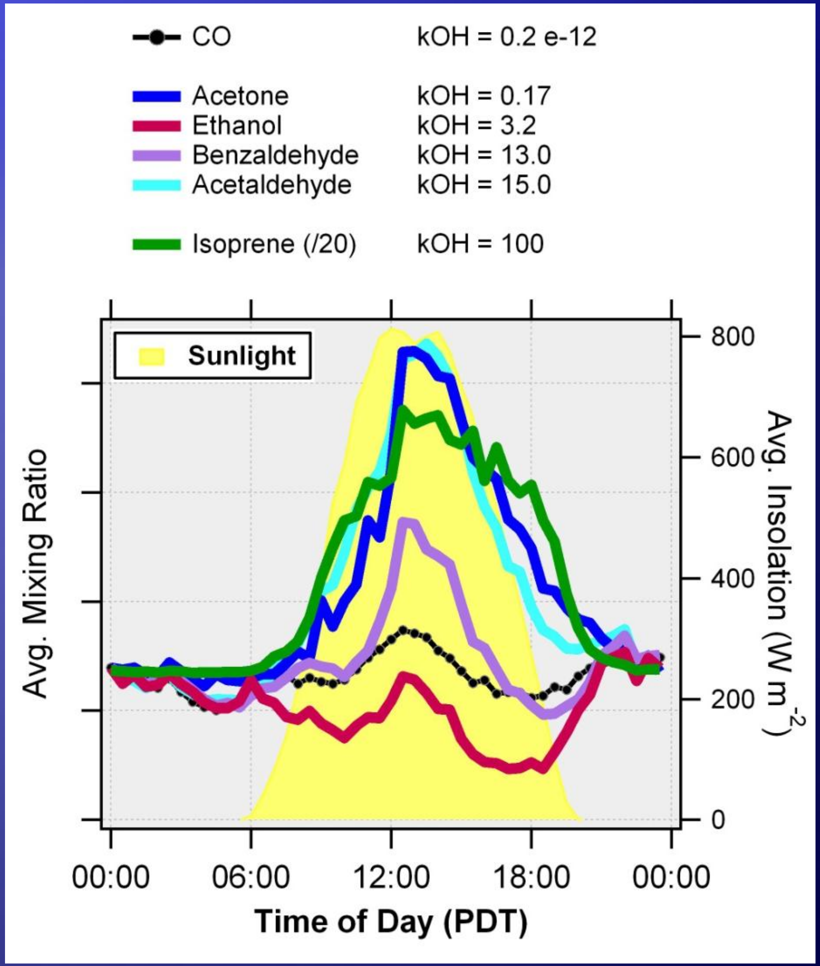
Secondary oxygenated VOCs:

- Photochemical production
  - Mid-day peak w/ solar noon
- Aldehydes and ketones

Biogenic VOCs:

- Light-dependent emissions
  - Mid-day peak w/ solar noon
- Primary: Isoprene
- Secondary: MVK and MACR

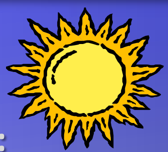
Oxygenated and Biogenic VOCs



k_{OH+VOC} (cm^3 $molec^{-1}$ s^{-1}) at 298 K and 1013 mbar

Characterizing the chemical evolution of VOCs

Primary sources of VOCs

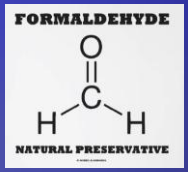


Anthropogenic:
Cars/Trucks/Industry

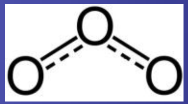
Biogenic:
Trees & Plants

+ NOx

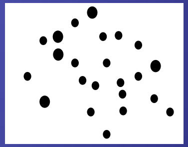
Secondary Products



Secondary OVOCs



Tropospheric Ozone (O_3)



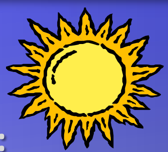
Secondary Organic Aerosol

Characterizing the chemical evolution of VOCs

Primary sources of VOCs

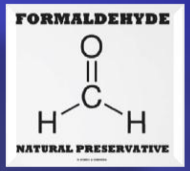
Anthropogenic:
Cars/Trucks/Industry

Biogenic:
Trees & Plants



+ NOx

Secondary Products



Secondary OVOCs

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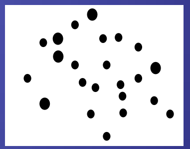


Secondary Organic Aerosol

[VOC abundance] x [Metric of interest] =

1. Carbon mass (µg C m^{-3}) Gas-phase carbon "budget"

Characterizing the chemical evolution of VOCs

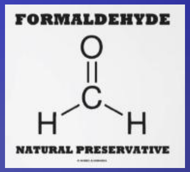
Primary sources of VOCs

Anthropogenic:
Cars/Trucks/Industry

Biogenic:
Trees & Plants

+ NOx

Secondary Products



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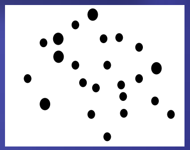


Secondary Organic Aerosol

[VOC abundance] x [Metric of interest] =

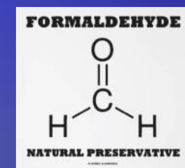
1. Carbon mass (μg C m^{-3}) Gas-phase carbon "budget"
2. OH reactivity (s^{-1}) Contrib. to potential O_3 production

Characterizing the chemical evolution of VOCs

Primary sources of VOCs

+ NOx

Secondary Products



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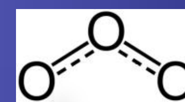

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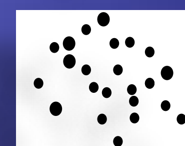


