A Measurement-Based Approach to Air Quality

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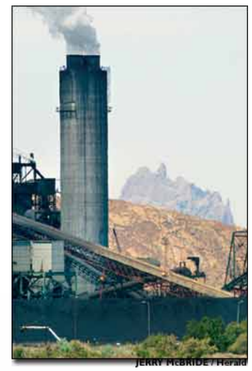
NOx Scientific Forum, Ozone Stakeholder Committee Mtg, RAQC, Denver, 18 December 2007

Outline

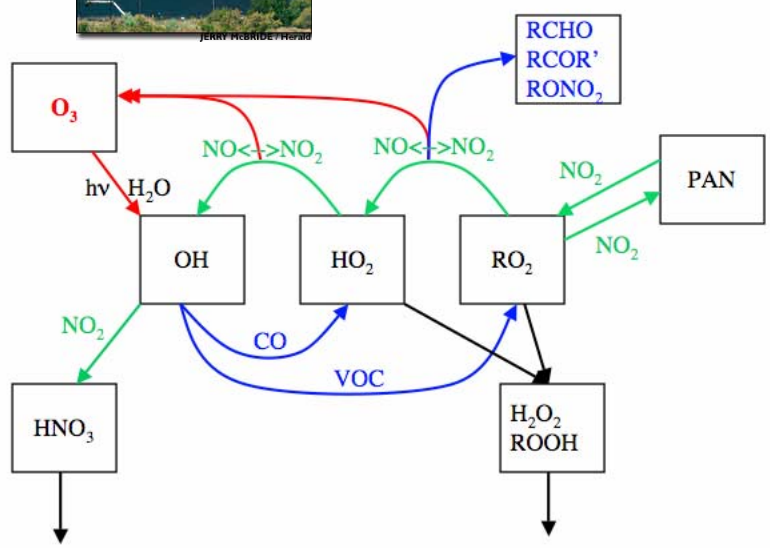
Measurement-based approach to air quality research
- Observational understanding of atmospheric processes
- Development of air quality models

Processes of interest in today's talk
- Emissions of ozone precursors (NO_x, VOCs, CO)
- Chemistry of ozone formation



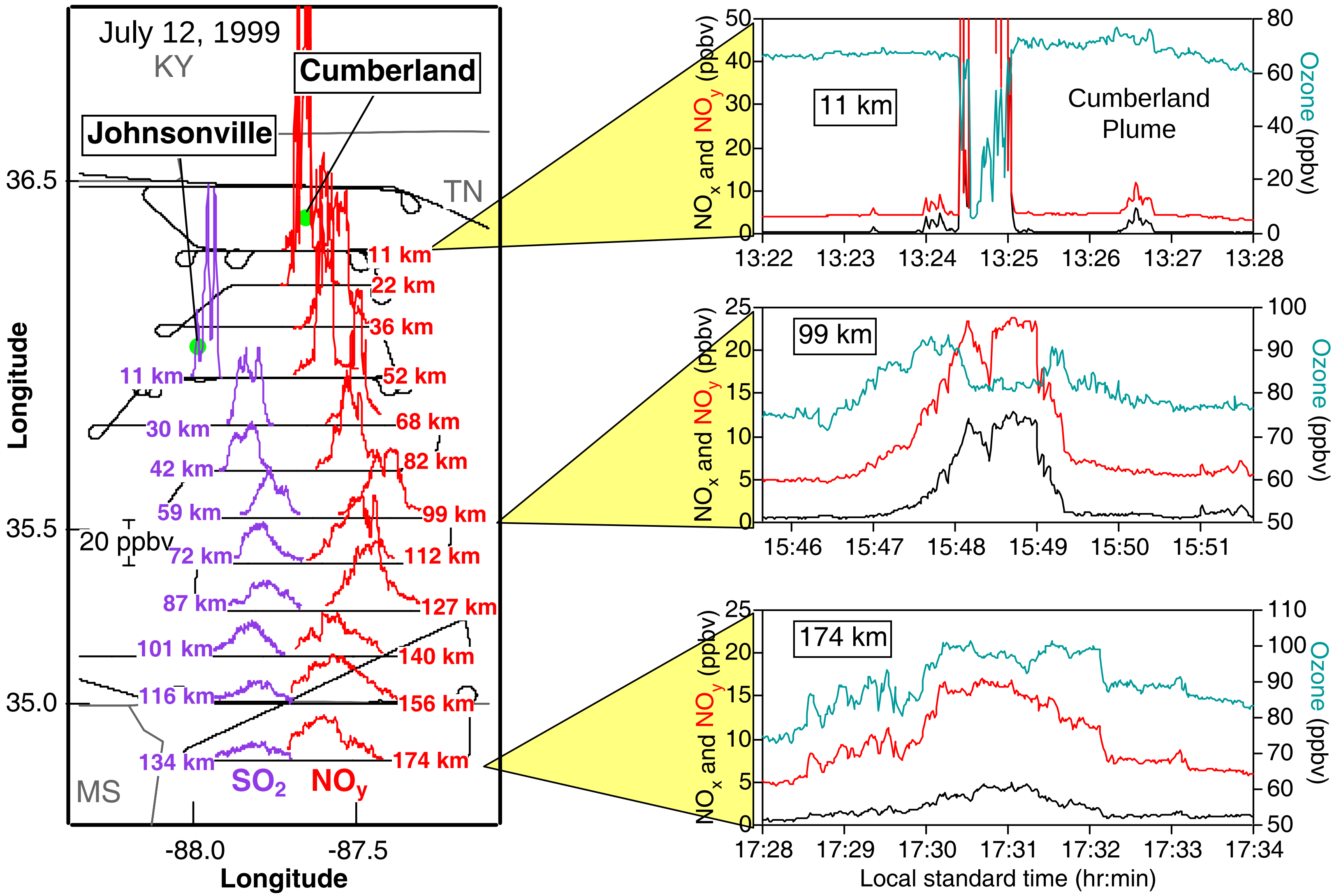
Case studies
- Power plants
- Refineries
- Urban mobile sources
- Oil & gas production

Examples across US, including Colorado



Power Plant Plume Sampling by Aircraft

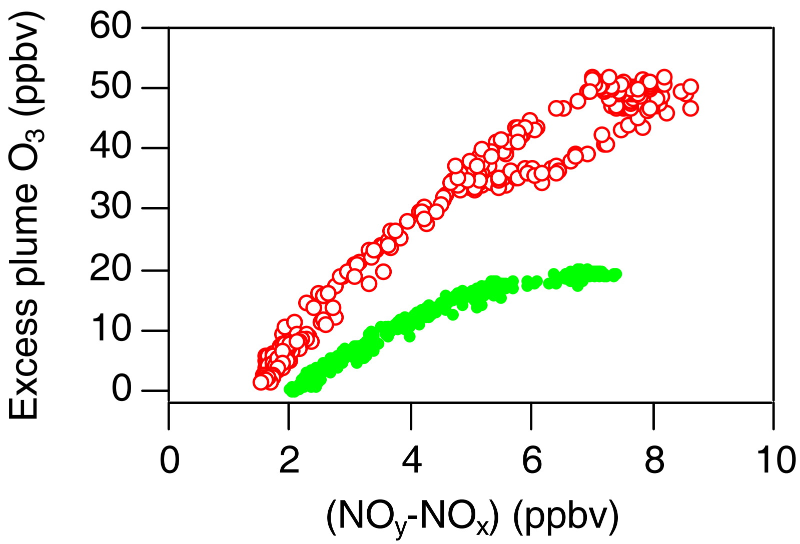
1999 Southern Oxidants Study (SOS99)

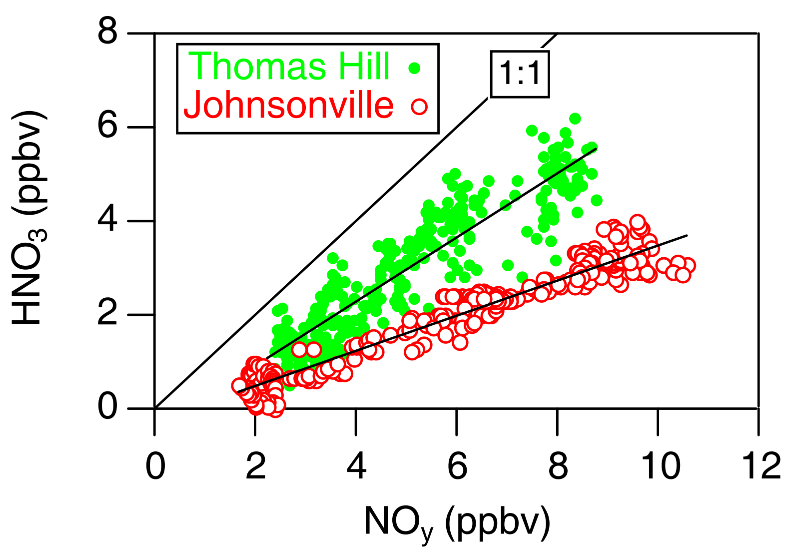


T. B. Ryerson et al., Science, 292, 719-723, 2001

Analysis of Power Plant Plume Ozone Formation

1999 Southern Oxidants Study





T. B. Ryerson et al., Science, 292, 719-723, 2001

•Sample plumes of similar age
•Comparable NO_x emissions at both plants
•Isoprene emissions at Johnsonville are 10X greater than at Thomas Hill

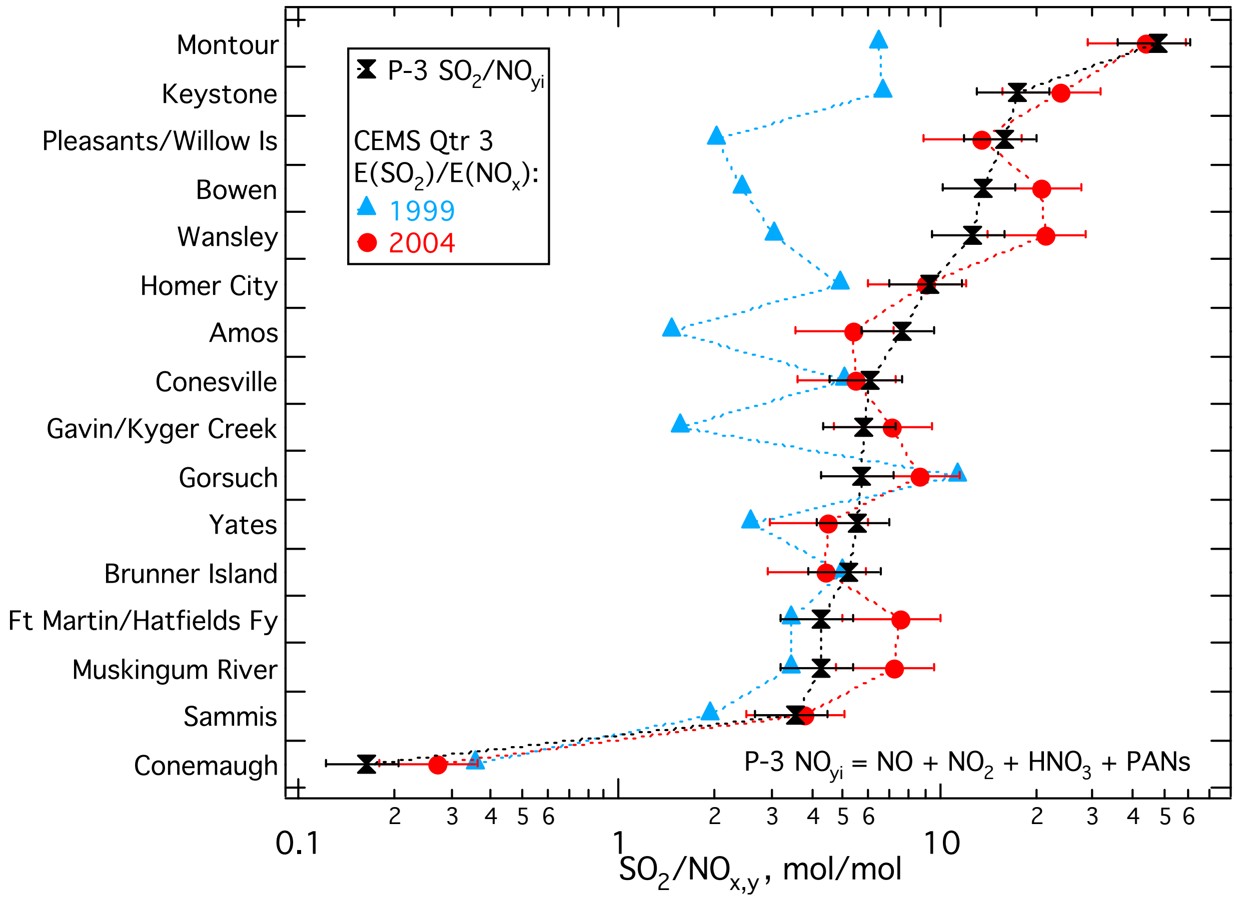
•Emit NO_x into more reactive VOC mix
$\Rightarrow$ more O_3 produced relative to HNO_3
•Emit NO_x into less reactive VOC mix
$\Rightarrow$ more HNO_3 produced relative to O_3

