2011 Air Chemistry Study at the Boulder Atmospheric Observatory

"Nitrogen, Aerosol Composition and Halogens on a Tall Tower" (NACHTT)

February 16 – March 13, 2011

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Photos: Rolf Sander

Scientific Goals – January 7, 2011

1. Understand winter halogen activation
2. Obtain an improved inventory for chloride
3. Improved understanding of inorganic aerosol thermodynamics and relationships to heterogeneous processes listed above
4. Characterize wintertime heterogeneous uptake efficiency of N_2O_5
5. Wintertime radical reservoirs and budgets

Post-Study Additions

6. Aerosol composition and sources within the Denver "Brown Cloud"
7. Emissions from the oil and gas industry

Instruments & Participants - BAO Tower

Species	Instrument	Investigators
NO, NO_2, NO_3, N_2O_5, O_3	CRDS	Wagner, Young, Dubé, Brown
$ClNO_2$, Cl_2, N_2O_5	CIMS (I^-)	Riedel, Thornton (UW)
HCl, HNO_3, HONO, etc.	CIMS (acetate)	Vandenboer, Roberts
Aerosol Composition	AMS	Ozturk, Bahreini, Middlebrook
Aerosol Size Distribution	UHSAS	Brock
Speciated VOCs	Canister samples	Sive (UNH / Appalachian State)
Height Data on Carriage	Counter, GPC	Dubé
Met Data on Carriage	Sonics, RH probe, etc.	Wolfe, Williams, Wagner
Tower server, ground communication & Control		Jameson, Wagner, Dubé

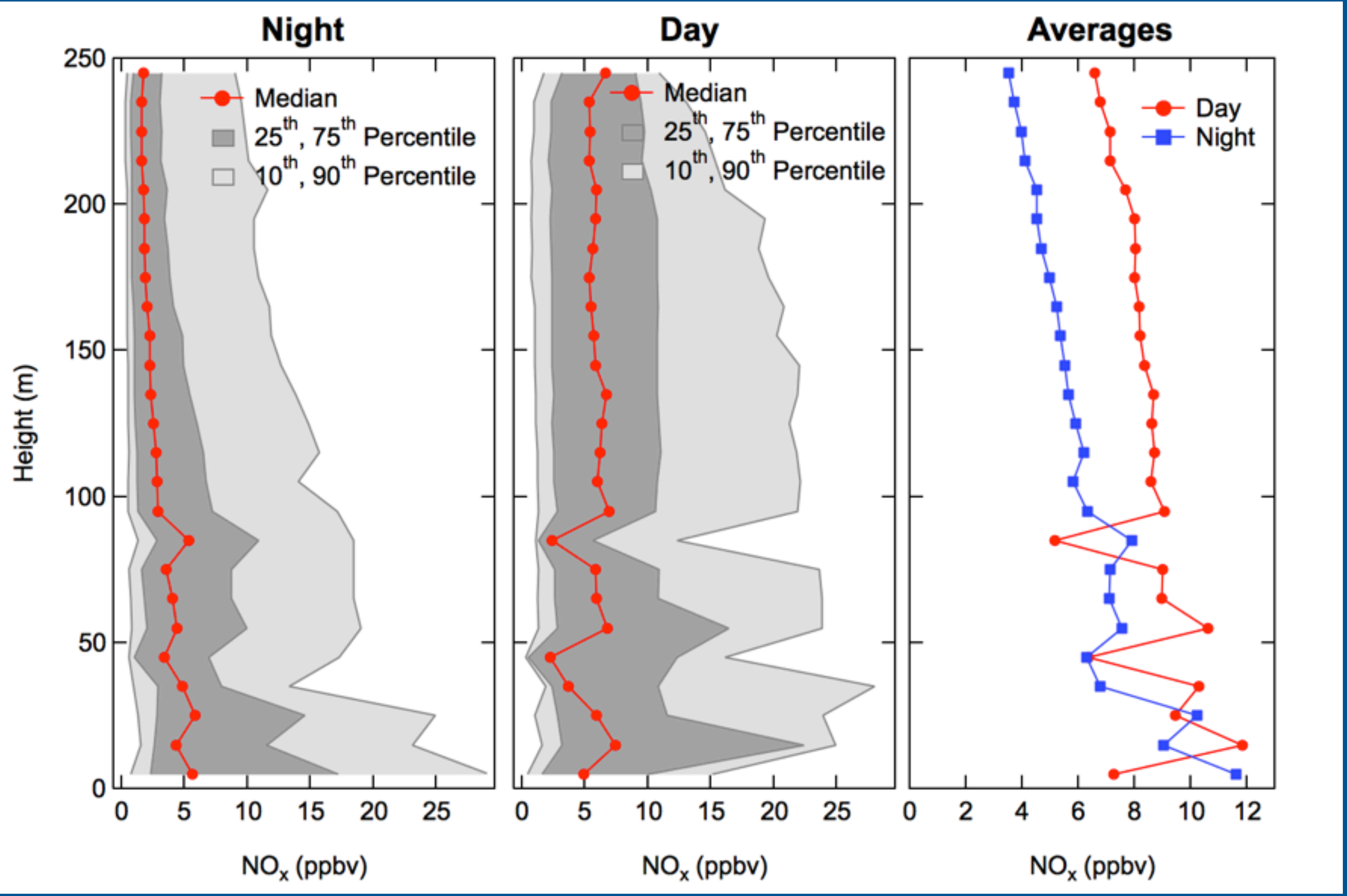
PISA + BAO Tower

Instruments & Participants - Ground Site

Species	Instrument	Investigators
HCl, HNO_3, NH_3, HCOOH, CH_3COOH, soluble Br^- (gas and particle phase)	Mist Chamber / IC	Pszenny (UNH), Keene (UVA)
Size resolved aerosol ionic composition, 0.25 - 20 µm	Cascade Impactor / IC	Pszenny (UNH), Keene (UVA)
HCl	CRDS	Yalin / Hagen (CSU)
Micrometeorology	Tethered balloon	Meillier (CU)
VOCs	PTR TOF / GC	Warneke, Gilman, Lerner, Graus de Gouw
VOCs	Canister samples	Sive (UNH)
OH	CIMS	Kim (NCAR)
Photolysis rates (NO_2, O_3)	Filter radiometer	Lerner
Ozone	UV absorption	Williams