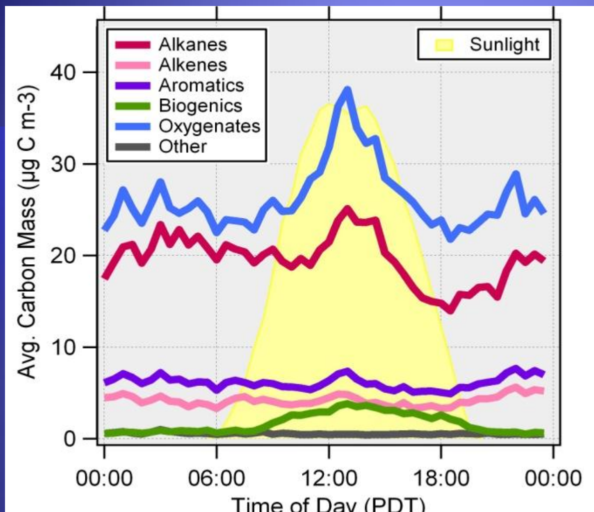
Secondary Organic Aerosol

[VOC abundance] x [Metric of interest] =

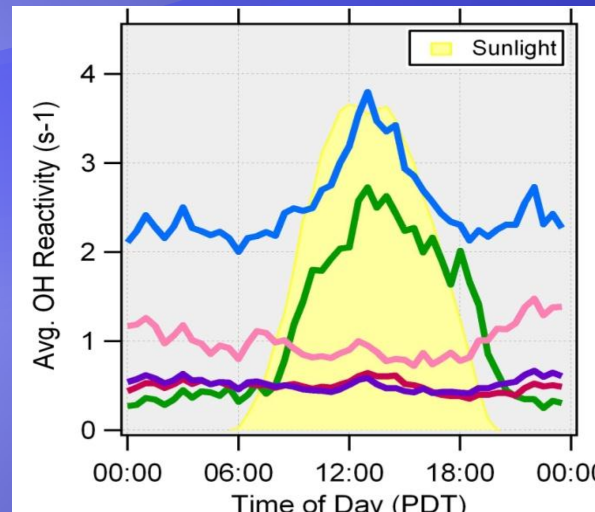
1. Carbon mass (μg C m^{-3}) — Gas-phase carbon “budget”
2. OH reactivity (s^{-1}) — Contrib. to potential O_3 production
3. SOA potential — Contrib. to potential SOA formation
   - Modeled SOA potential relative to Toluene (Derwent et al., 2010)

Characterizing the chemical evolution of VOCs

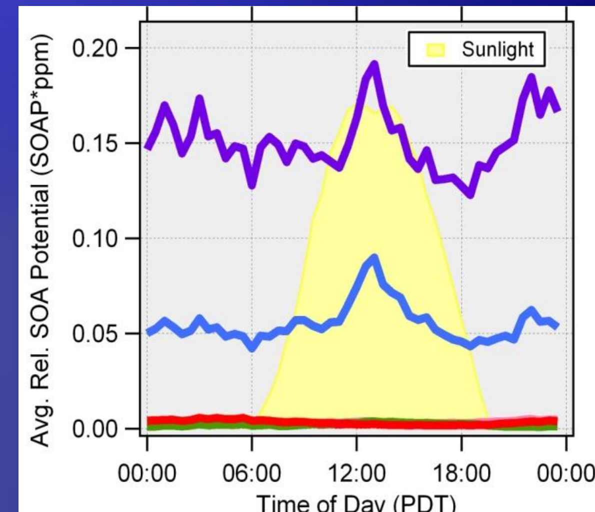
Carbon Mass (µg C m^{-3})



OH Reactivity (s^{-1})



Relative SOA potential



Oxygenates:
- Secondary: Acetone + MEK
- Primary: Ethanol

Oxygenates:
- Secondary: HCHO + Acetal
- Primary: Ethanol

Aromatics
- Primary: Toluene + Benzene
- Mid-day max = "LA plume"

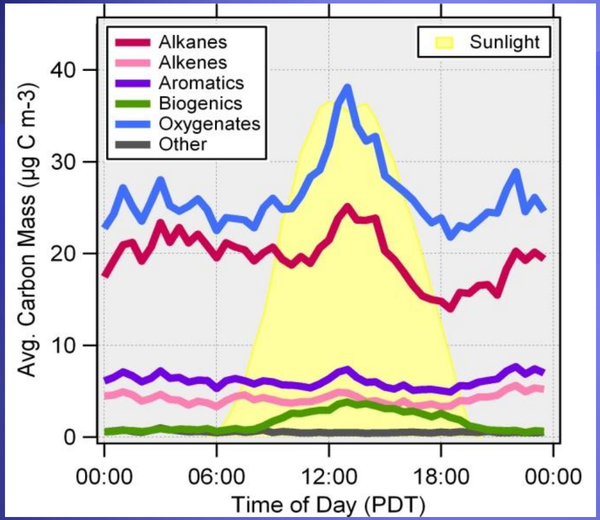
Alkanes:
- Primary: Ethane + Propane
- Mid-day max = "LA plume"

Biogenics:
- Primary: Isoprene
- Secondary: MVK + MACR

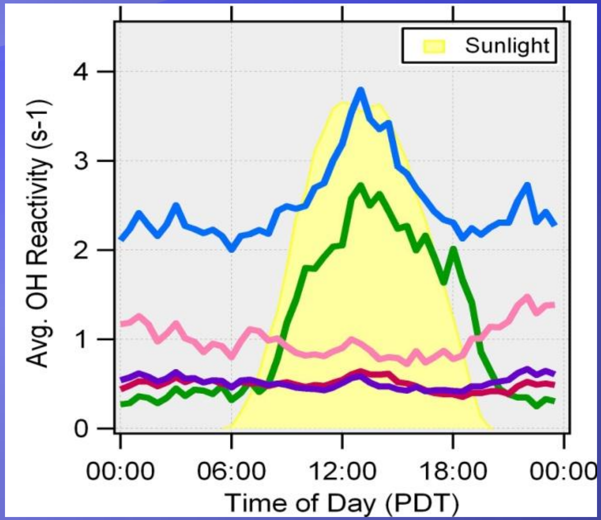
Oxygenates:
- Primary: Benzaldehyde
- Toluene oxidation product

Characterizing the chemical evolution of VOCs

Carbon Mass (µg C m^{-3})



OH Reactivity (s^{-1})



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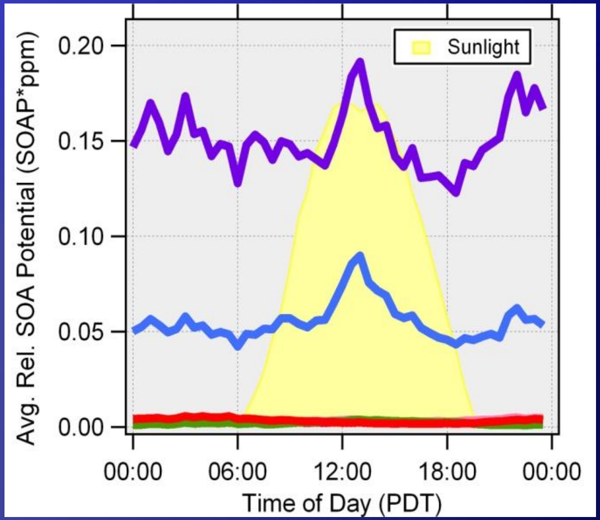