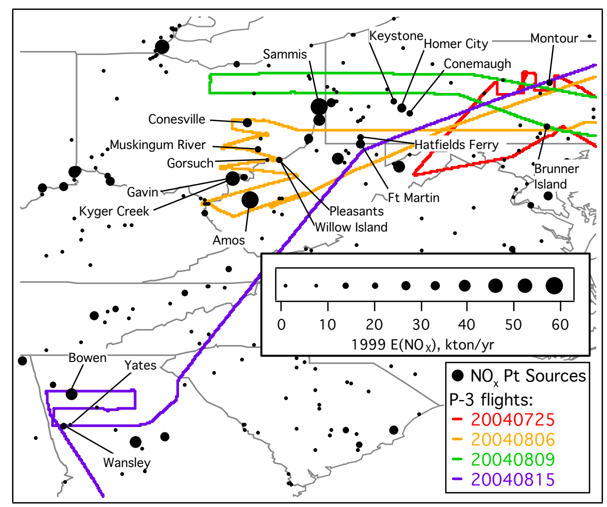
Comparison of CEMS to Aircraft Observations in Power Plant Plumes

NEAQS - ITCT 2004

(New England Air Quality Study - Intercontinental Transport & Chemical Transformation)

- CEMS emission ratios agree with P-3 observations
- Decline in $E(NO_x)$ resulting from pollution controls detected in power plant plumes



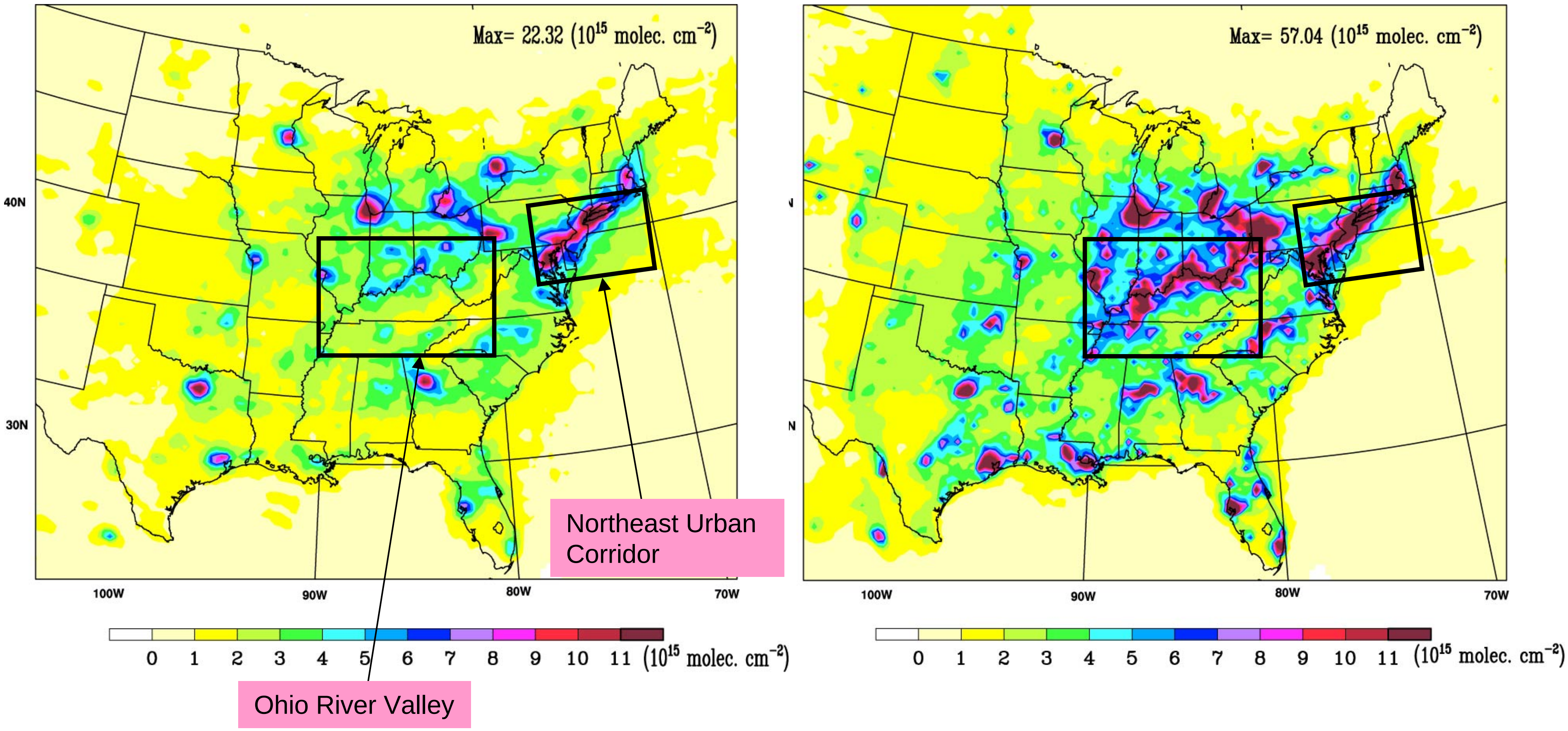


G. J. Frost et al. (2006), J. Geophys. Res., 111, D12306, doi:10.1029/2005JD006354

Eastern US Power Plant NO_x Emission Reductions Detected by Satellite

Summer 2004 Average NO_2 Vertical Columns

SCIAMACHY **WRF-Chem Model, Reference Emissions (NEI 99)**



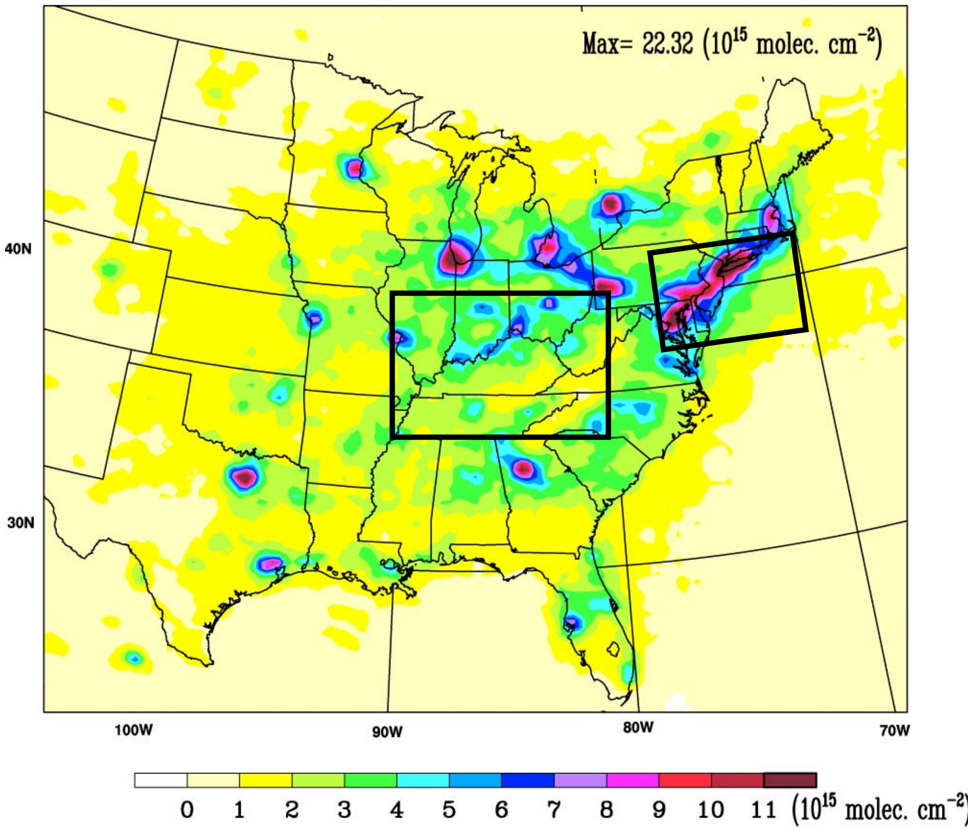
- Model reproduces satellite NO_2 vertical columns over urban areas
- Model NO_2 columns too large over power plants using 1999 emissions

S.-W. Kim et al. (2006), Geophys. Res. Lett., 33, L22812, doi:10.1029/2006GL027749

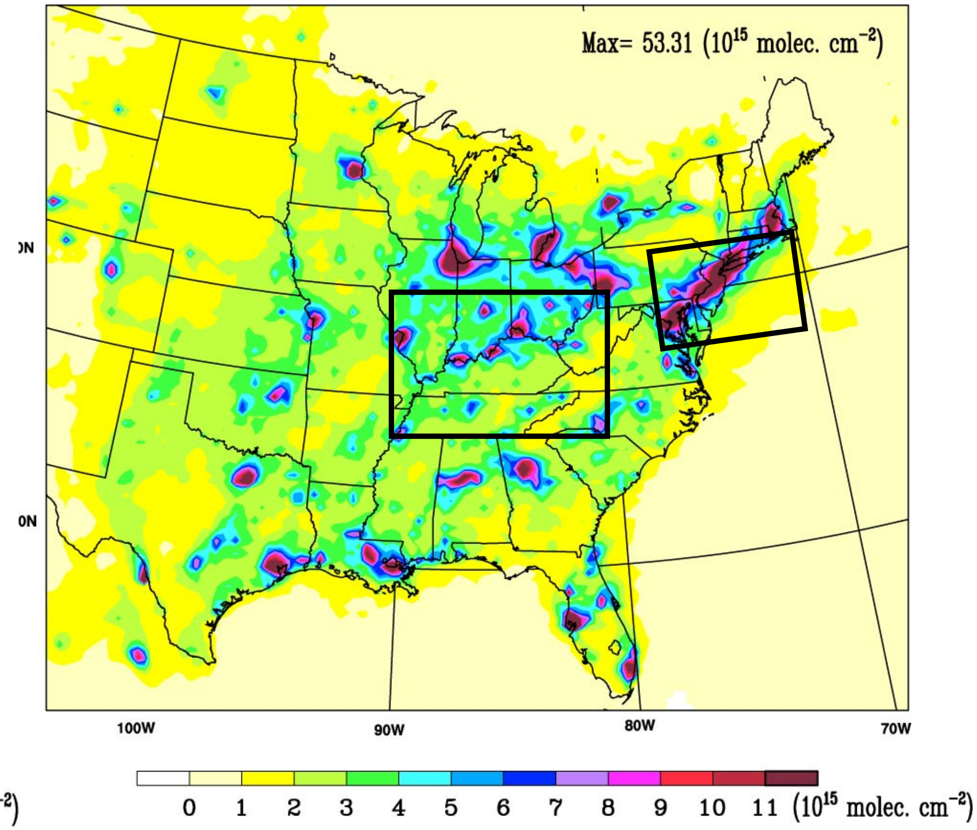
Eastern US Power Plant NO_x Emission Reductions Detected by Satellite