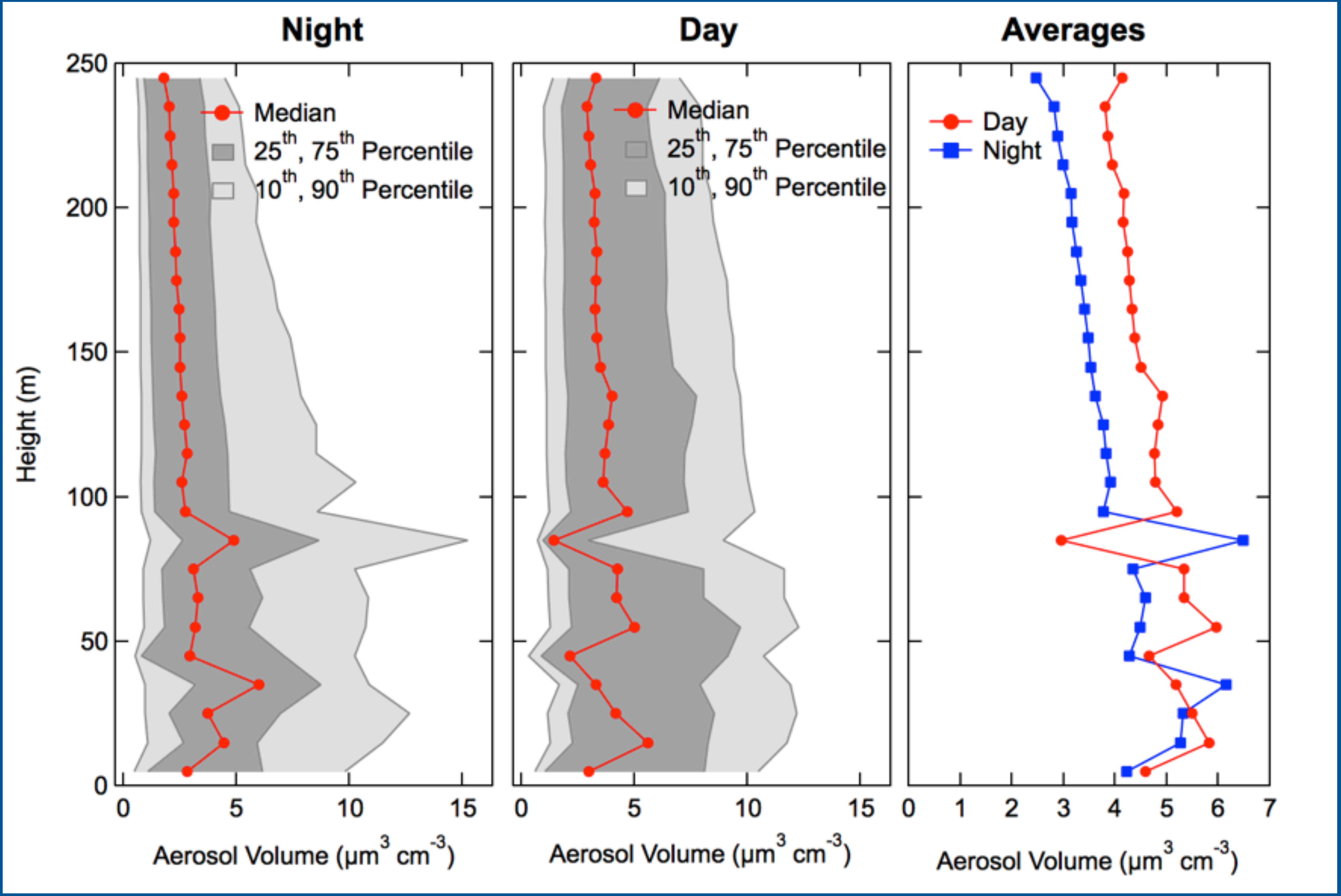
Ground Site Layout

NO_x Profiles



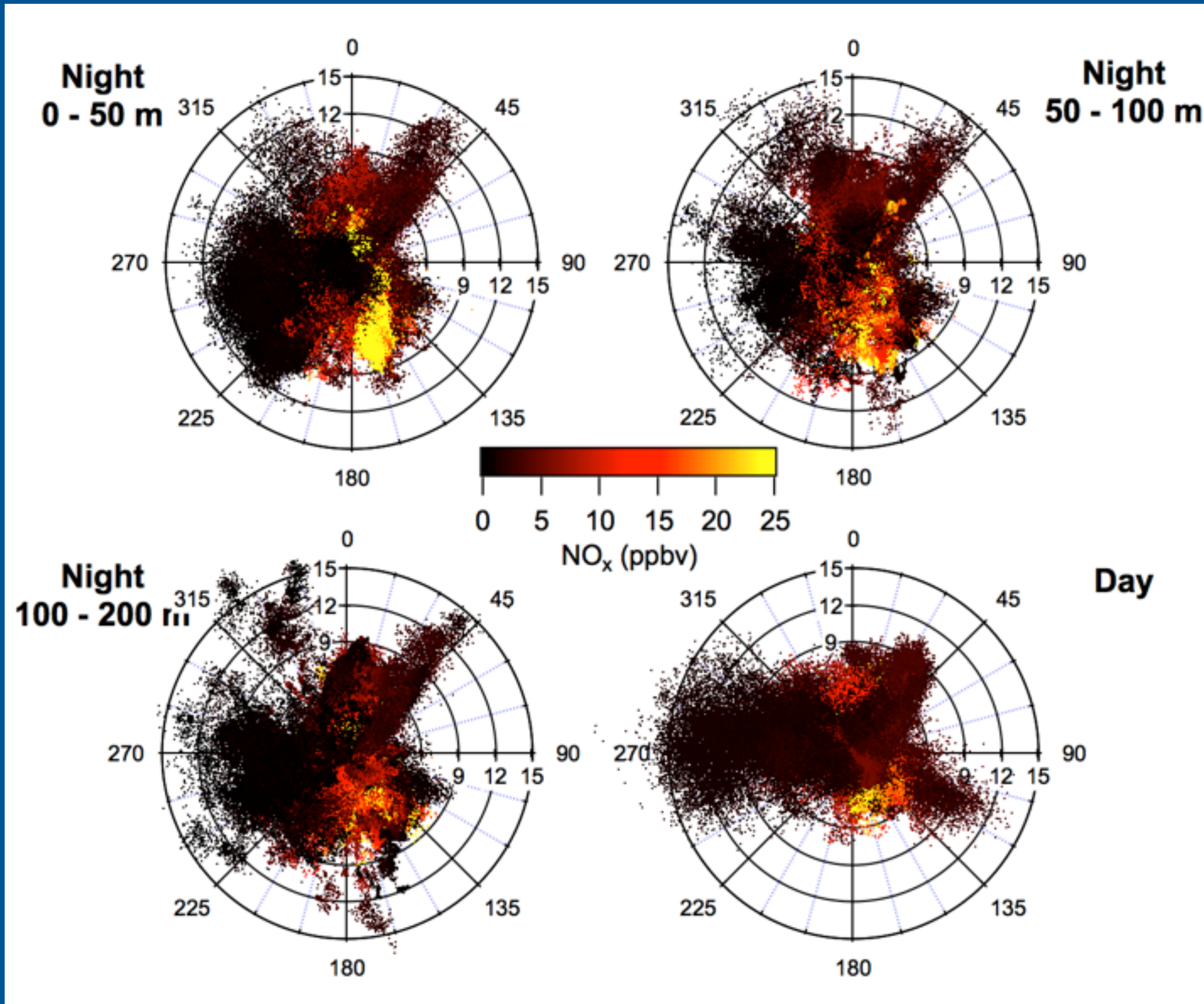
$NO_x = NO + NO_2$

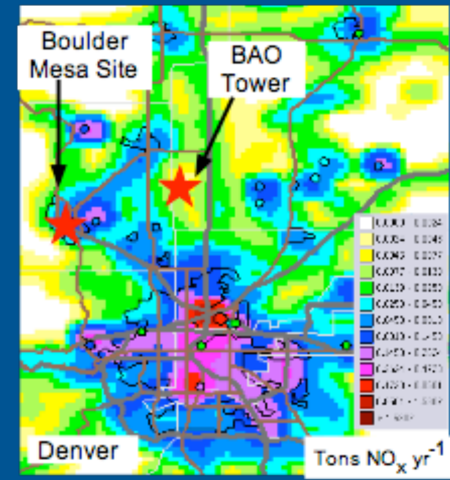
Aerosol Profiles



Note: Dry aerosol volume - substantial RH correction would skew nighttime distribution