Oxygenates:
- Secondary: Acetone + MEK
- Primary: Ethanol

Alkanes:
- Primary: Ethane + Propane
- Mid-day max = "LA plume"

Include carbon mass from organic aerosols

Oxygenates:
- Secondary: HCHO + Acetal
- Primary: Ethanol

Biogenics:
- Primary: Isoprene
- Secondary: MVK + MACR

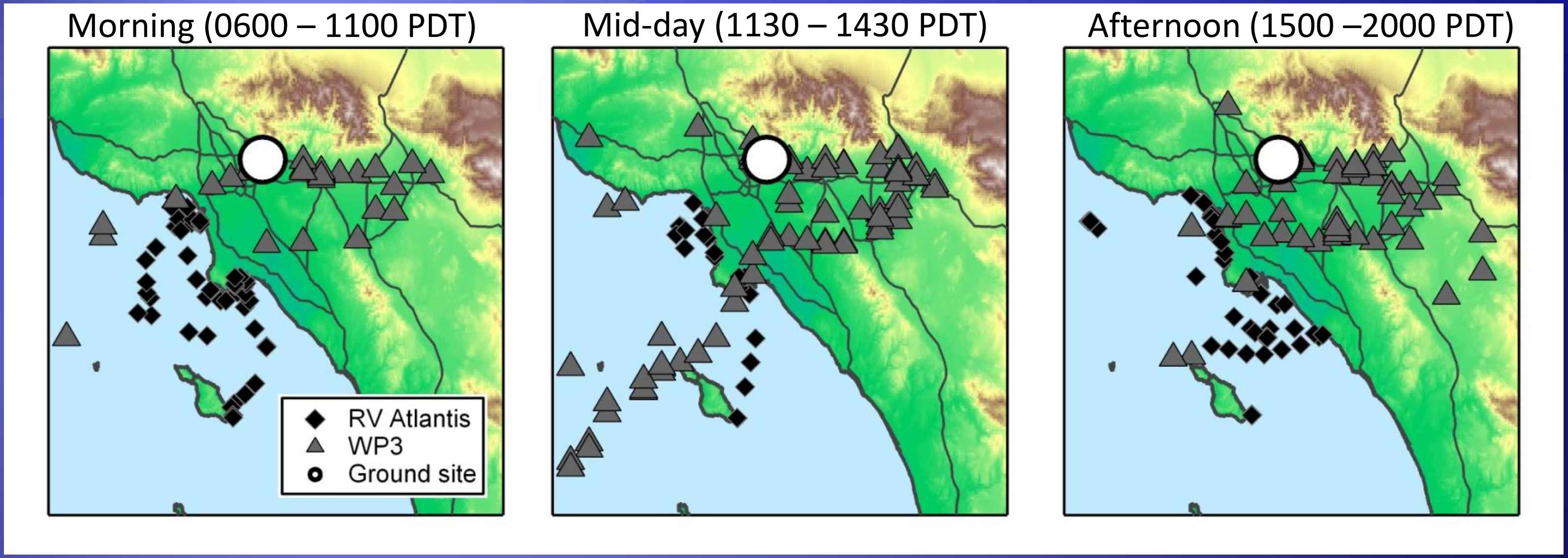
Compare to measured OH reactivity at ground site

Aromatics
- Primary: Toluene + Benzene
- Mid-day max = "LA plume"

Oxygenates:
- Primary: Benzaldehyde
- Toluene oxidation product

Compare to measured potential aerosol mass (PAM)

Characterizing the chemical evolution of VOCs
in the greater Los Angeles basin



Characterizing the chemical evolution of VOCs
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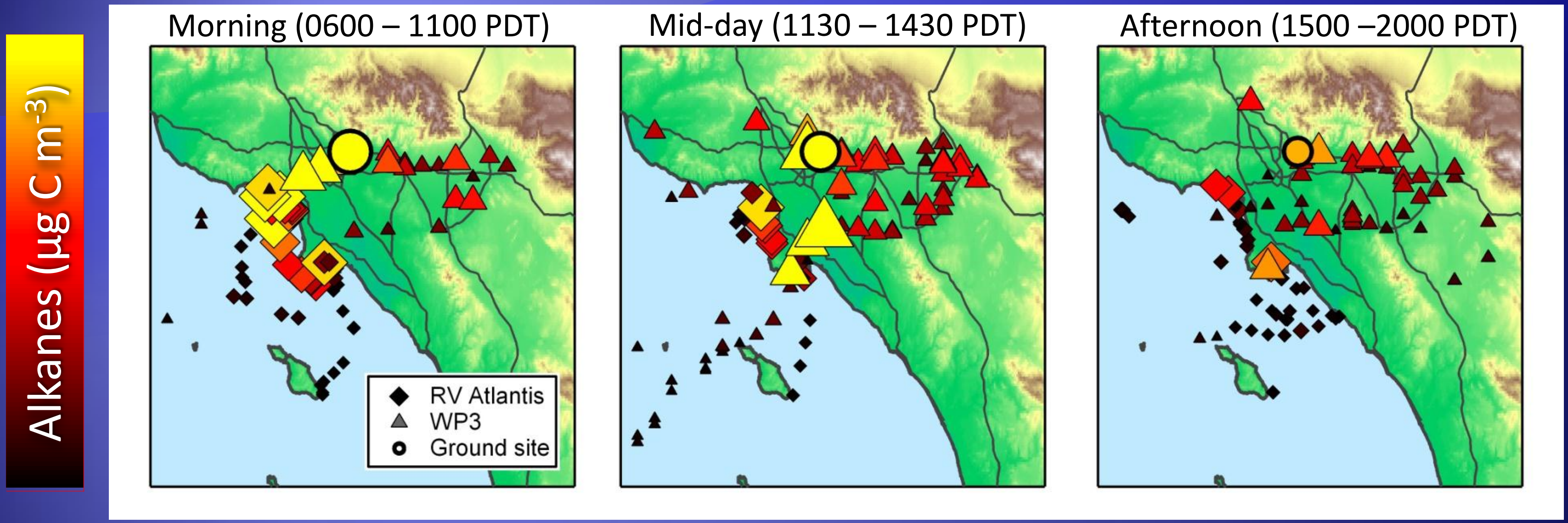