Summer 2004 Average NO_2 Vertical Columns

SCIAMACHY



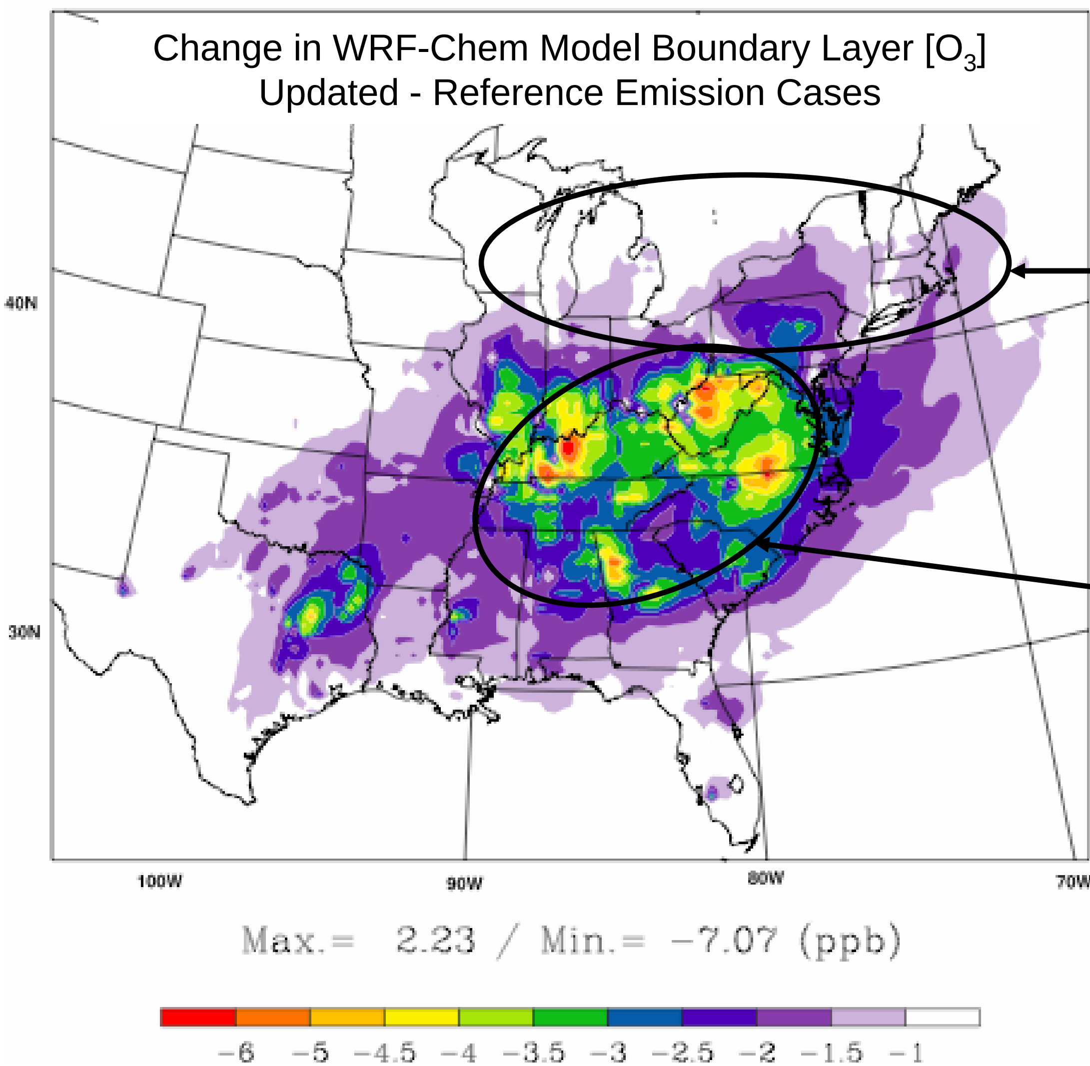
WRF-Chem Model, 2004 Power Plant Emissions



- Model with summer 2004 power plant emissions agrees much better with satellite NO_2 columns over power plants
- *Satellite detects changes in Ohio River Valley from recent power plant NO_x emission controls*

S.-W. Kim et al. (2006), Geophys. Res. Lett., 33, L22812, doi:10.1029/2006GL027749

O_3 Response to NO_x Emission Reductions - Air Quality Model



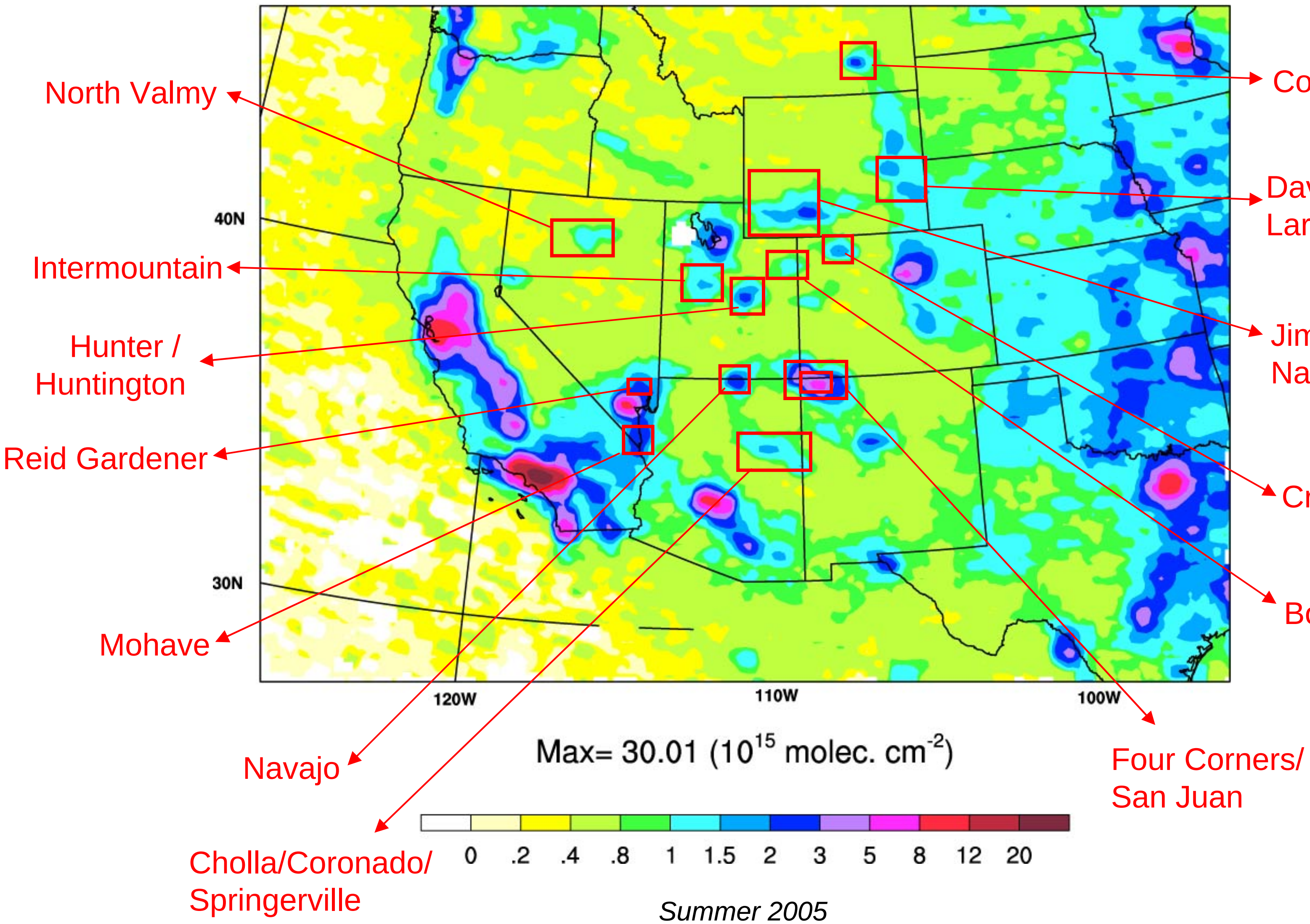
Average of all model output between 0 & 1 km at 20 UTC (1500 EST) for all days June-August 2004

- *O_3 generally decreases in response to power plant NO_x emission reductions*
- *Small $\Delta[O_3]$ in northern US $\Rightarrow$ persistent cold fronts and unusually cold conditions in summer 2004*
- *Up to 10% [O_3] decreases in Ohio River Valley, VA, NC, and GA*

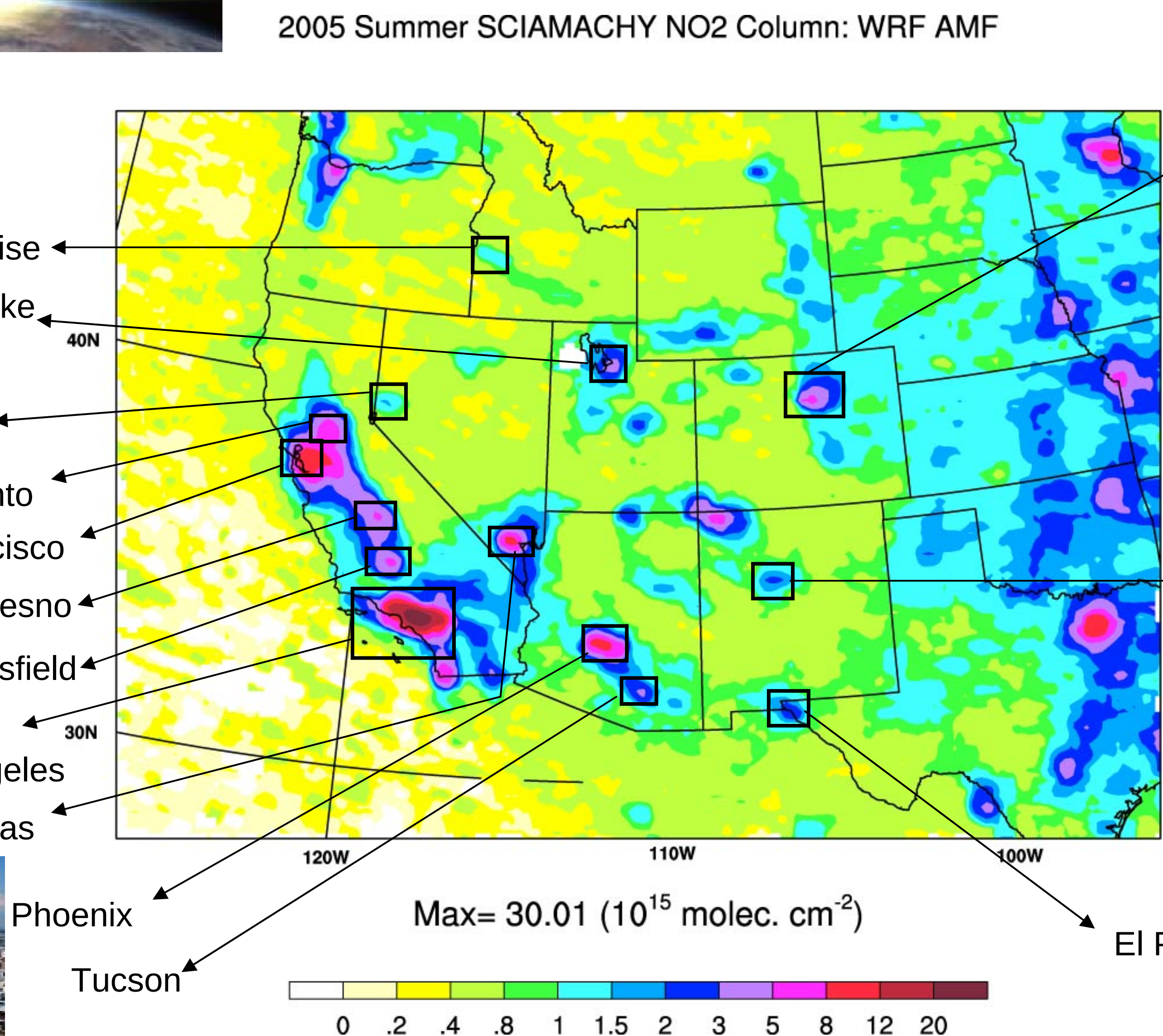
S.-W. Kim et al. (2006), Geophys. Res. Lett., 33, L22812, doi:10.1029/2006GL027749

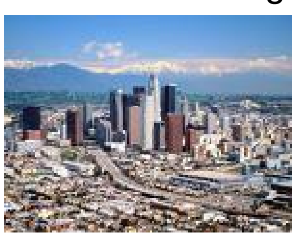
Western US Power Plant NO_x Plumes Detected by Satellite Instruments