NO_x vs. Wind Direction

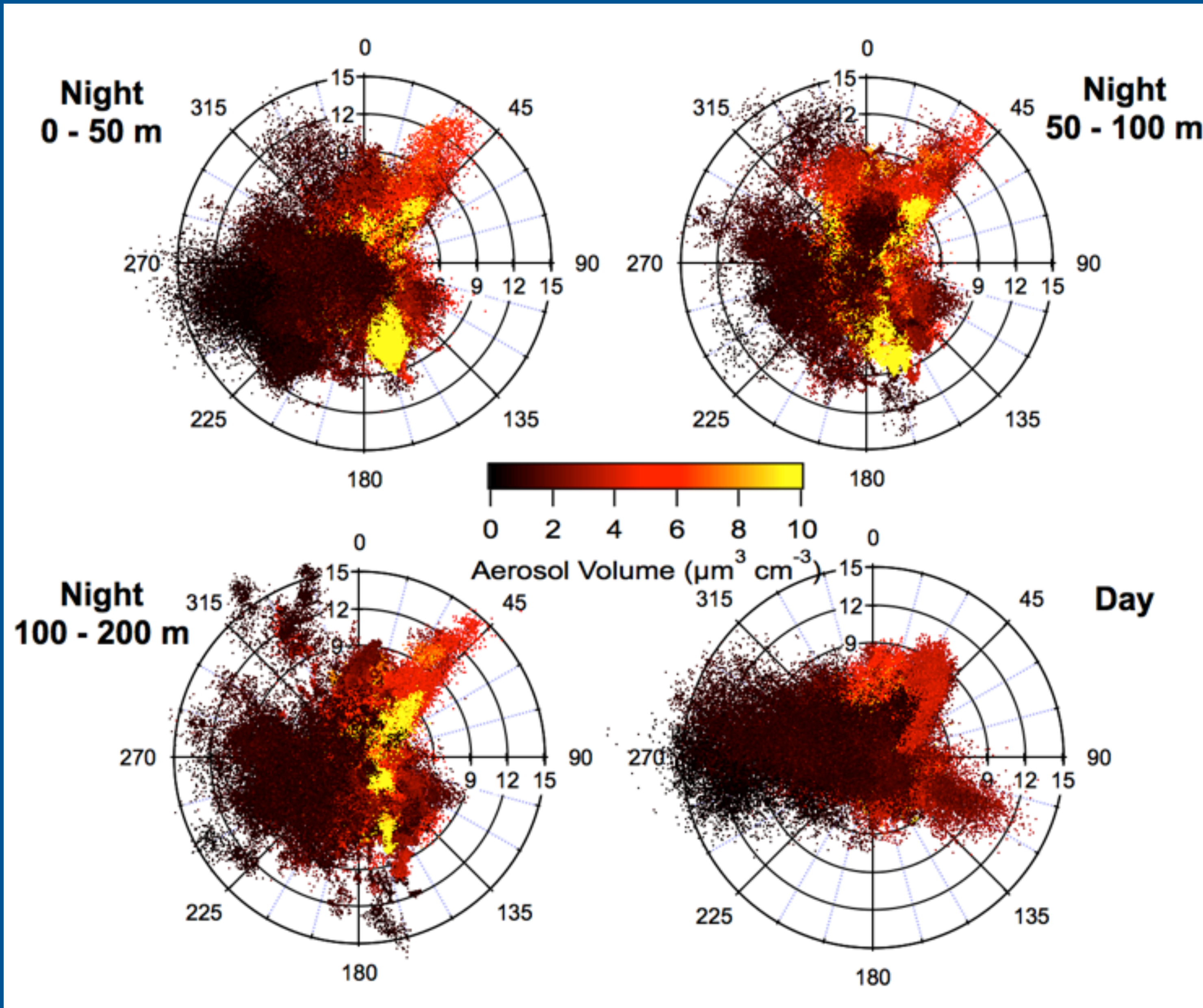




- Westerly (downslope) flow observed both day and night, uniformly warm

- Night has:
SW (warm),
SE (cooler) and
NE (cold) sectors

Aerosol Volume / Mass vs. Wind Direction



- Day:

W = Downslope flow, low aerosol

E = Upslope flow, higher aerosol

NE = Highest aerosol

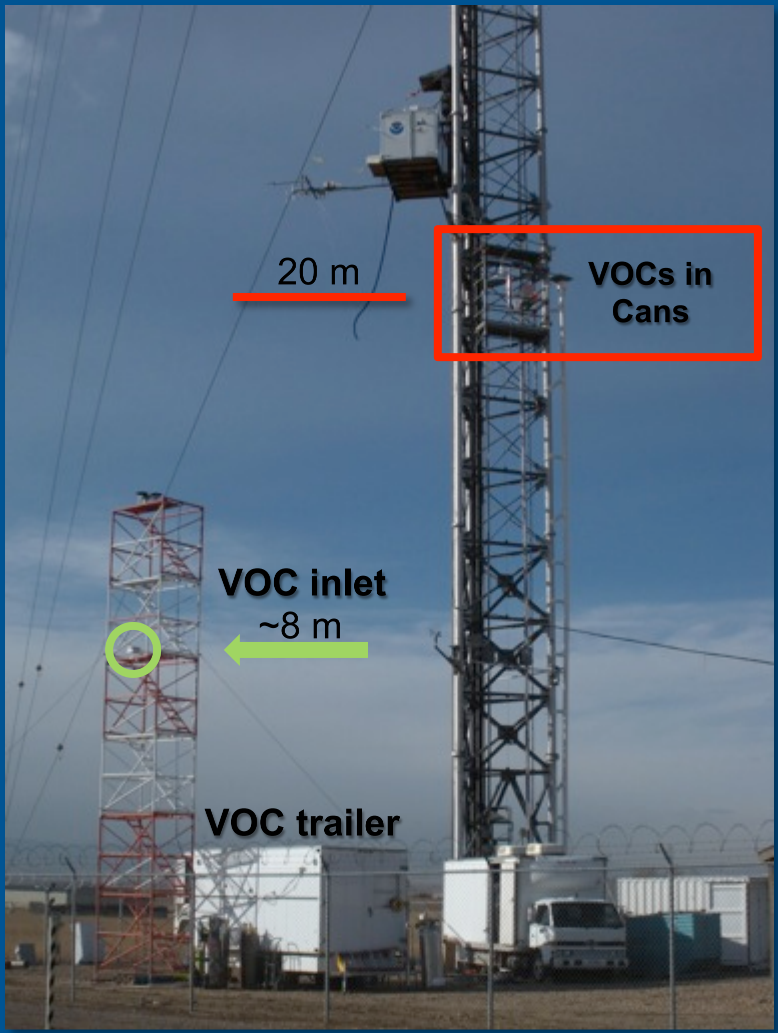
- Night:

SW = Clean

SE, NE = Both high aerosol

Eastern plains (NE) source of high aerosol but moderate NO_x. Ammonia source ?

Erie VOCs: Ground-based observations



In-situ GC-MS:

- 5 min sample acquisition
- 1 sample every 30 min
- 44 species analyzed for NACHTT
  - C2 to C12 hydrocarbons
  - C6-C9 aromatics, OVOCs, etc.