Characterizing the chemical evolution of VOCs
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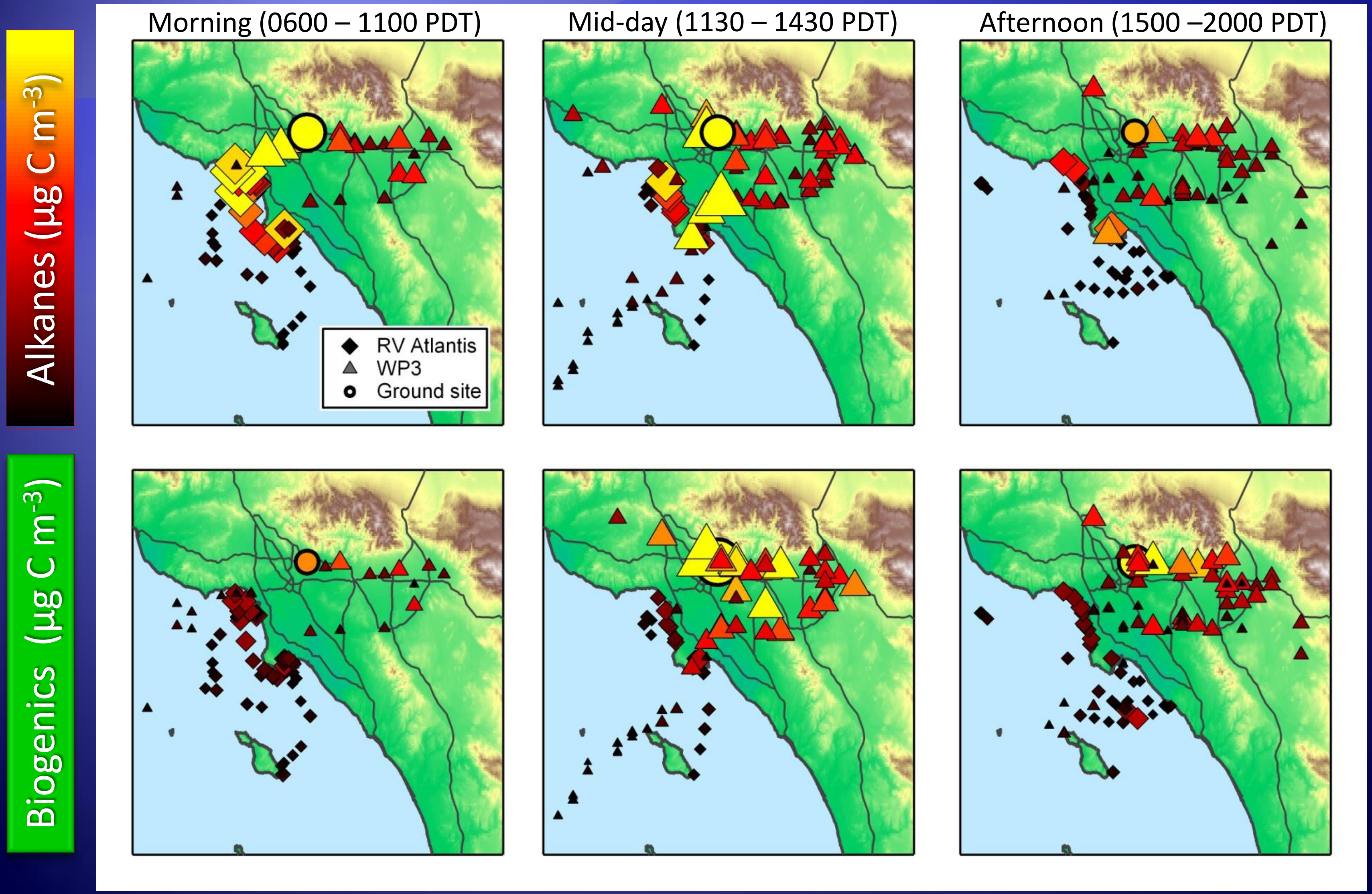

Summary:

1. VOC measurements for platforms compare well
   - Similar VOC sources throughout greater Los Angeles basin
2. Diurnal profiles of VOCs at Pasadena ground site
   - **Mid-day peak:** Primary anthropogenic emissions in "LA plume"
     Primary biogenic emissions (e.g., isoprene)
     Secondary production (e.g., acetaldehyde and acetone)
   - **Afternoon minimum:** Reaction and dilution of highly reactive VOCs
3. Characterizing the chemical evolution of VOCs
   - Oxygenated VOCs are a large fraction of carbon mass, OH reactivity, and potential SOA production (benzaldehyde)
   - Combine platforms to follow chemical evolution in the greater LA basin