2005 Summer SCIAMACHY NO2 Column: WRF AMF



Western US Urban Area NO_x Plumes Detected by Satellite Instruments



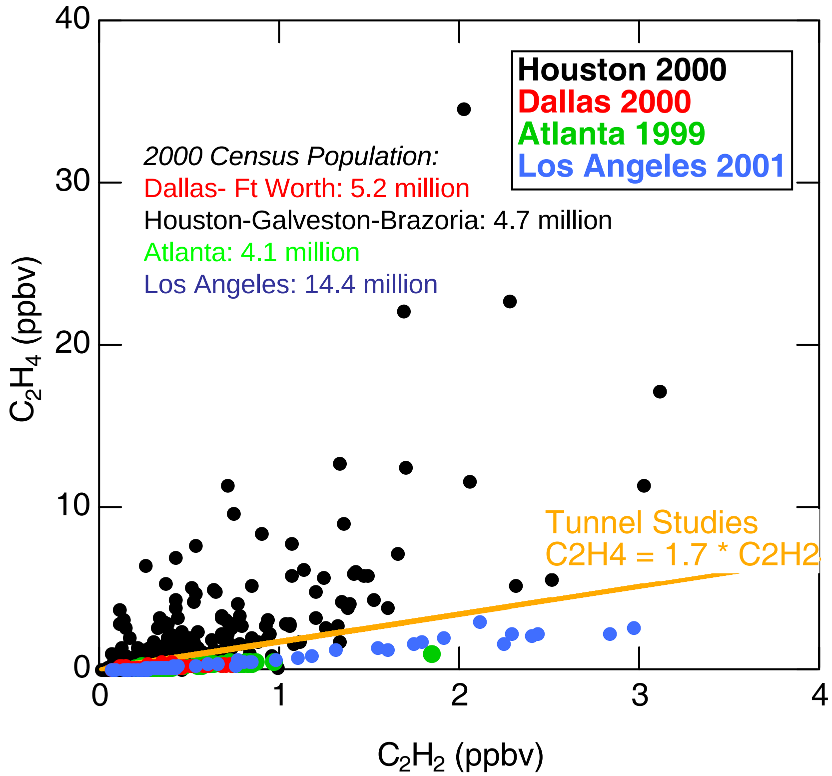


Houston Hydrocarbons and Alkene Reactivity

2000 Texas Air Quality Study (TexAQS2k)

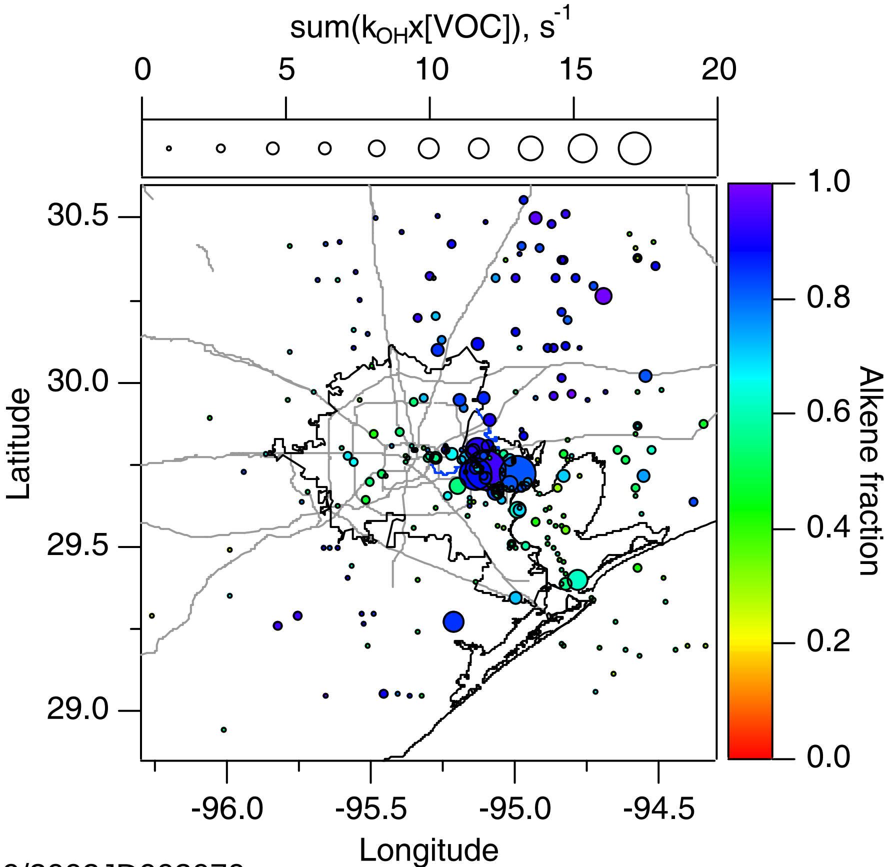
Ambient hydrocarbon concentrations over Houston much larger than expected for typical automotive urban emissions

Houston measurements: NCAR Whole Air Sampler



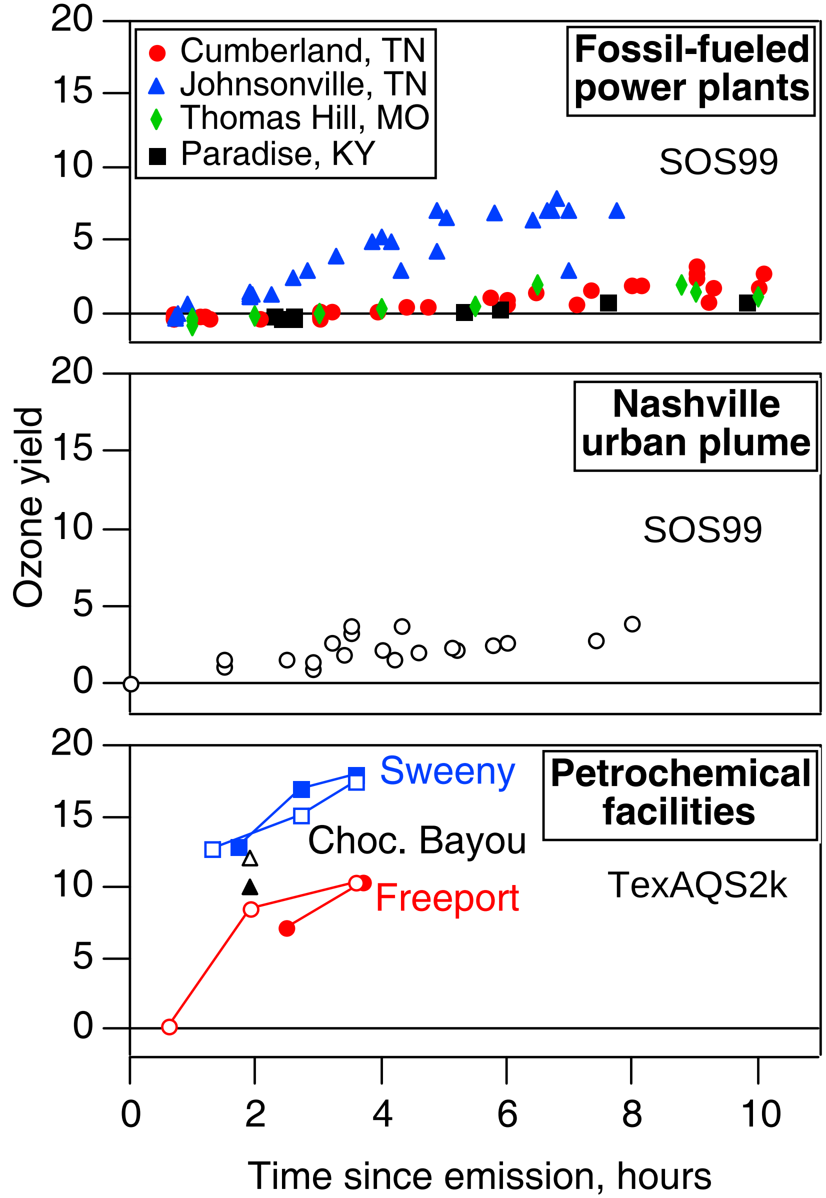
High alkene contribution to reactivity is widespread throughout Houston metro area

All in-situ and Whole Air Sampler canister measurements below 1.5 km altitude



Ryerson et al. (2003), *J. Geophys. Res.*, 108, D8, 4249, doi:10.1029/2002JD003070

Ozone Production in Power Plant, Urban, and Refinery Plumes

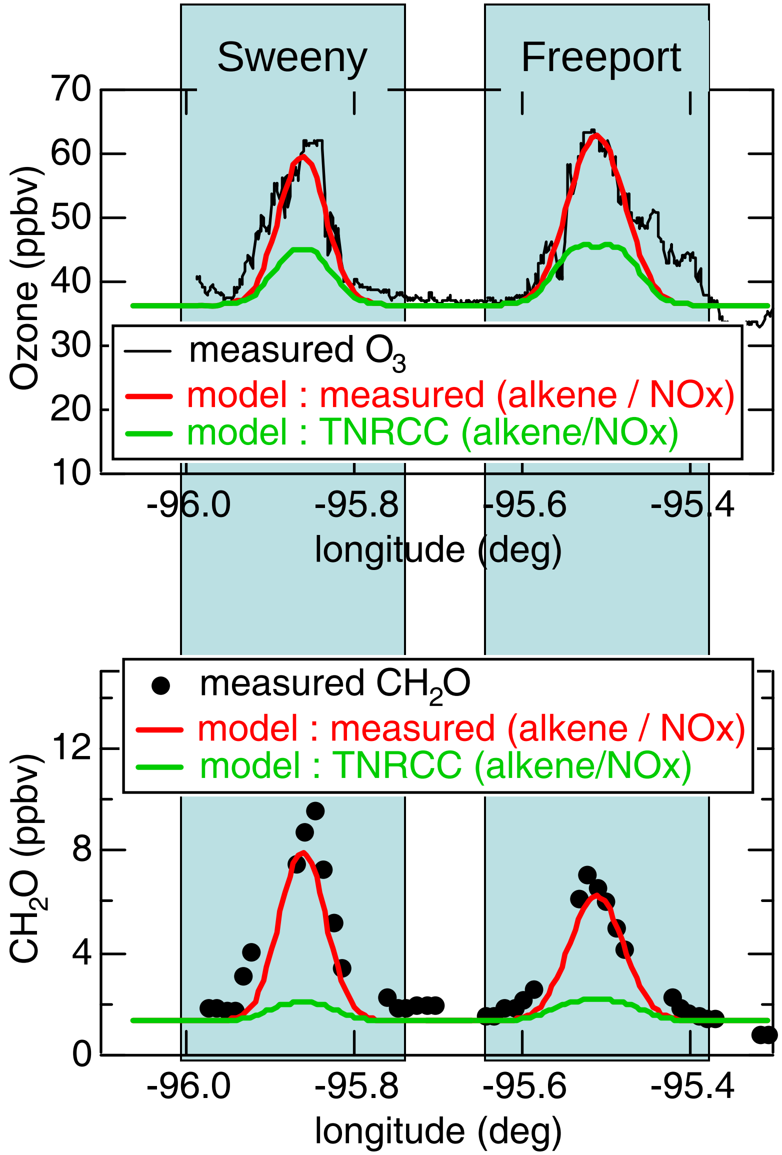


Ryerson et al. (2003), *J. Geophys. Res.*, 108, D8, 4249, doi:10.1029/2002JD003070

- Emissions of NO_x: power plants > petrochem > urban
- Emissions of VOC & CO:
  - low for most power plants, except Johnsonville (local isoprene emissions)
  - higher for urban plume
  - very high for petrochemical facilities
- Power plant NO_x must mix with VOCs from surrounding area
- Urban and petrochemical plumes: NO_x and VOCs are co-emitted

Petrochemical facilities produce more O_3 and produce it faster than other sources studied

Aircraft Data - Plume Model Comparisons in Isolated Refinery Plumes



2000 Texas Air Quality Study (TexAQS2k)

•Ethylene/NO_x and Propylene/NO_x emission ratios scaled to match observations
⇒Observed alkene/NO_x = 50-200 X inventory

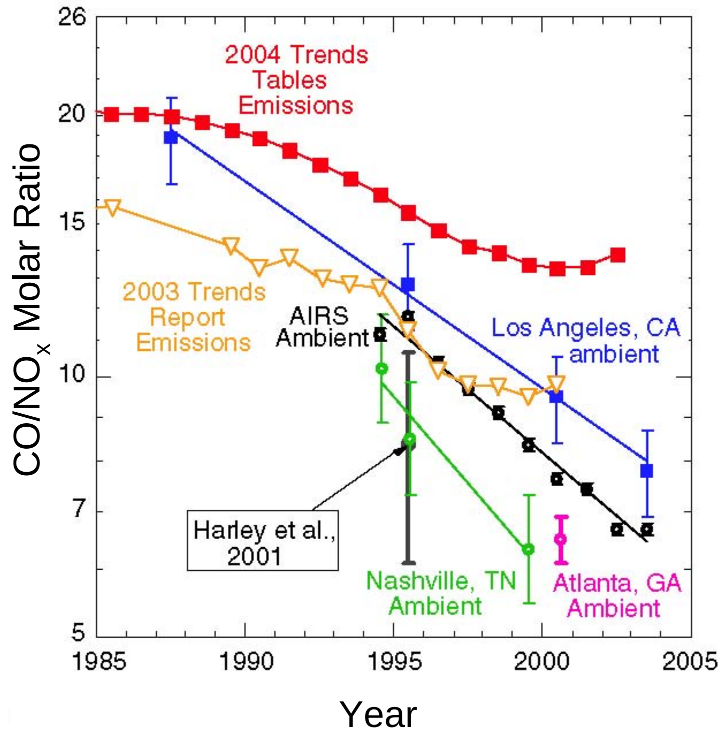
•Plume model reproduces products of alkene oxidation
⇒O_3, CH_2O
⇒not shown: CH_3CHO, PAN