PTR-MS:

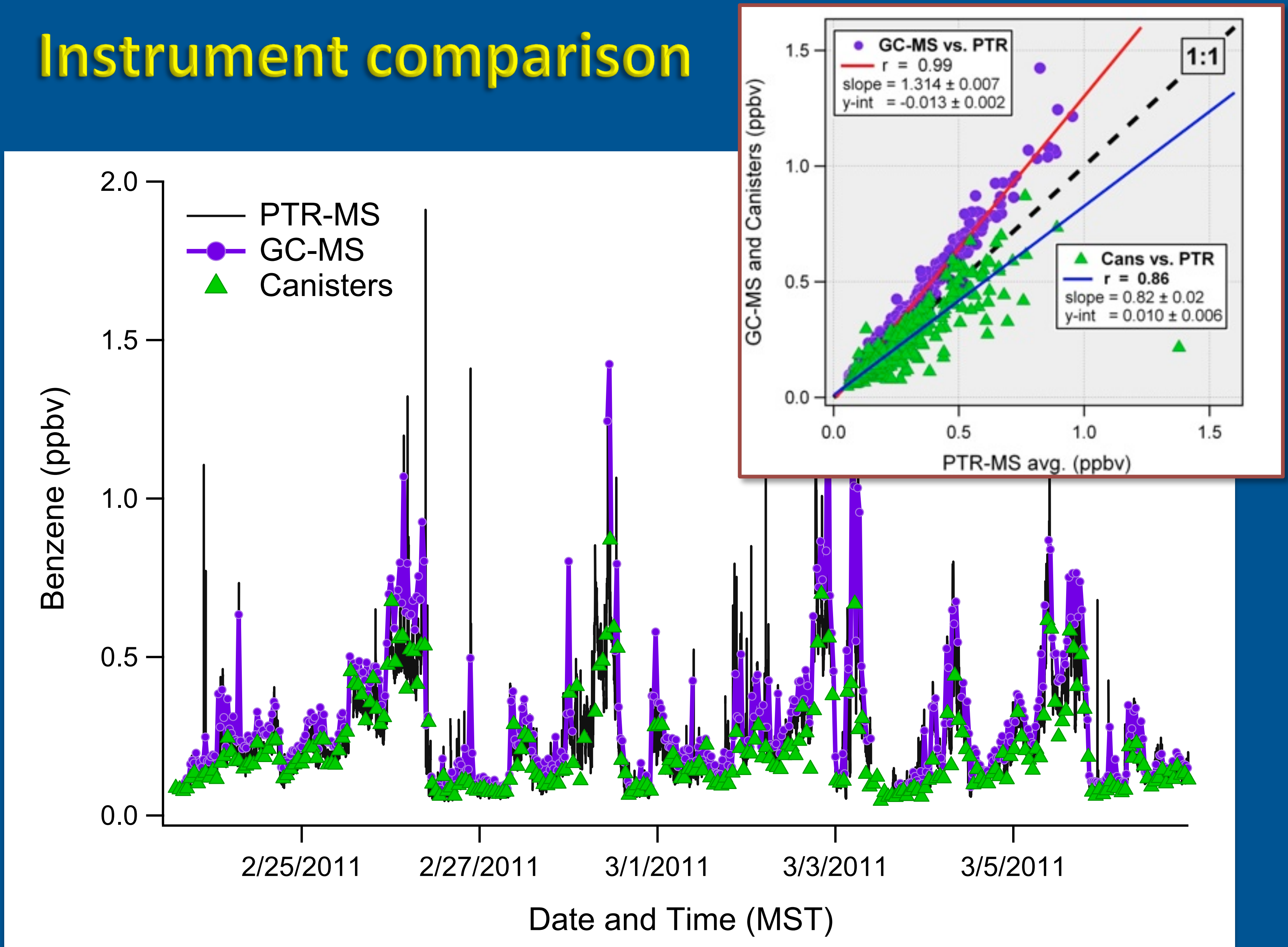
1. Quadrupole MS
   - 1 min time base posted
   - 14 masses scanned
   - Unit mass resolution
2. HR Time-of-flight MS
   - Full mass spectra
   - High mass resolution

Canister Samples:

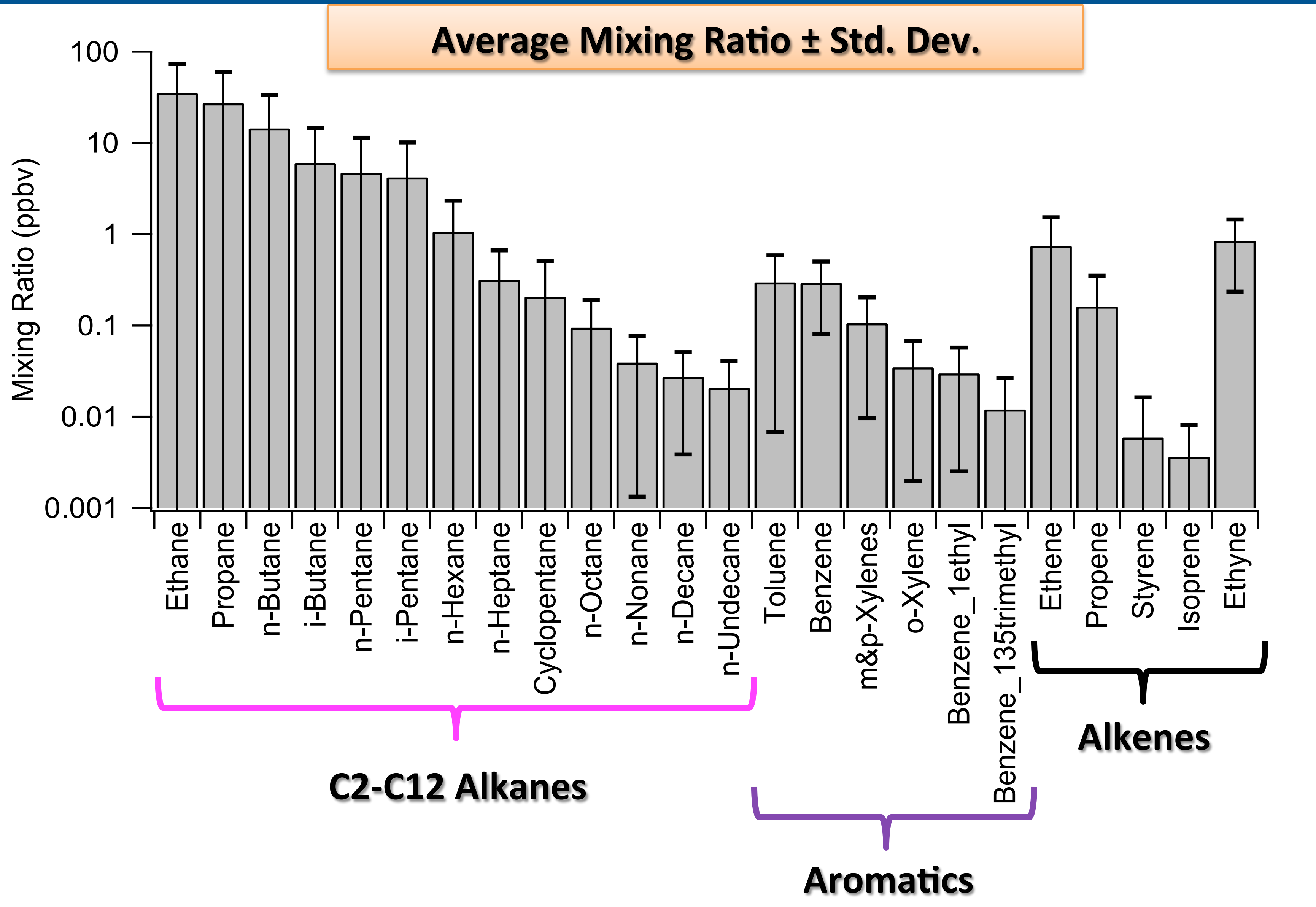
-

VOC data courtesy of: Jessica Gilman, Carsten Warneke, Brian Lerner, Martin Graus, Joost de Gouw