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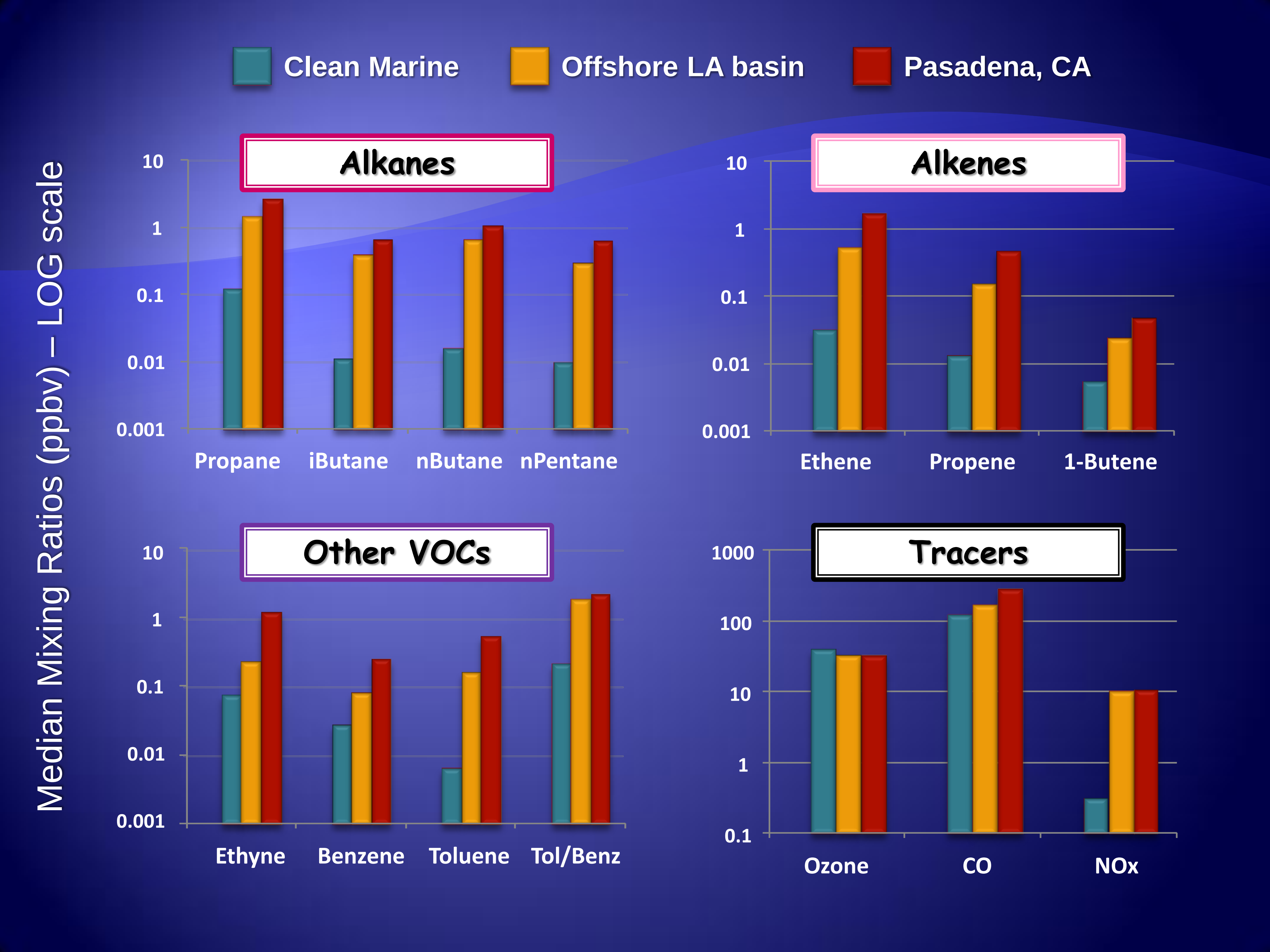
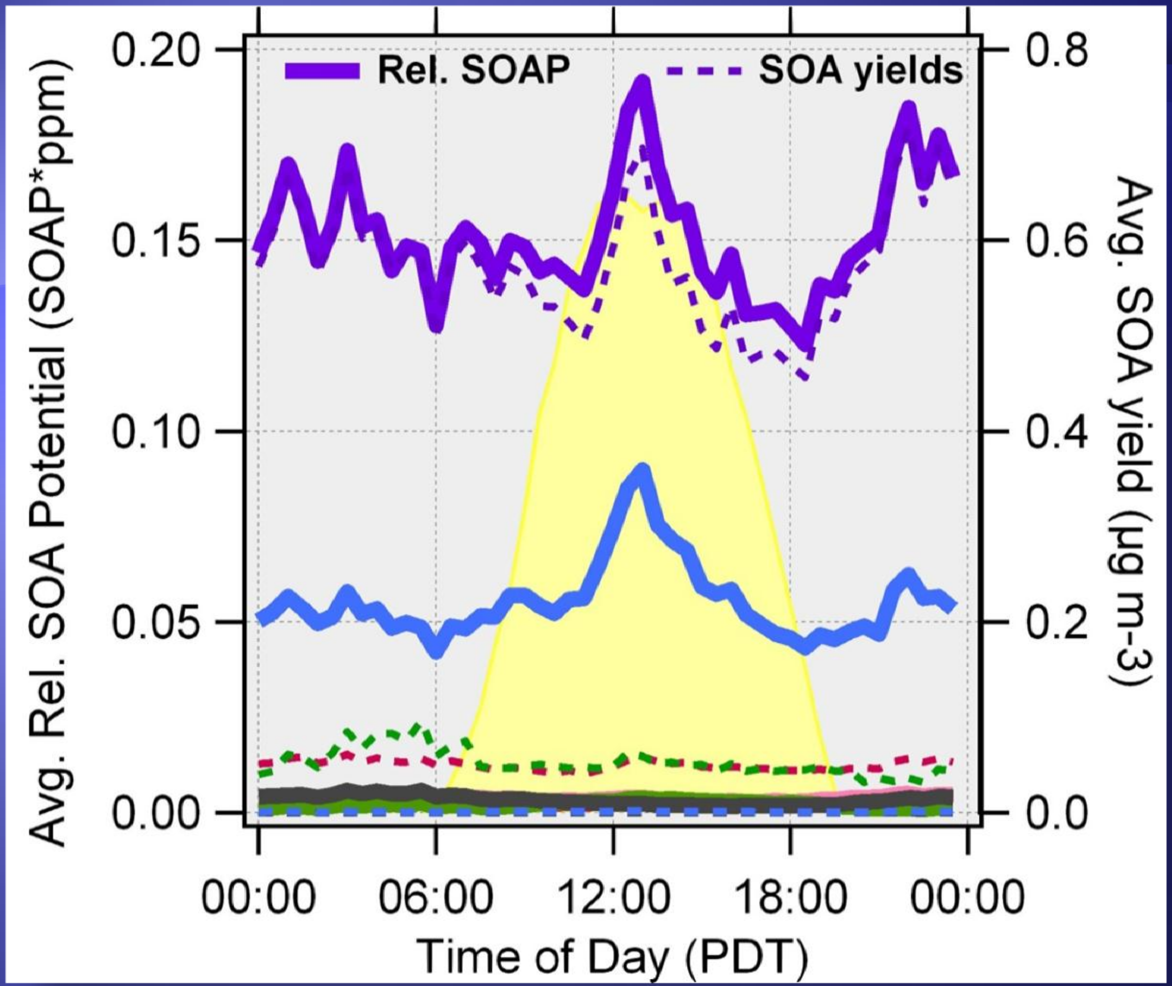
Sunset on LA Harbor from RV Atlantis
Photo by D. Bon