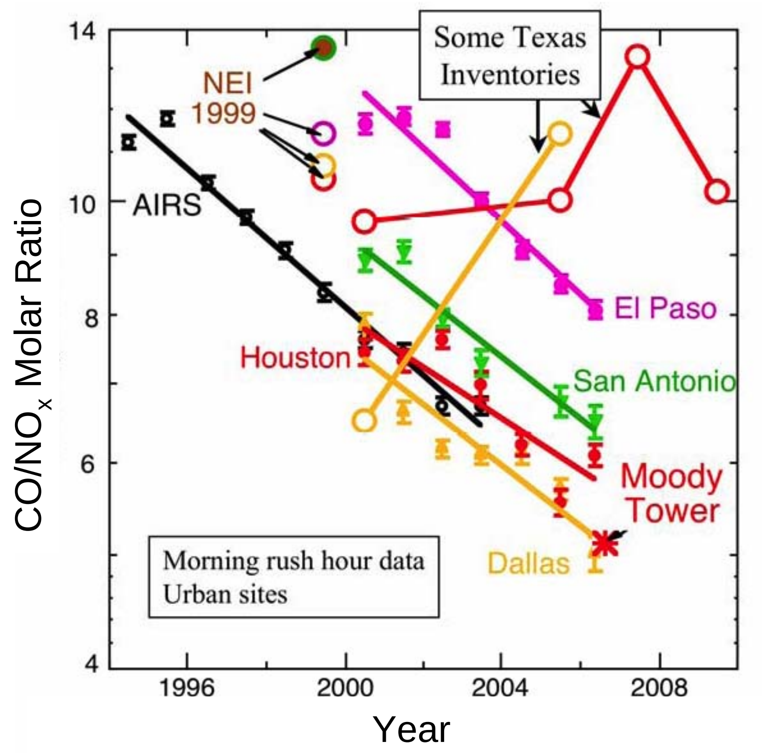
Emissions of reactive VOCs from petrochemical refineries are substantially underestimated by inventories

Models drastically under-predict O_3 and other smog constituents using existing inventories

Wert et al. (2003), *J. Geophys. Res.*, 108, D3, 4104, doi:10.1029/2002JD002502

Urban Mobile Source CO/NO_x Emissions: Measured vs. Inventory





US Urban Areas

•Rapid decrease (6.6%/yr) in CO/NO_x nationally

➢slower decrease in CO emissions (4.6%/yr)

➢significant increase in NO_x emissions (~ 2%/yr)

Texas Inventory Assessment

•Inventory overestimates mobile source CO/NO_x

➢factor of 2 overestimate in CO emissions

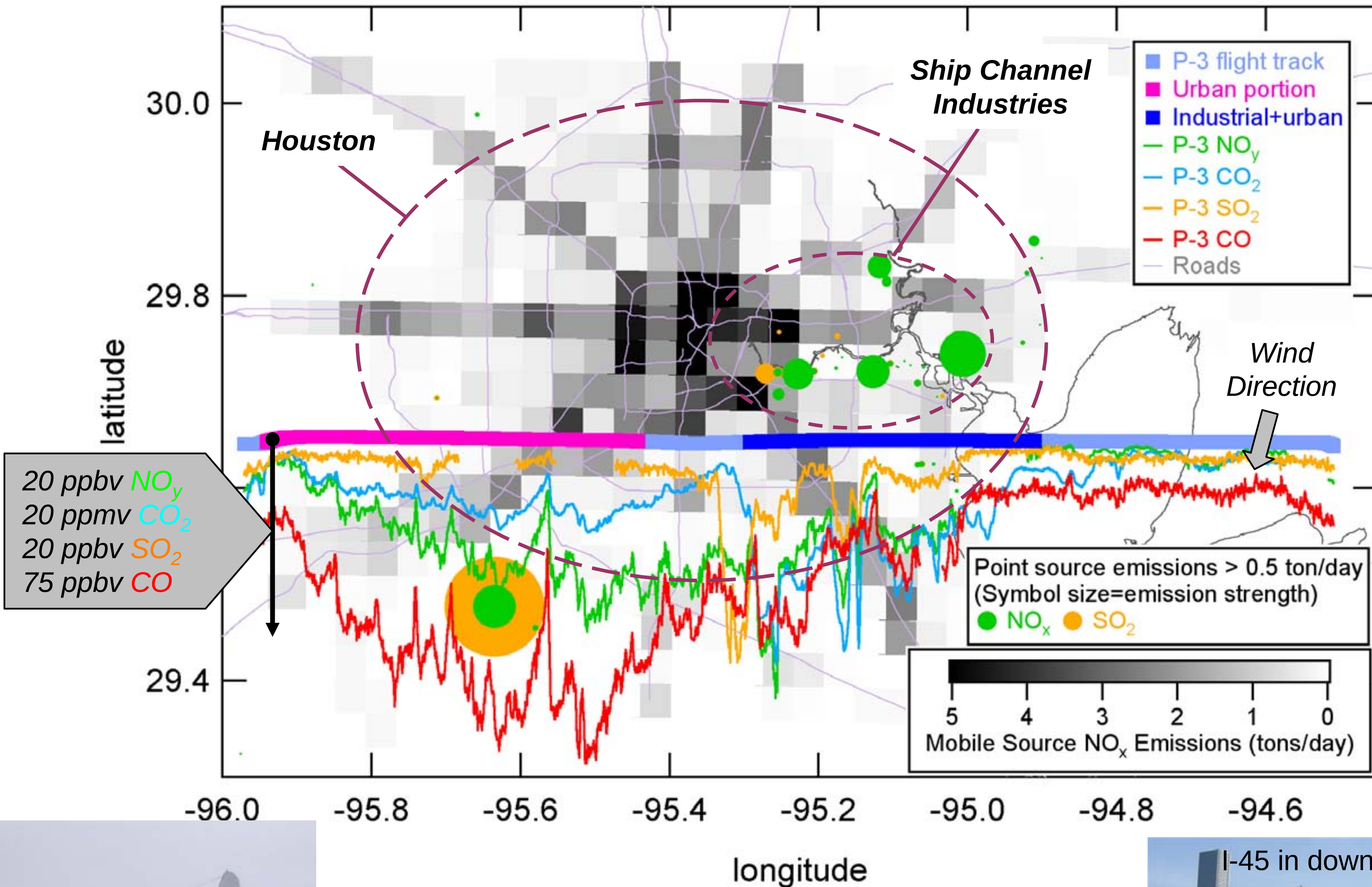
➢underestimate in NO_x emissions

➢In most urban areas, generally dominated by on-road mobile emissions, inventories will underestimate NO_x/CO and NO_x/VOC

D. D. Parrish (2006), Atmos. Environ. 40, 2288-2300

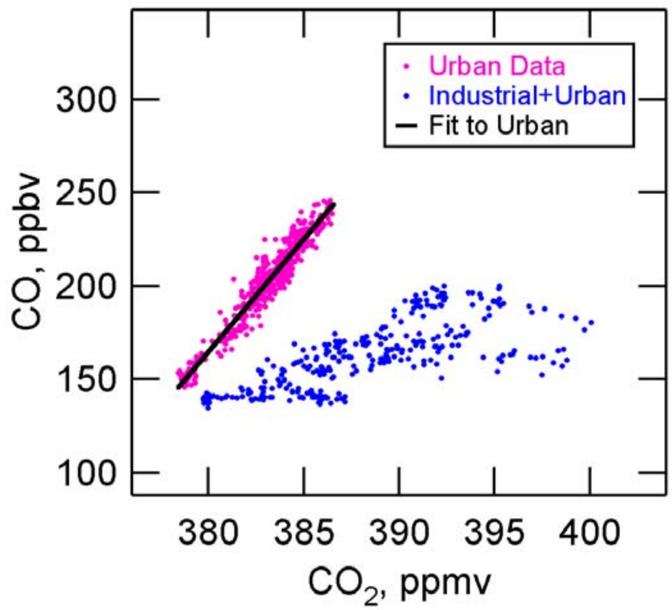
Aircraft Observations of Mobile Source Emissions

2006 Texas Air Quality Study (TexAQS2k6)



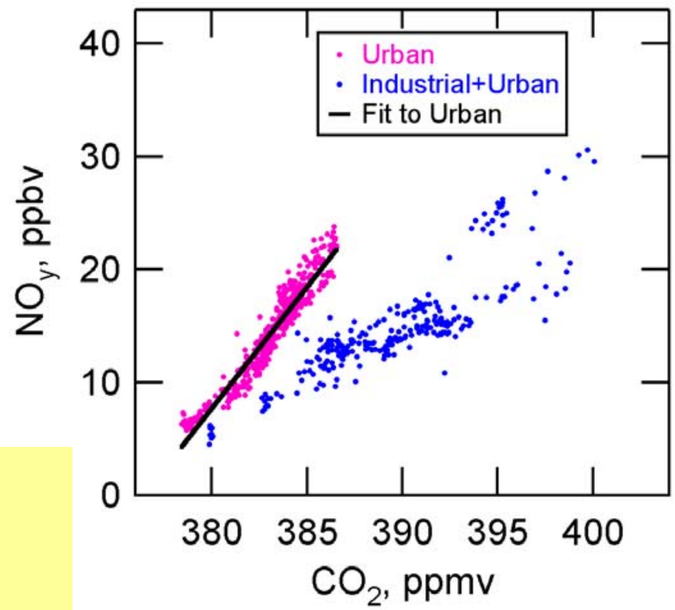
Tuesday, 26 September 2006, 1258-1318 CDT, 400-500 m altitude

Aircraft Observations of Mobile Source Emissions

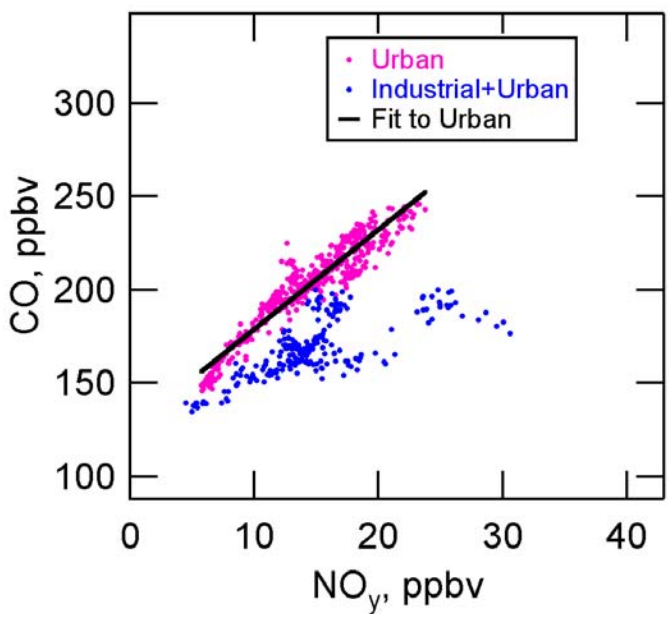


TexAQS2k6

NOAA WP-3D



Slopes of Linear Fits
Units = mole/mole
(r = correlation coefficient)
CO/CO_2 = 0.0121 (r = 0.96)
NO_y/CO_2 = 0.00215 (r = 0.96)
CO/NO_y = 5.32 (r = 0.95)