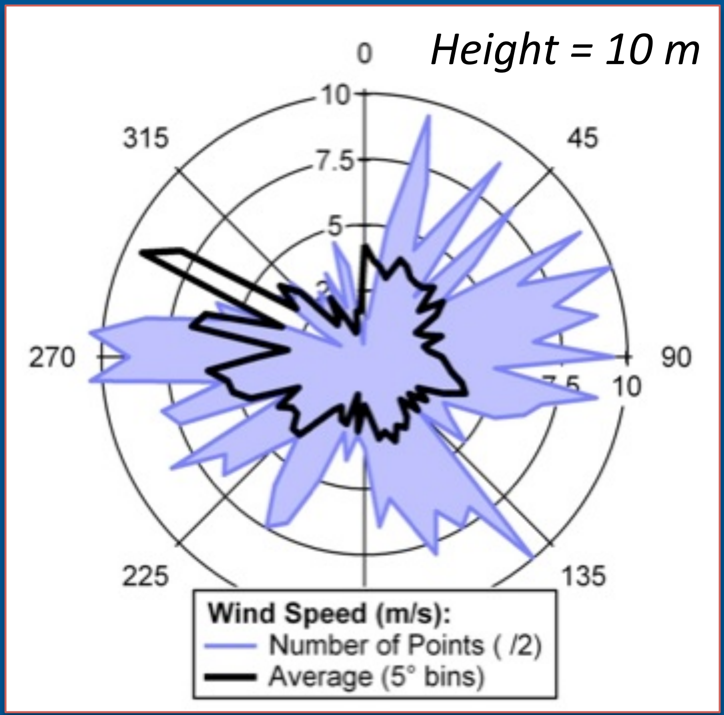
Instrument comparison

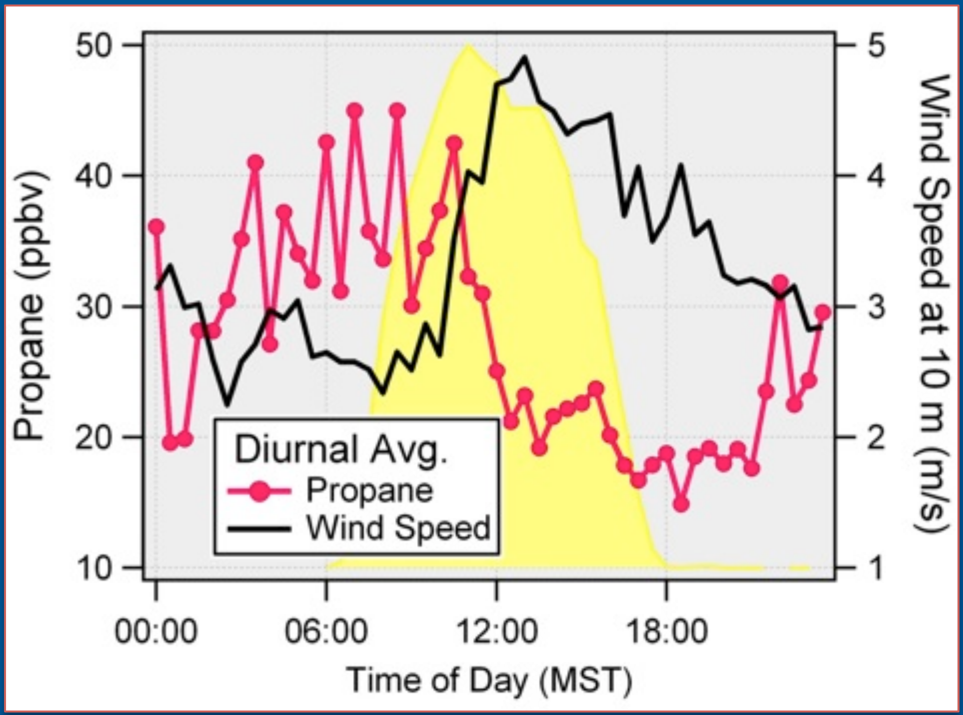


Erie Statistics



Meteorology: Wind Speed





- The site experienced wind from all sectors
  - Highest winds were predominately from the west

- Lower wind speeds from 12 am to 12 pm, higher wind speeds in the afternoon

VOC Source Signature: Correlations

- Look for correlations between VOCs in order to identify a source signature
  - Local
  - Ground-level
  - Continuous emissions
  - Primary source
  - Enriched in alkanes