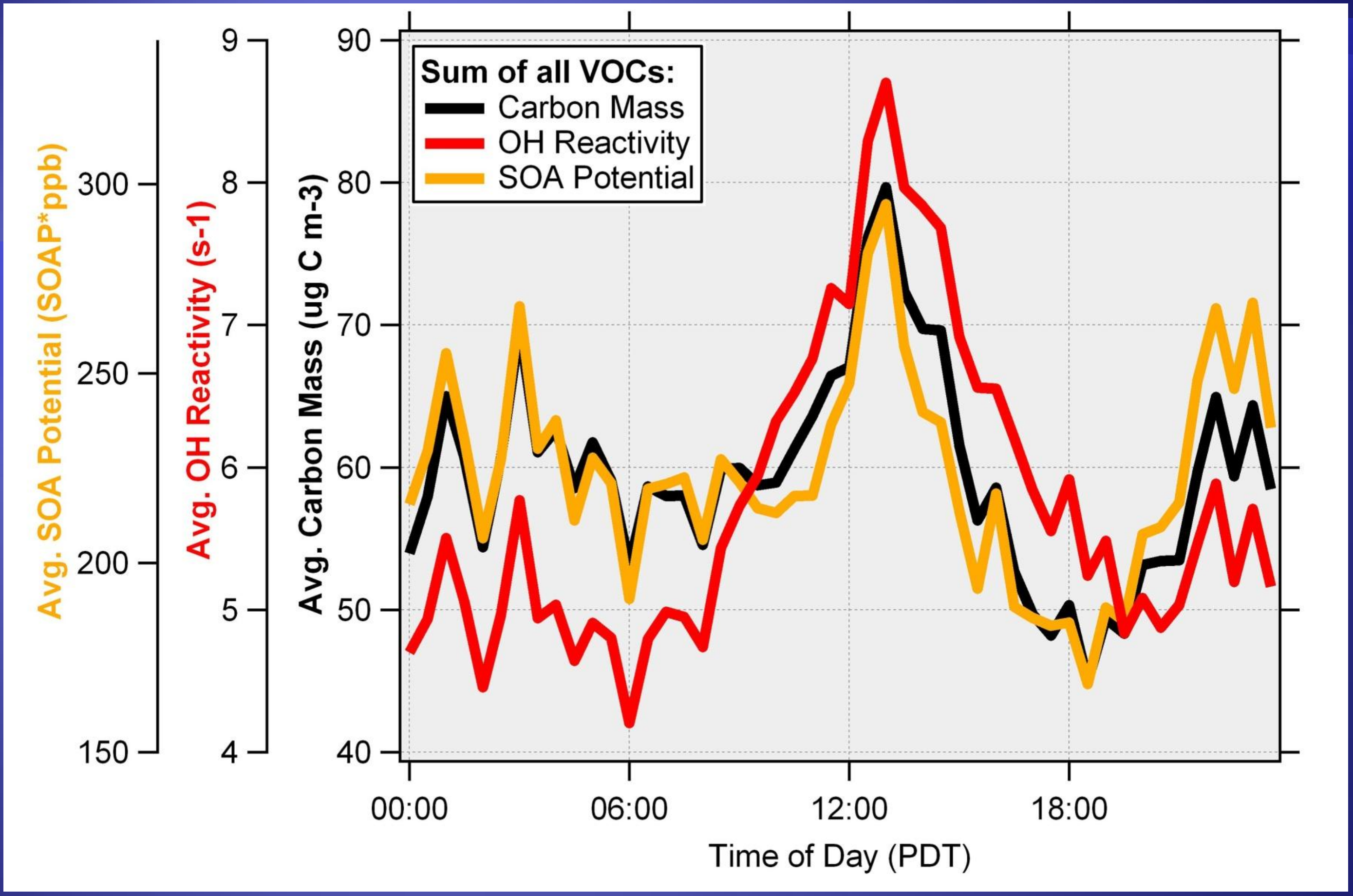
End



Clean Marine
Offshore LA basin
Pasadena, CA
Median Mixing Ratios (ppbv) – LOG scale
Alkanes
10
1
0.1
0.01
0.001
Propane
iButane
nButane
nPentane
Alkenes
10
1
0.1
0.01
0.001
Ethene
Propene
1-Butene
Other VOCs
10
1
0.1
0.01
0.001
Ethyne
Benzene
Toluene
Tol/Benz
Tracers
1000
100
10
1
0.1
Ozone
CO
NOx



Rel. SOAP
SOA yields
Avg. Rel. SOA Potential (SOAP*ppm)
Avg. SOA yield (µg m-3)
0.20
0.15
0.10
0.05
0.00
0.8
0.6
0.4
0.2
0.0
00:00
06:00
12:00
18:00
00:00
Time of Day (PDT)


Sum of all VOCs:
Carbon Mass
OH Reactivity
SOA Potential
Avg. SOA Potential (SOAP*ppb)
Avg. OH Reactivity (s-1)
Avg. Carbon Mass (ug C m-3)
Time of Day (PDT)
00:00
06:00
12:00
18:00
150
200
250
300
4
5
6
7
8
9
40
50
60
70
80
90

Classification of air masses via gas-phase markers

Clean Marine:

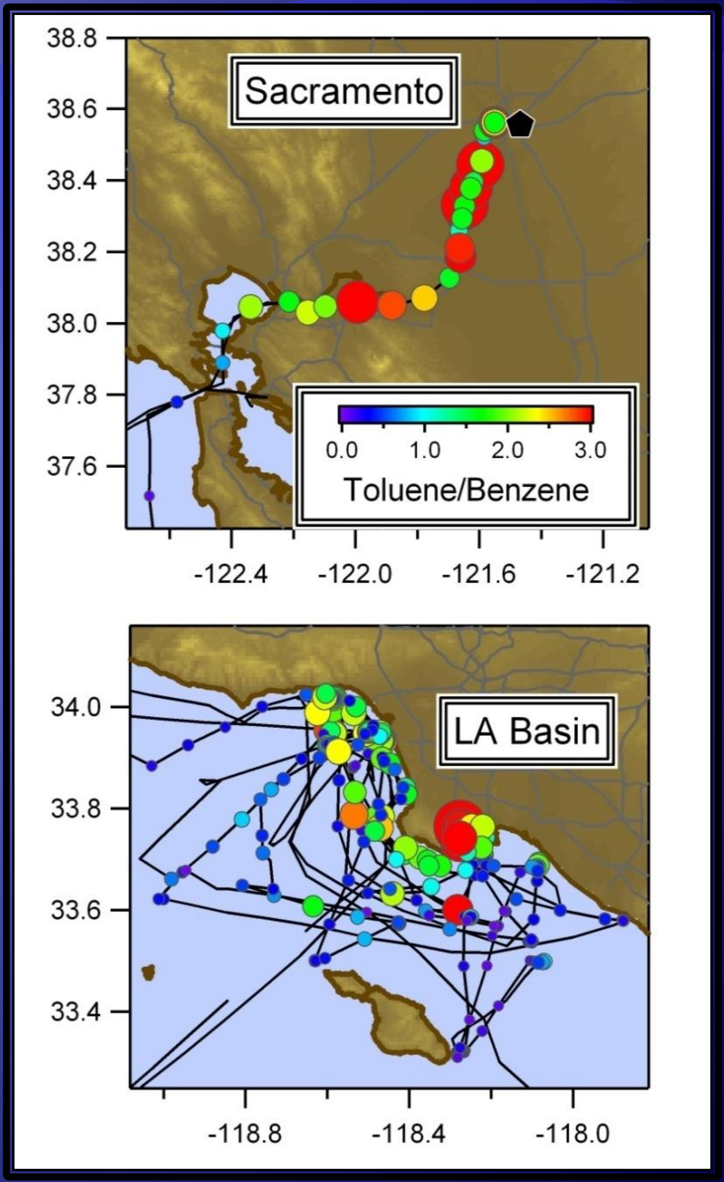
- Low CO, NO_x, Radon
- Low VOCs
- Small Toluene/Benzene ratio
    - Typically < 1.0