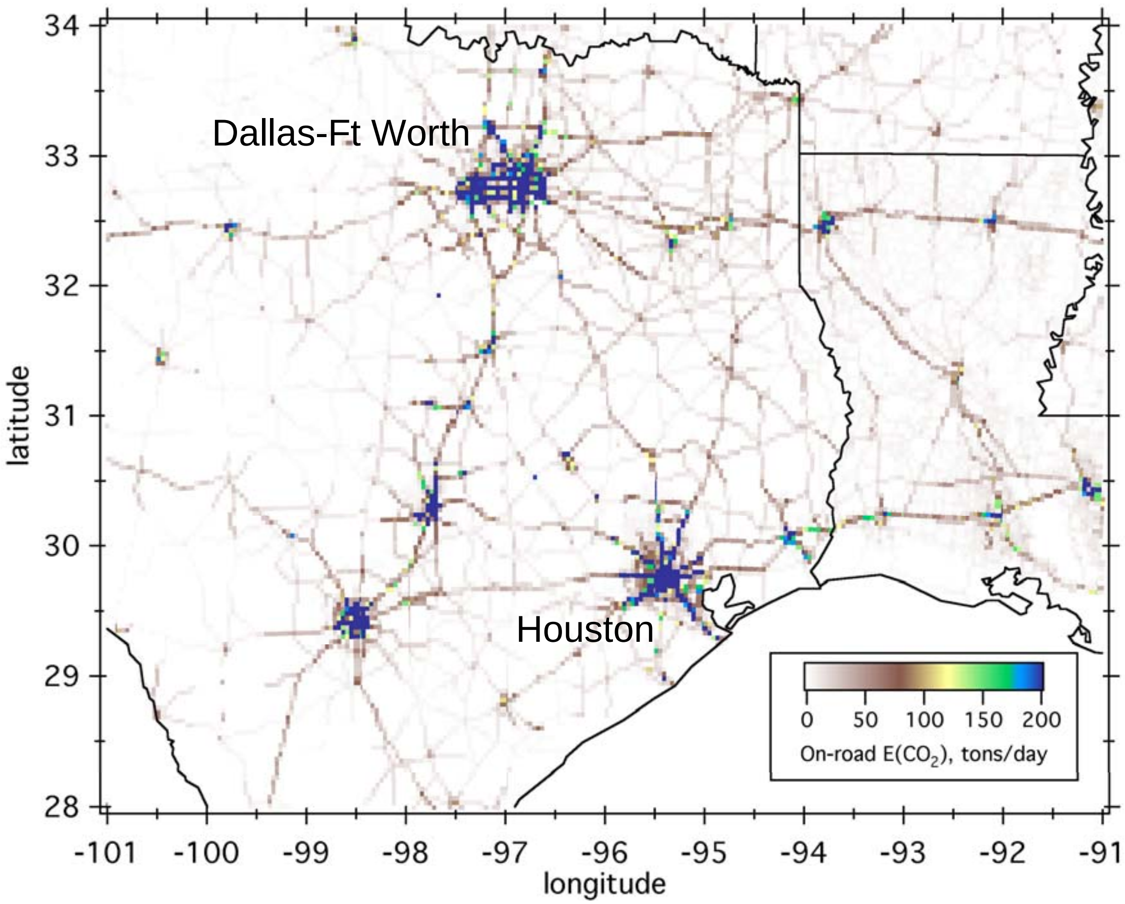
La Porte Freeway & Shell Deer Park Refinery in background

Tuesday, 26 September 2006, 1258-1318 CDT, 400-500 m altitude

US On-road Mobile Source Inventory for CO_2 & Criteria Pollutants

On-road Mobile E(CO_2) in Texas & Louisiana

4x4 km^2 Grid, 1999 Summer Daily Average



•S□tructure and grid from EPA 1999 National Emission Inventory (NEI99)

- ➢NO_x, SO_2, CO, VOCs, NH_3, $PM_{2.5}$, PM_{10}
- ➢horizontal resolution: 4x4 km^2
- ➢hourly emissions
- ➢summer ozone season day

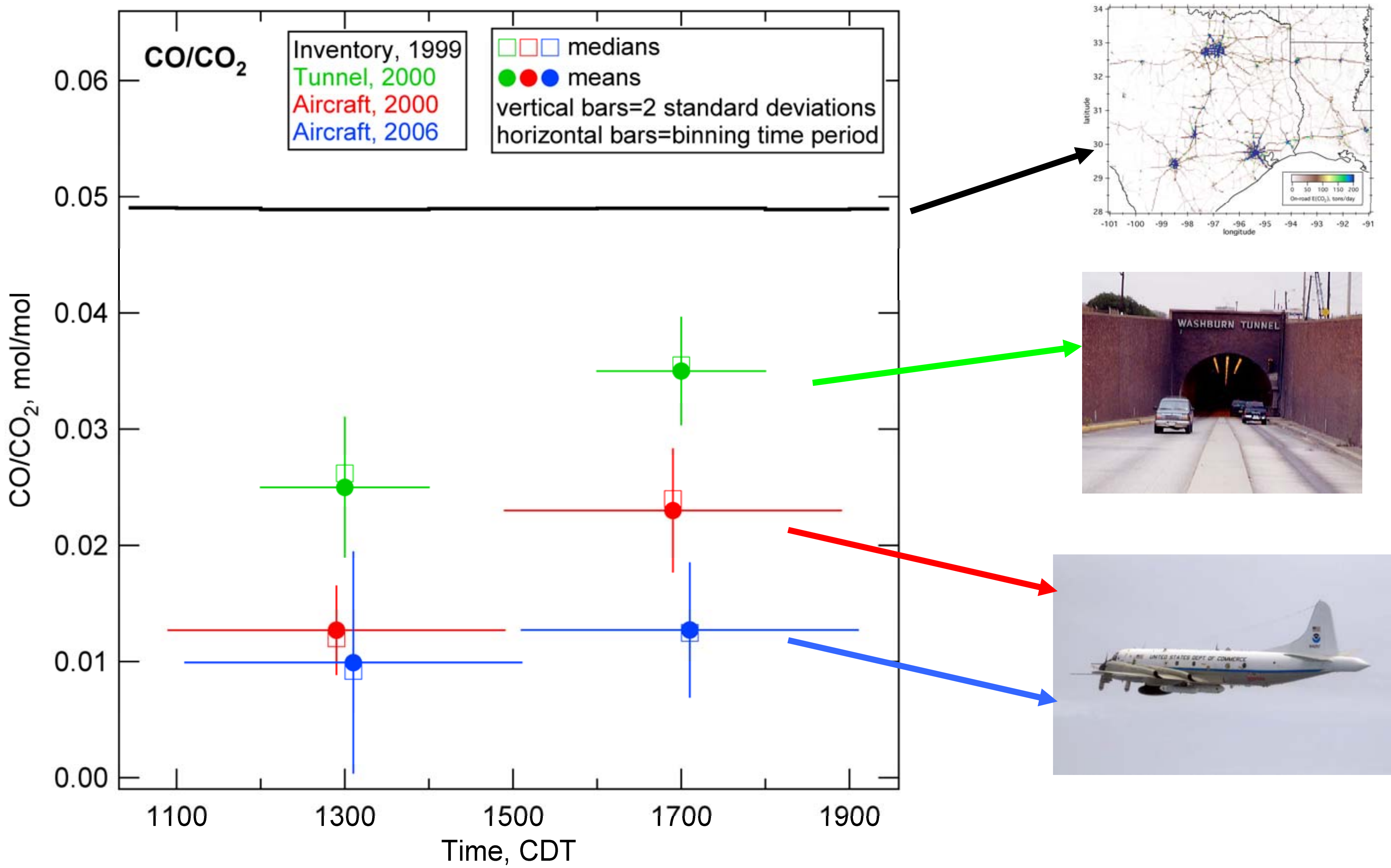
• Benefits*:*

- •*Multi-pollutant fossil fuel emission inventory*
- •*High spatial and temporal resolution*
- •*Useful for both air quality and climate studies*

Dallas-Ft Worth from International Space Station

Houston & Dallas-Ft Worth Mobile Emissions: Observations vs. Inventory

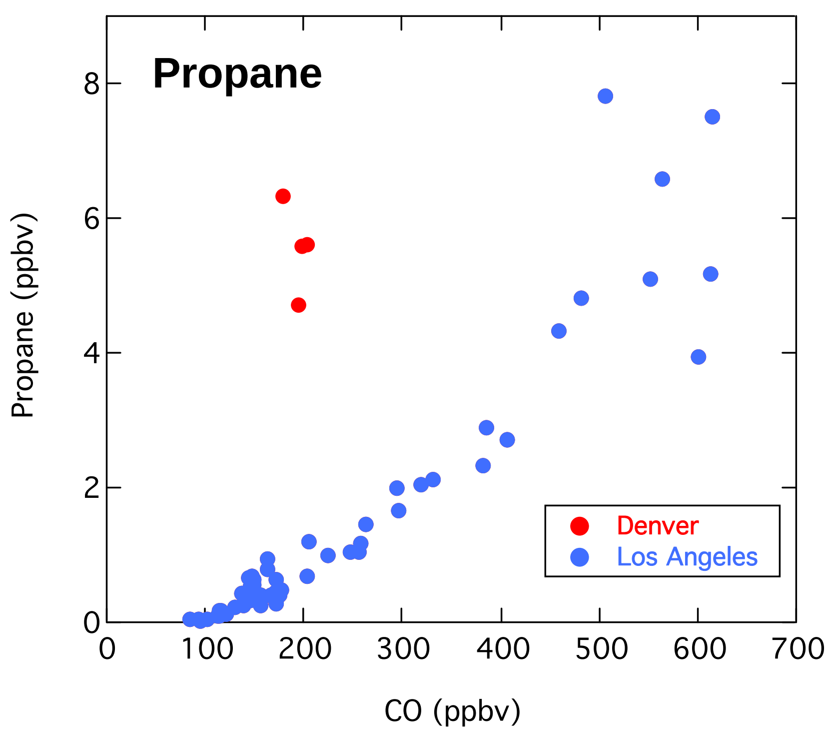
Average Molar Emission Ratios

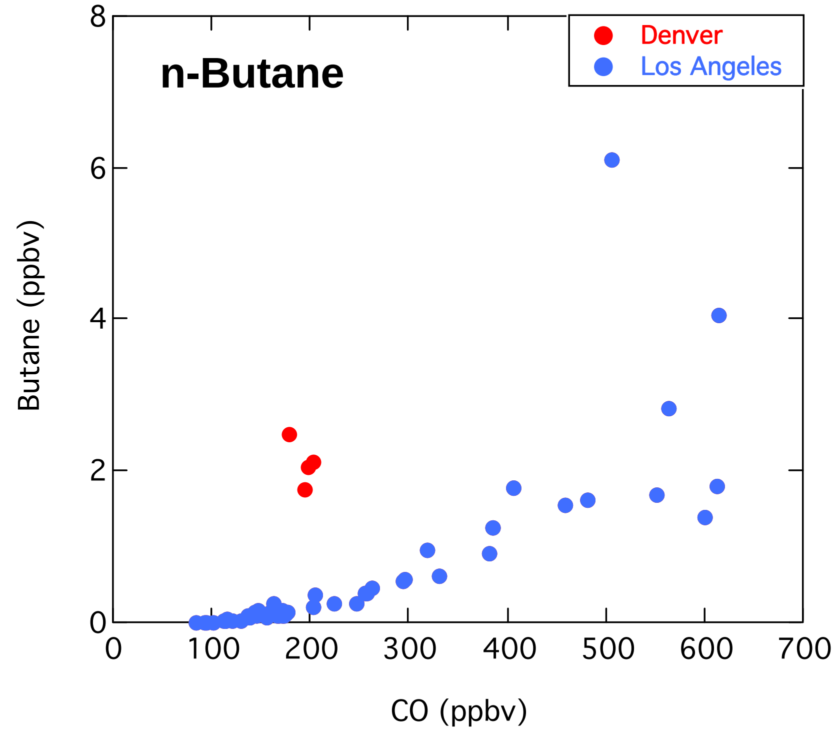


Oil & Gas Production in Colorado

Los Angeles: Urban hydrocarbon profile <==> Denver: Elevated light alkanes

Signature of emissions from oil and natural gas production





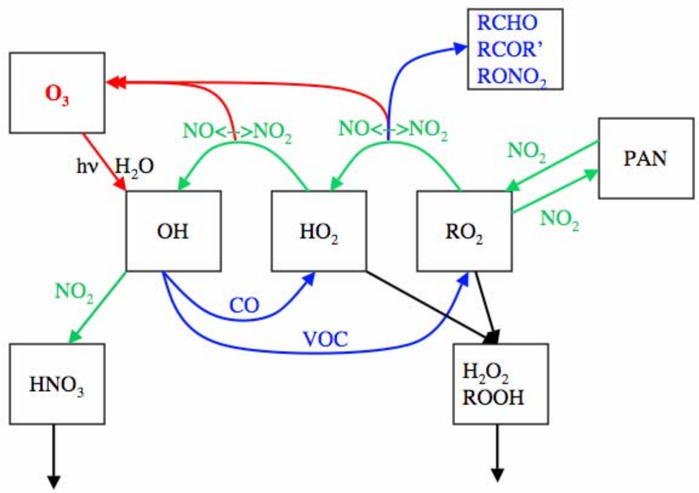
ITCT2k2 (Intercontinental Transport & Chemical Transformation 2002)