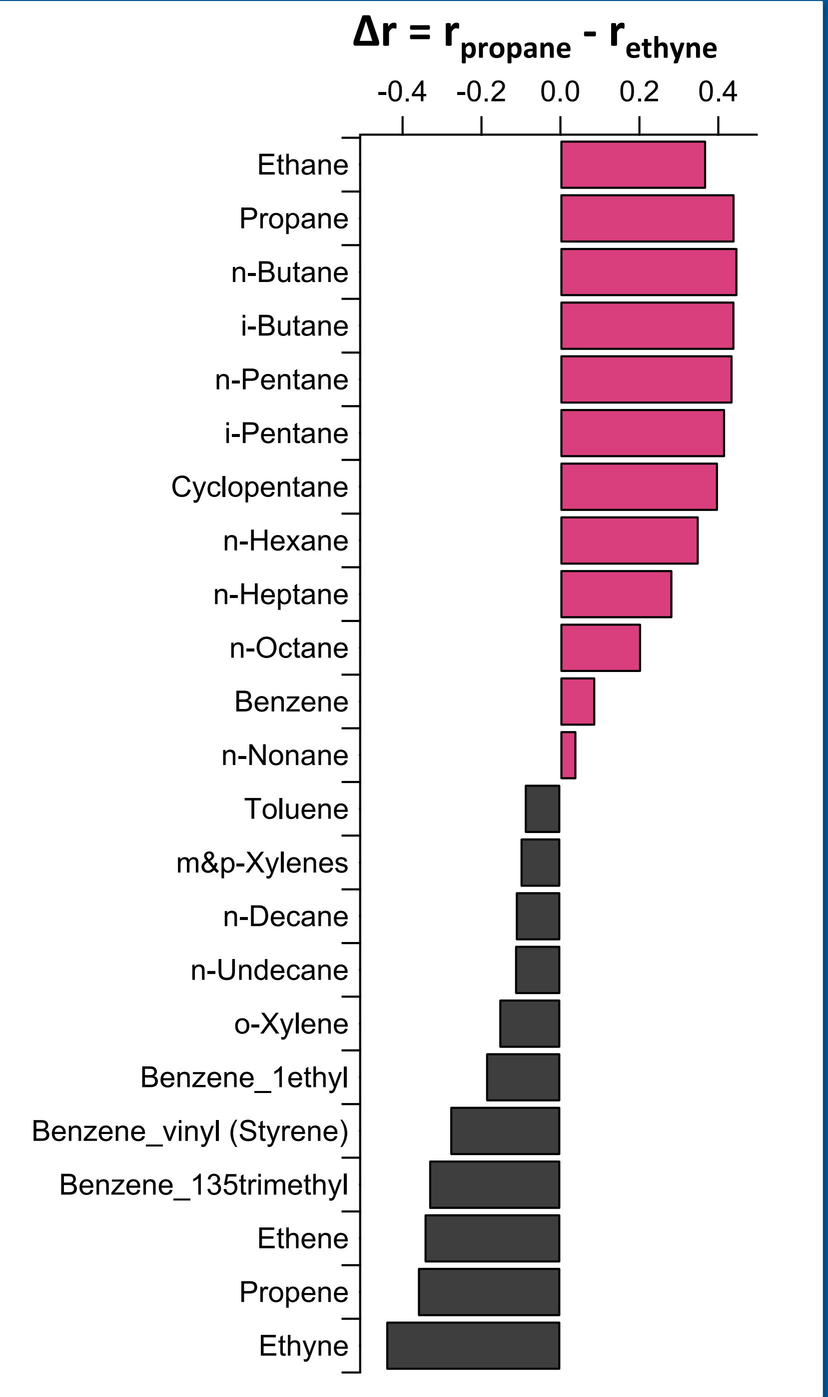
Propane: Natural gas tracer

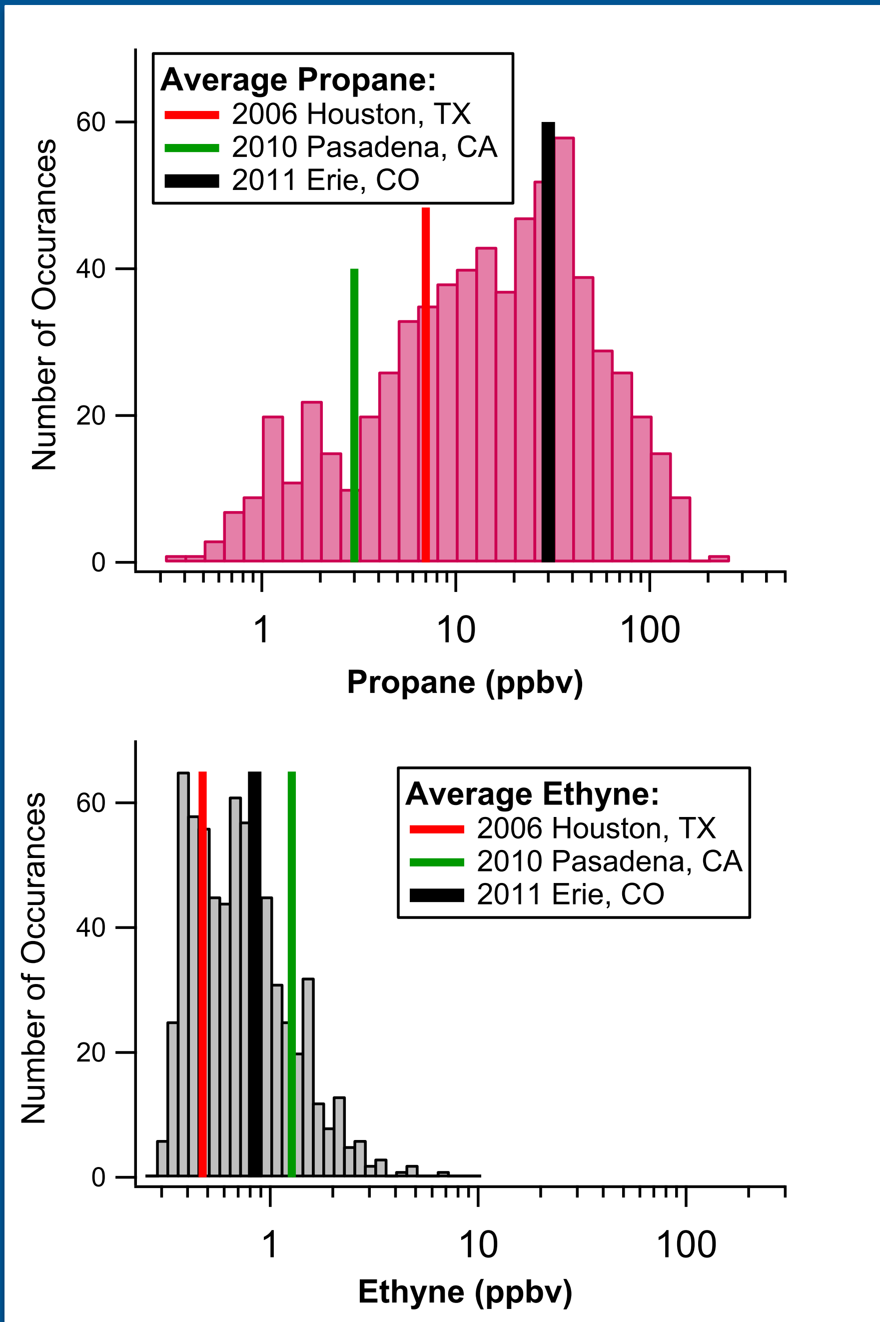
C2-C9 alkanes and Benzene

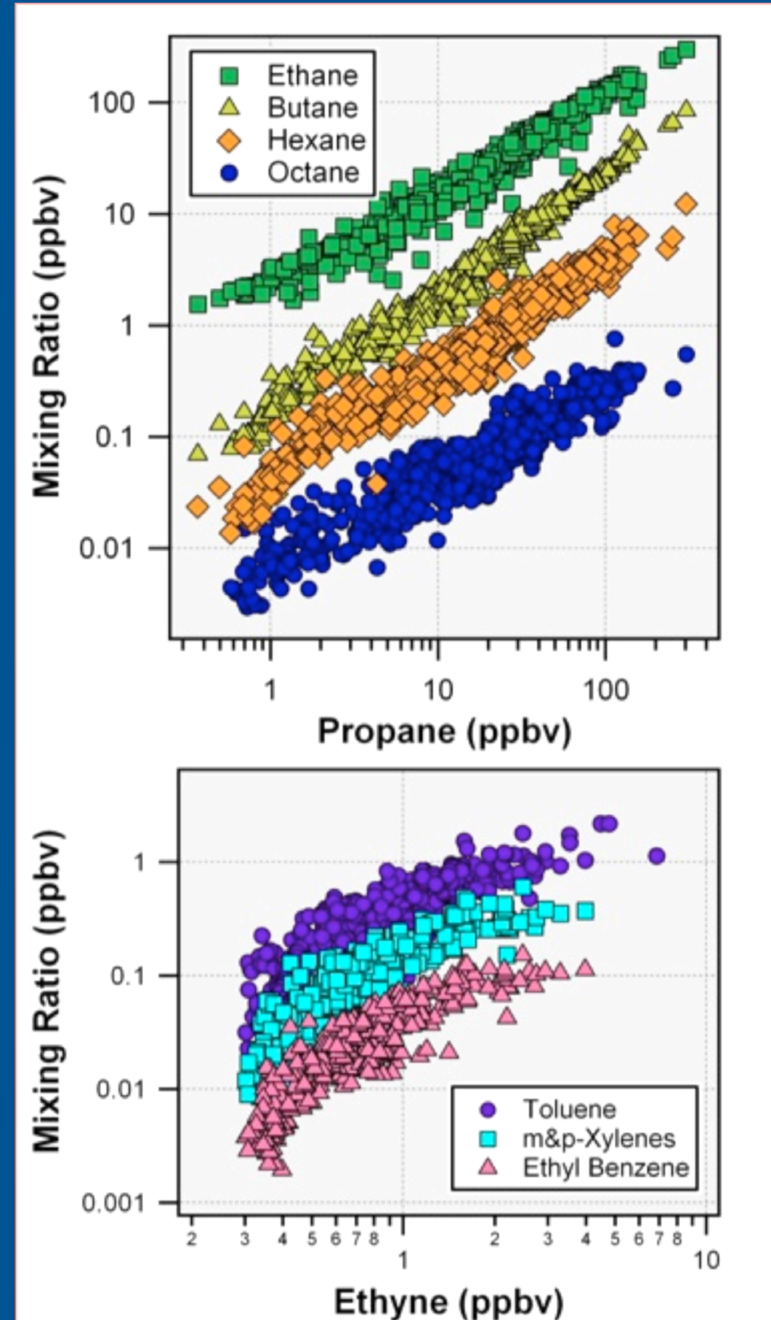
Ethyne: Urban/on-road tracer

Alkenes and C10+ alkanes

Toluene and C8, C9 aromatics




Average Propane:
2006 Houston, TX
2010 Pasadena, CA
2011 Erie, CO
Number of Occurances
0
20
40
60
1
10
100
Propane (ppbv)
Average Ethyne:
2006 Houston, TX
2010 Pasadena, CA
2011 Erie, CO
Number of Occurances