Urban Outflow:

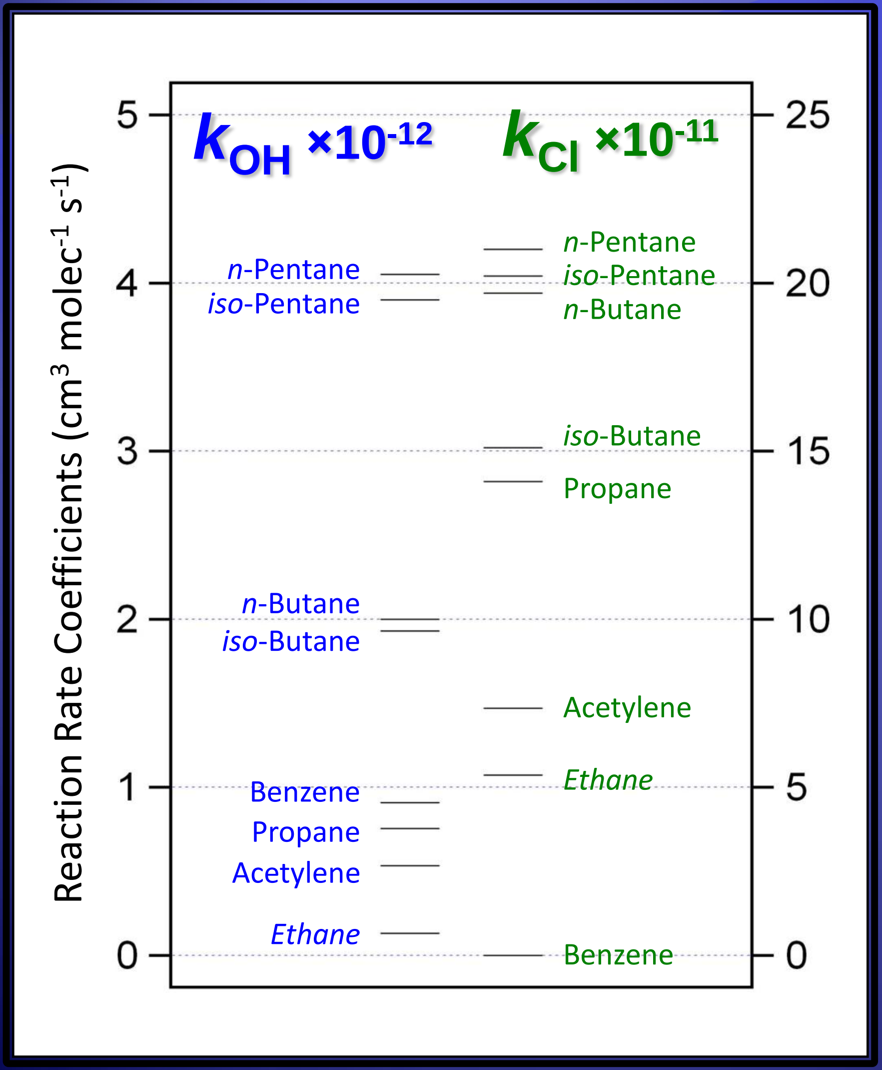
- Increased CO, NO_x, Radon
- O_3 anti-correlates with CO, NO_x
- Increased VOCs, correlate with CO
- Larger Toluene/Benzene ratios
    - Usually > 2.0

Atlantis Exhaust/Ship Air:

- Relative WD
- Large CO and NO
- Spike in Toluene, low VOCs
- Ship hits have been removed



What can VOCs tell us about oxidation chemistry?



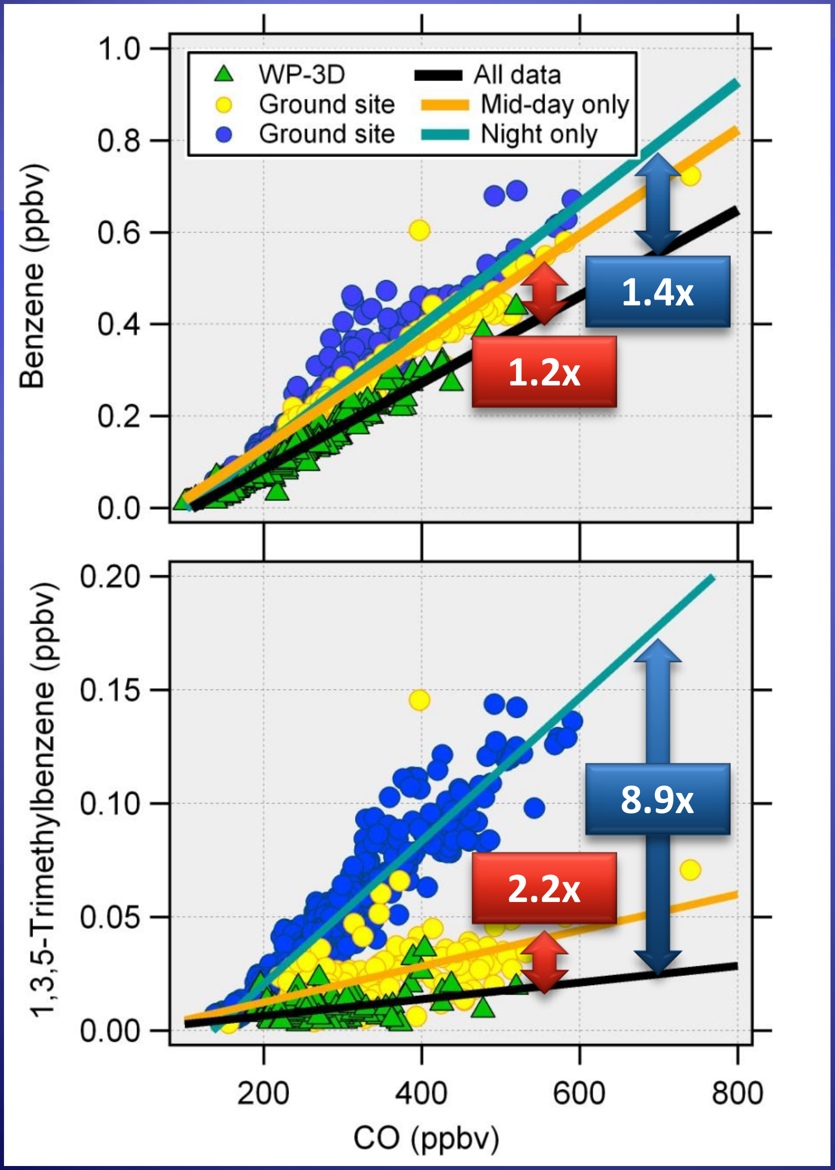
- Oxidation of VOCs can lead to the production of O_3
- VOCs react with OH and Cl