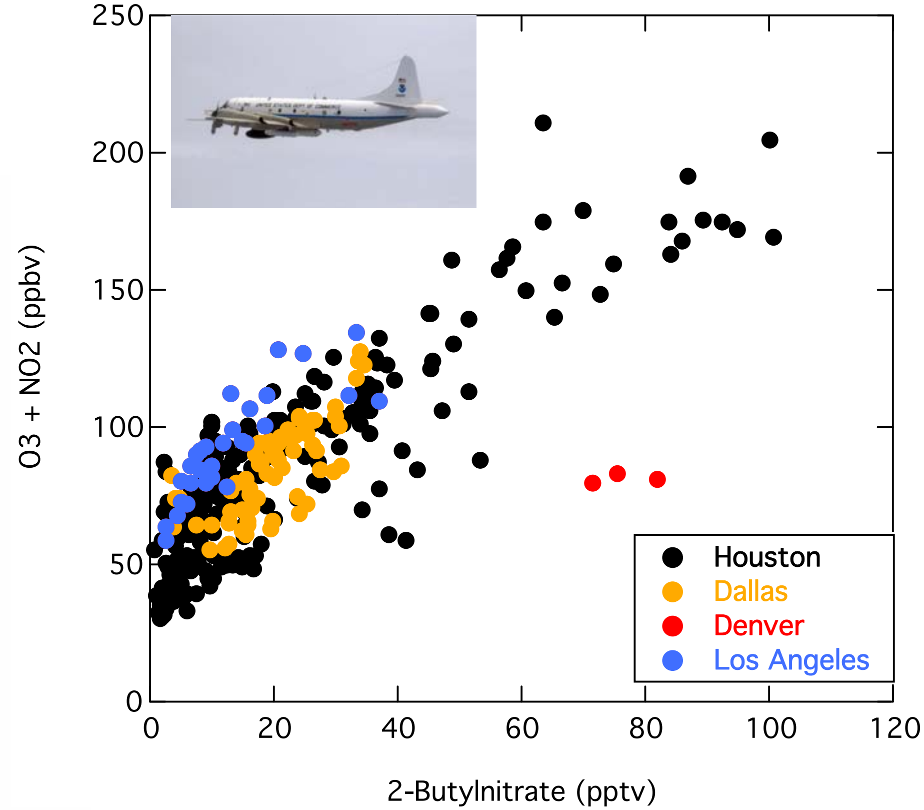
Evaluating Chemical Mechanisms for Ozone Formation

Correlation of ozone with other secondary products of photochemistry

Propane and branched alkanes produce:
•Acetone, i-Propylnitrate

N-butane produces:
•Methylethylketone, 2-Butylnitrate

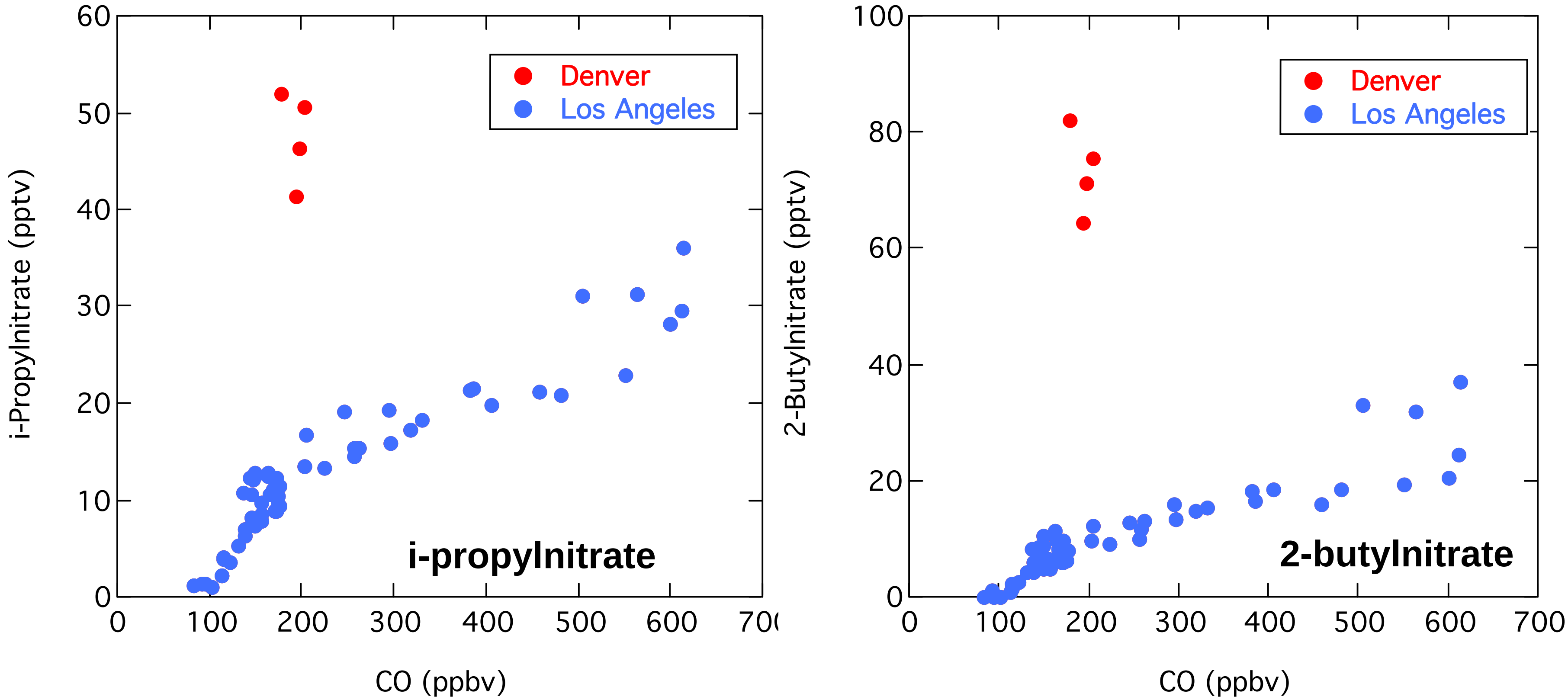




Direct contribution of butane oxidation to ozone is small

Evaluating Chemical Mechanisms for Ozone Formation

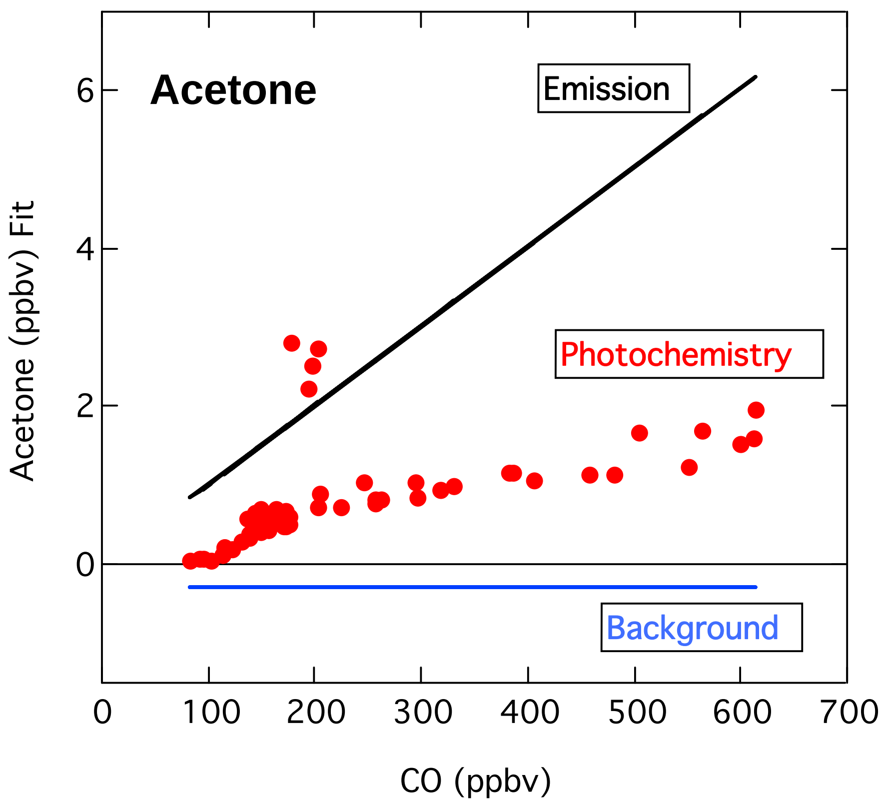
Denver:
High light alkane concentrations ==> high alkyl nitrate concentrations☐

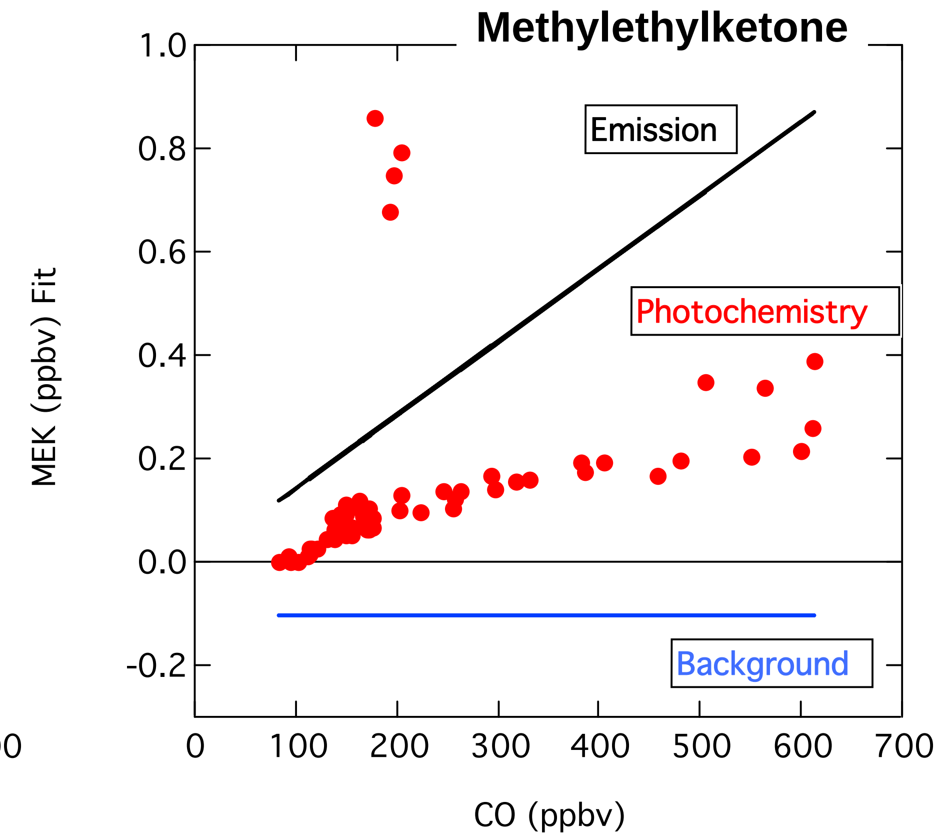


ITCT2k2 (Intercontinental Transport & Chemical Transformation 2002)

Evaluating Chemical Mechanisms for Ozone Formation

Denver: High light alkane concentrations ==> higher ketone concentrations
Acetone and Methylethylketone:
==> signature of chemical formation and direct emissions
Fit to [ketone] = a1*[CO] + a2*[RONO2] + a3
Emission + Photochemistry + Background





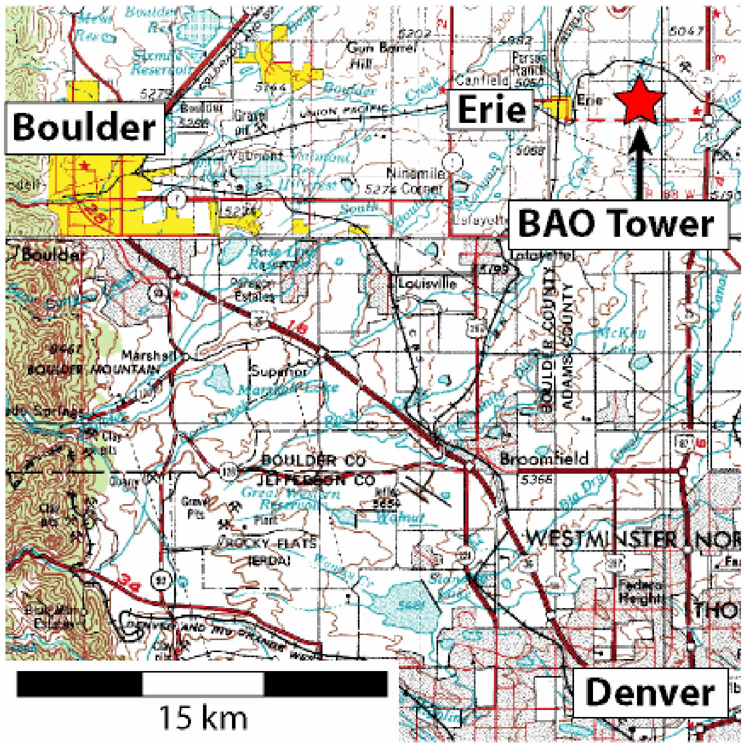
Acetone(ppbv) = 0.01***CO**(ppbv)
+ **54E-3*iPropONO2**(pptv) - **.28**
R = .95