0
20
40
60
1
10
100
Ethyne (ppbv)


Ethane
Butane
Hexane
Octane
Mixing Ratio (ppbv)
100
10
1
0.1
0.01
1
10
100
Propane (ppbv)
Toluene
m&p-Xylenes
Ethyl Benzene
Mixing Ratio (ppbv)
1
0.1
0.01
0.001
2
3
4
5
6
7
8
1
2
3
4
5
6
7
8
10
Ethyne (ppbv)

VOC Measurements from the Tower

18 February – 13 March 2011

Hourly samples from 20 m

Profile samples throughout campaign (usually 2-3 per day)

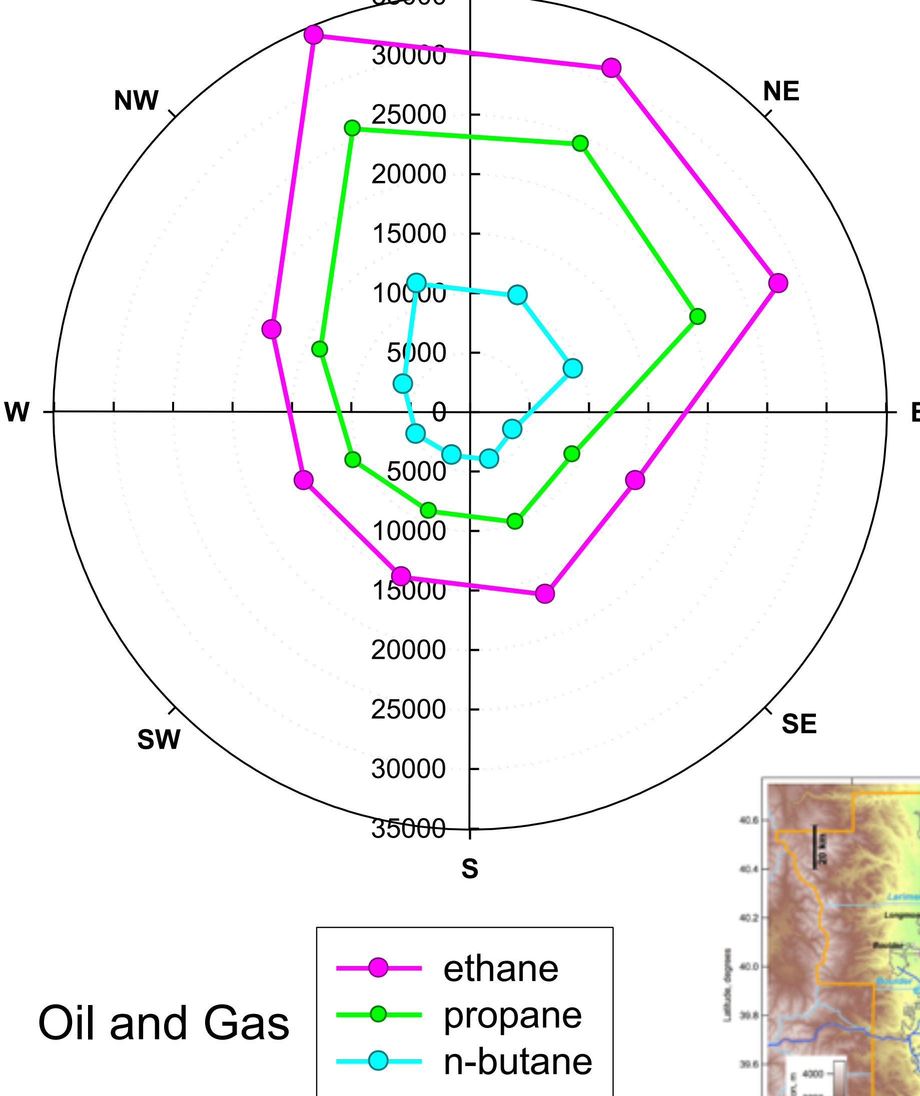
Sample heights (m): 50, 100, 150, 200, 250