$$-\,d[VOC]/dt = k_{OH}[OH]+k_{Cl}[Cl]$$

  - $k_{OH} < k_{Cl}$
  - [OH] >> [Cl]
- Changes in VOC ratios can be used to decipher oxidation chemistry
  - Ratios are less sensitive to mixing and dilution than absolute mixing ratios

Parrish, et al. (1992), Helmig, et. al (2008)

How well do the VOC to CO ratios compare?



Benzene vs. CO

- Strong correlations (r > 0.96)
- Small differences
  - Mid-day vs. Night
  - Ground site vs. WP-3D aircraft

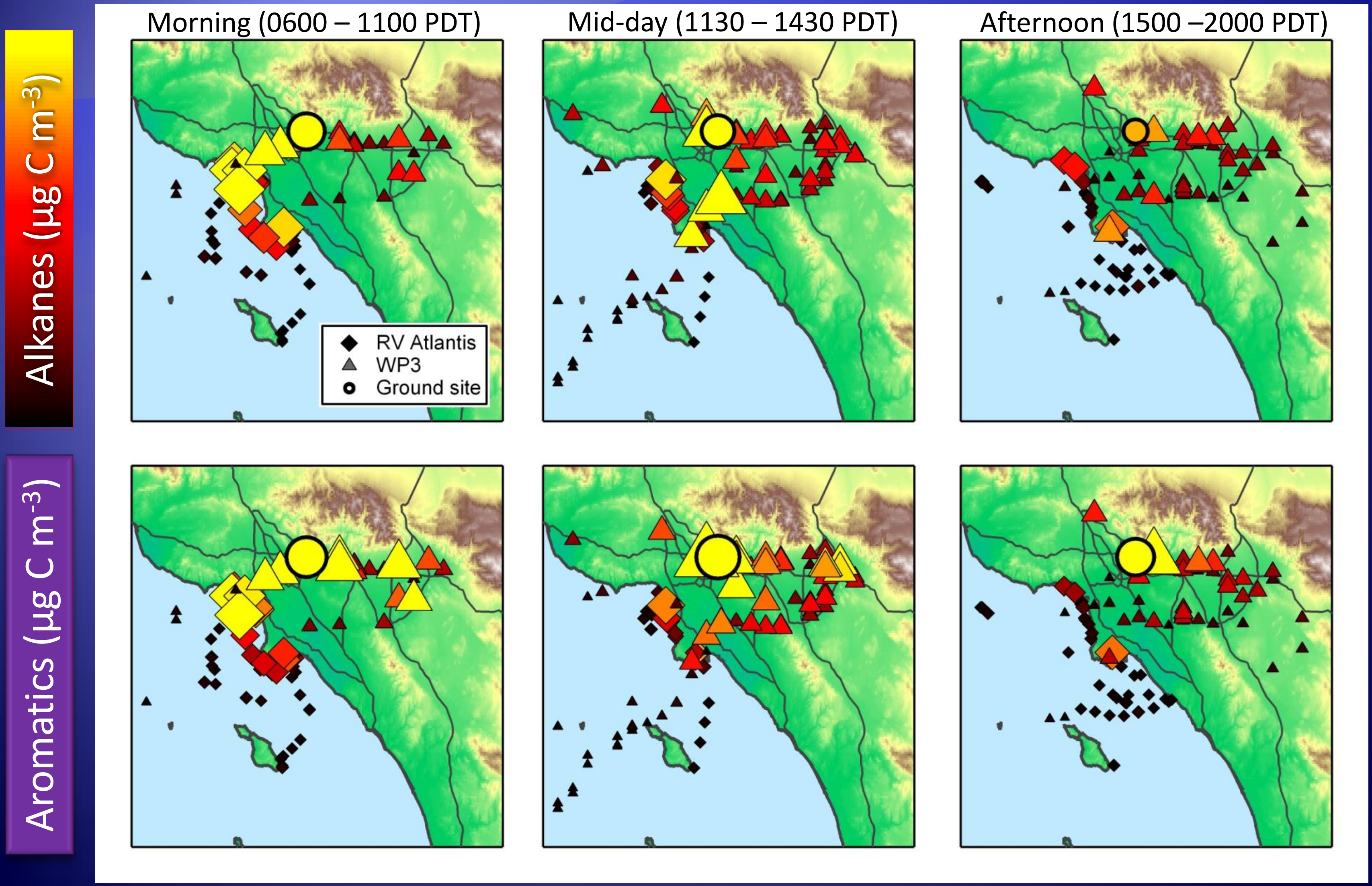
Benzene is well mixed throughout the boundary layer in the greater LA basin

1,3,5-Trimethylbenzene vs. CO

- Mid-day (1130 to 1430 PDT):
  - Weak correlations (r < 0.46)
  - Ground site 2.2x higher than WP-3
- Nighttime (2030 to 0530 PDT):
  - Strong correlations (r > 0.95)
  - Higher enhancement ratio

1,3,5-Trimethylbenzene has strong diurnal and vertical gradients

Characterizing the chemical evolution of VOCs
in the greater Los Angeles basin



Diurnal profiles: VOC sources, transport, dilution, reaction

Primary anthropogenic VOCs