All samples pressurized to ~30 psig using a metal bellows pump

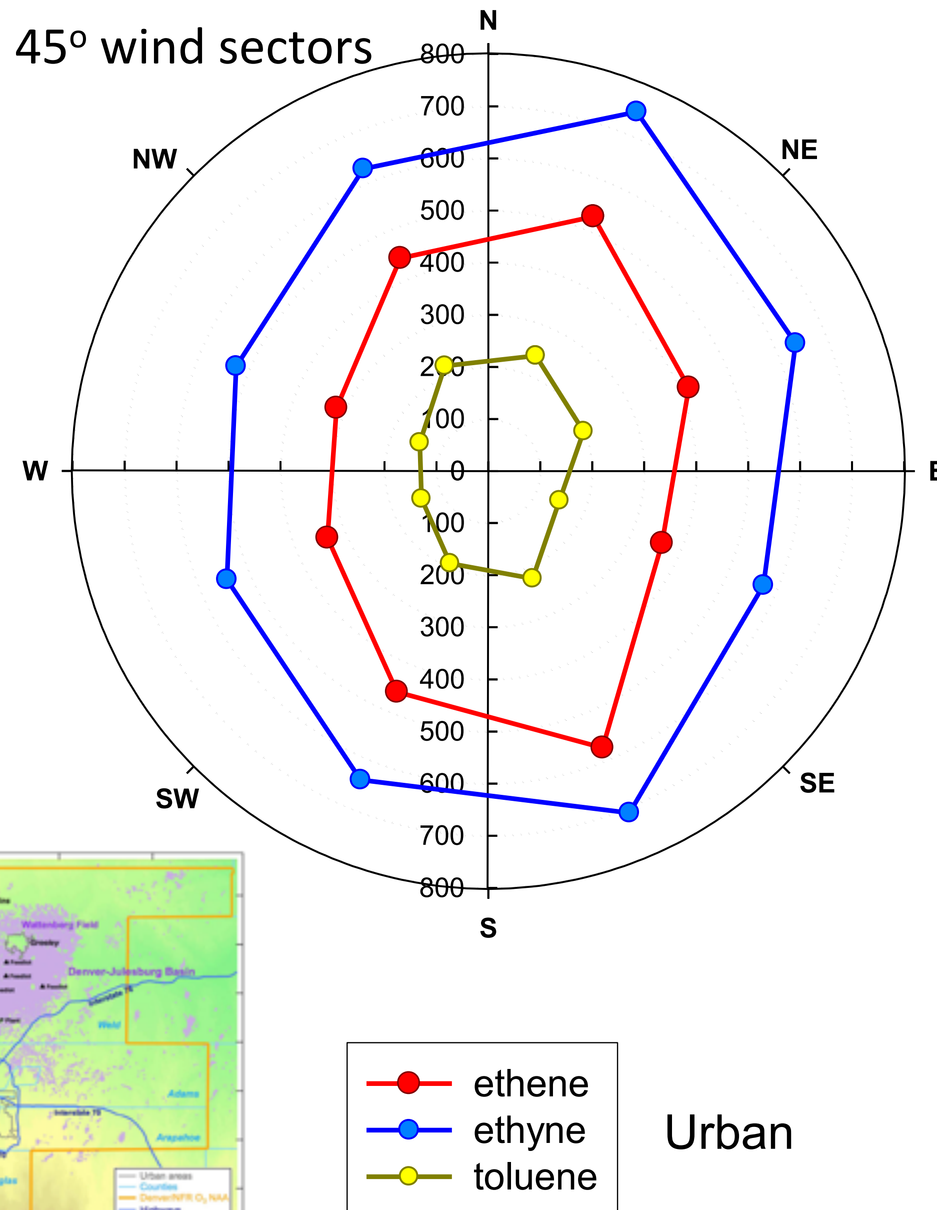
Rachel Russo, Andrew Hart, Bob Swarthout, Yong Zhou, Barkley Sive

Wind Rose

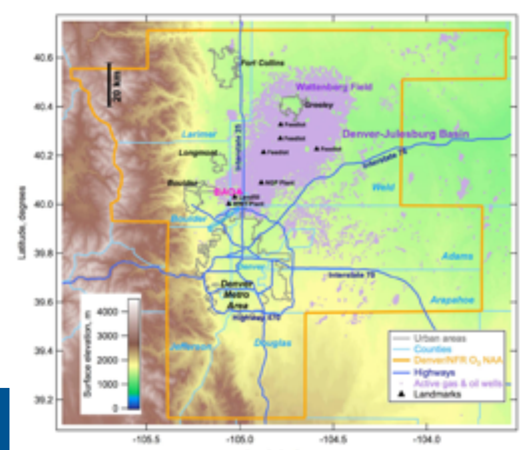
Mean mixing ratios in 45° wind sectors



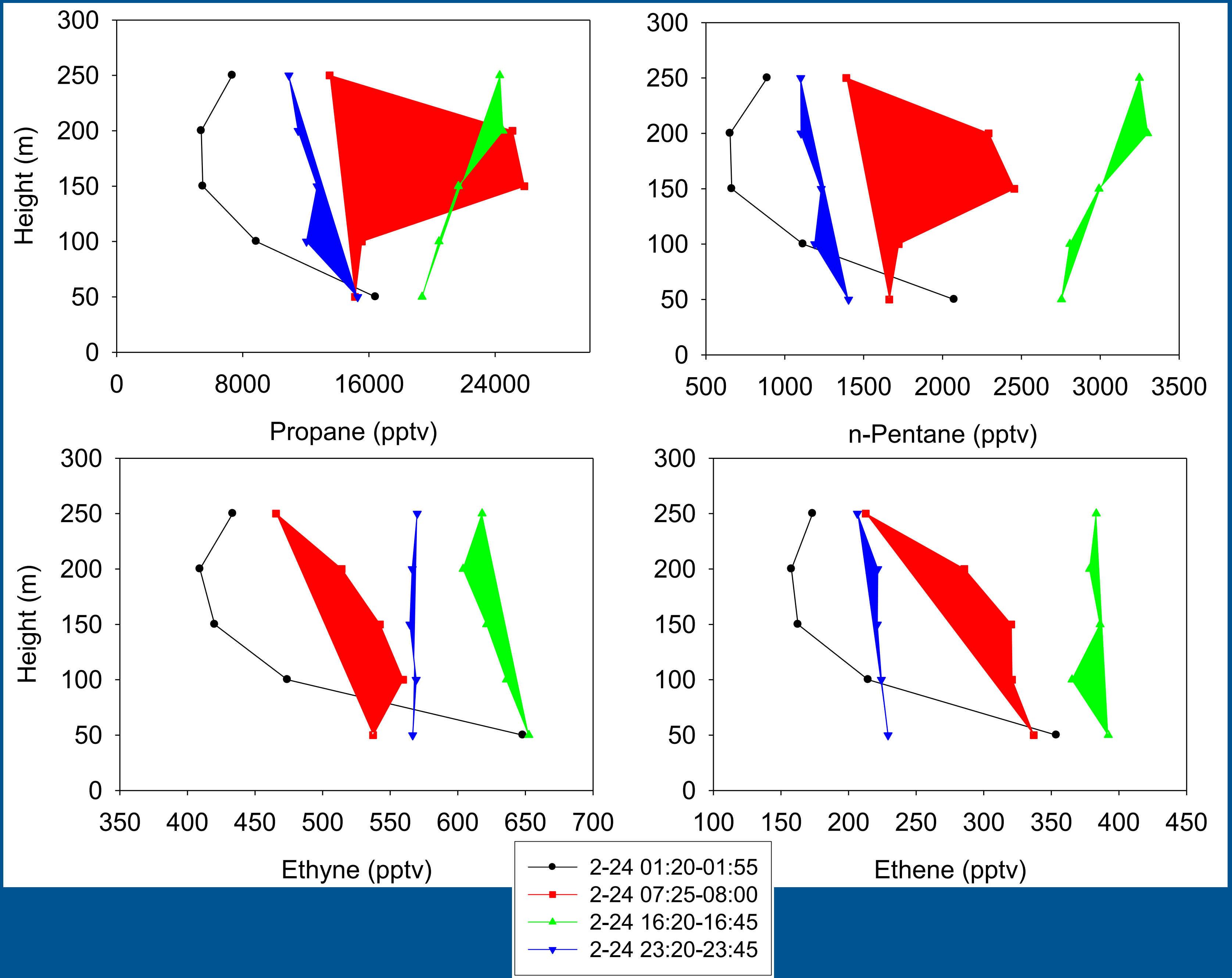
Oil and Gas



Urban



NMHC Profiles



Oil and Gas

Urban

Summary

- Ground-based measurements can be “de-coupled” from tower
  - Low surface winds and shallow mixed layers, particularly at night
  - Higher mixing ratios and greater variability of VOCs closer to the surface
- Large source of alkanes from local natural gas operations
  - Ethane and Propane: Averages over 10 ppb with maximums over 100 ppb
  - Strong correlation among C2-C9 alkanes and benzene
- Typical, winter-time “urban” background
  - Stronger correlations among C7-C9 aromatics, alkenes, and ethyne
- VOC oxidation appears to be minimal
  - Primary emissions will have longer atmospheric lifetimes
  - Decreased production of secondary by-products such as OVOCs and ozone