Methylethylketone(ppbv) = **1.4E-3*CO**(ppbv)
+ **11E-3*2ButylONO2**(pptv) - **.11**
R = .96

ITCT2k2 (Intercontinental Transport & Chemical Transformation 2002)

Measuring Front Range Air Quality at the Erie Tall Tower

2007 Erie Campaign
July 29 - August 10, 2007



Goals

- Nighttime chemistry
- VOC's & SOA
- Front Range Air Quality
  (NO_x, VOC, O_3, particulates)

Erie Tower Advantages & Capabilities

- Tower is unique facility for vertical profiling and atmospheric sampling
- Erie part of rapidly developing suburban area
- Downwind of Denver
- Nearby oil and gas drilling
- Unique facility to study pollutants in stable boundary layers
- Located in an area not covered by the Front Range O_3 monitoring network

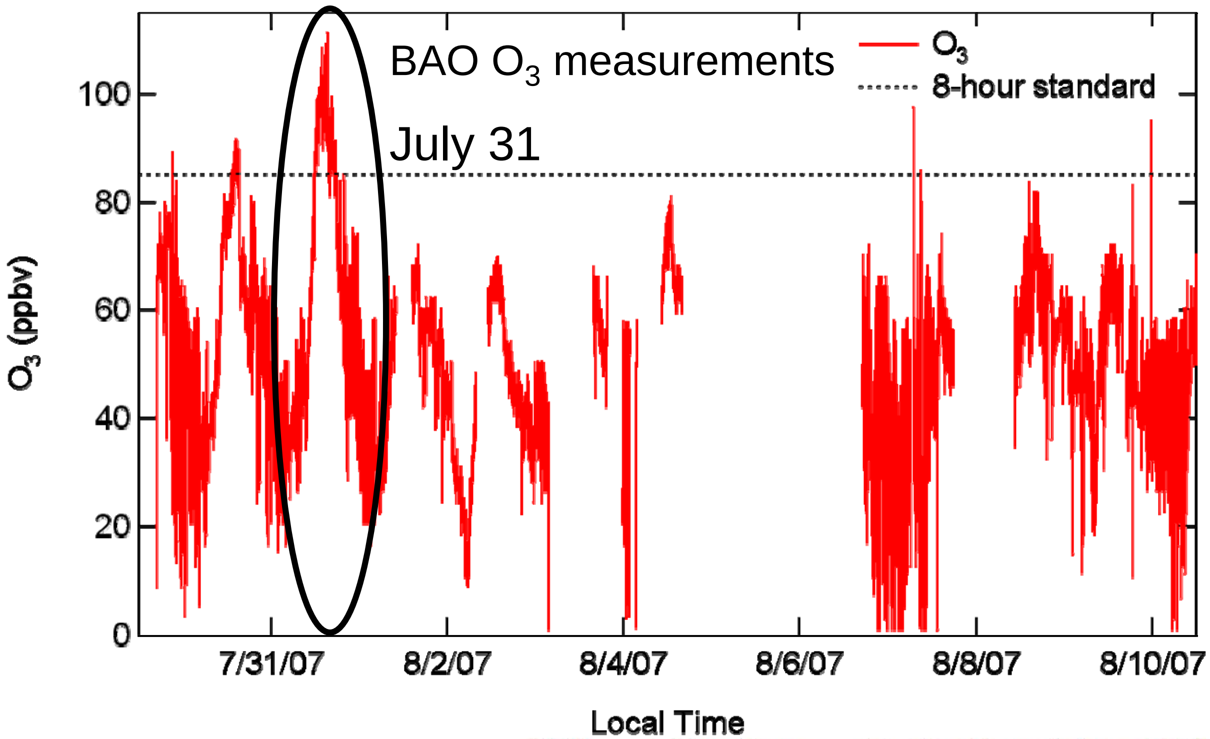
Boulder Atmospheric Observatory (BAO)

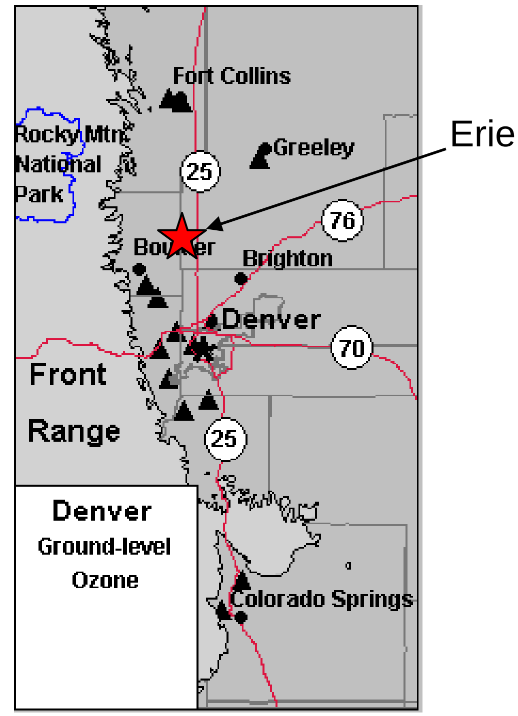
- Height = 300 m
- Movable carriage with > 1 ton capacity
- Transit time for vertical profile ≈ 9 min
  (vertical resolution = 0.6 m @ 1 Hz)

Instrumentation Summer 2007

Instrument	Location
$NO_2/NO_3/N_2O_5$ - Ring-down	Carriage
NO/O_3 - Chemiluminescence / UV Abs	Carriage
VOC - PTRMS	Carriage
Aerosol Number, Surface	Carriage
Actinc Flux - Filter Radiometers	Boom
Met Data	Boom
CO/CO_2 - GMD Carbon Tracker	3 Levels
Sonic Anemometers - U. Mass	6 Levels
Speciated VOC - GC MS	Ground
Micromet - SODAR, Tethered Balloon	Ground

2007 Campaign Highlights: O_3 Exceedances

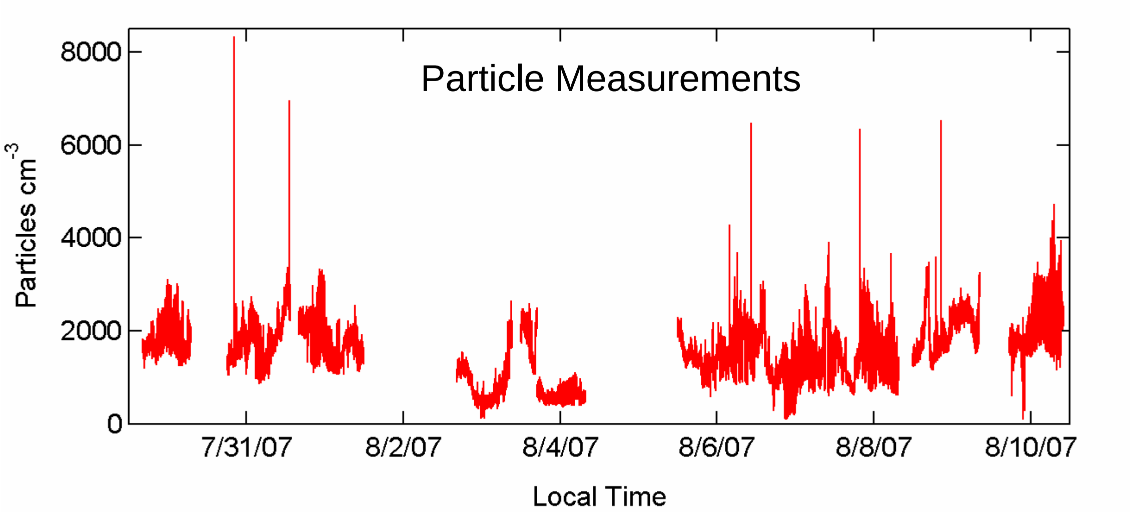


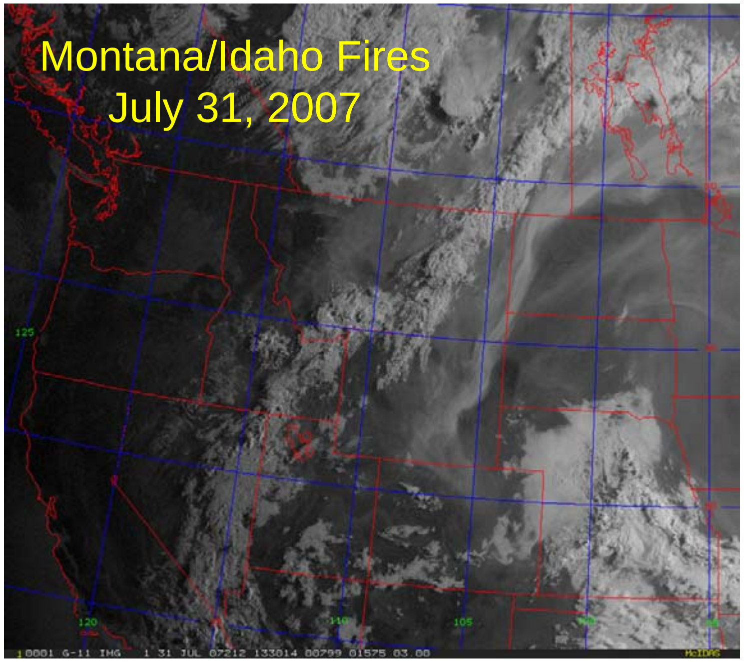


2007 8-Hour Ozone (updated through August 31, 2007)

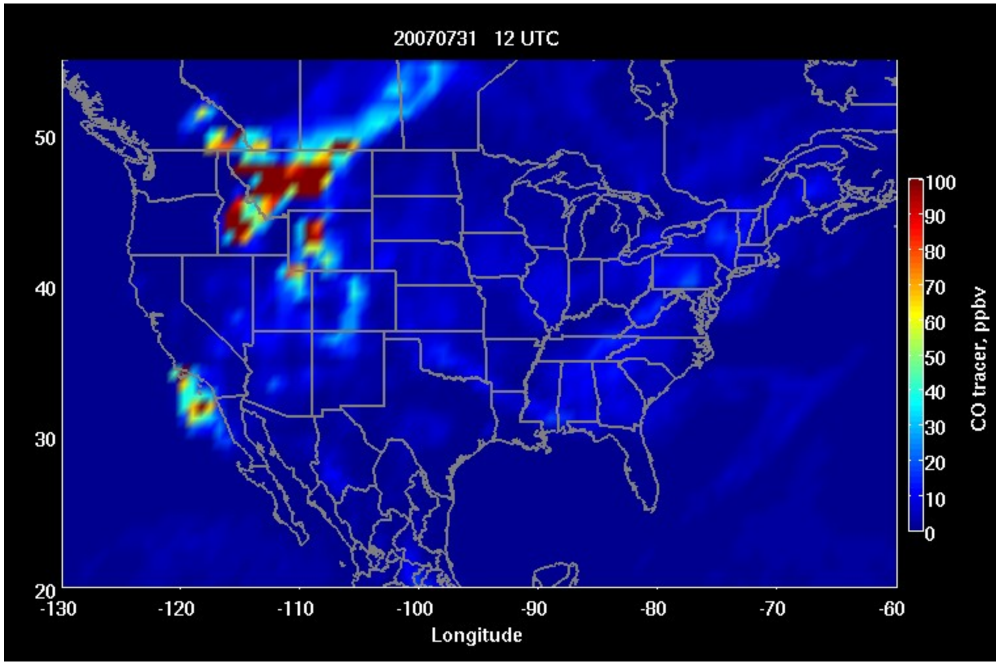
AQS Number	Site Name	1st Max 8-Hour (ppm)	Date 1st Max 8-Hour	2nd Max 8-Hour (ppm)	Date 2nd Max 8-Hour	3rd Max 8-Hour (ppm)	Date 3rd Max 8-Hour	4th Max 8-Hour (ppm)	Date 4th Max 8-Hour	5th Max 8-Hour (ppm)	Date 5th Max 8-Hour
08-001-3001	Welby	0.086	07/31	0.078	07/09	0.072	07/21	0.070	06/15	0.070	06/30
08-005-0002	Highland	0.083	07/09	0.079	07/02	0.075	06/30	0.075	07/31	0.074	04/19
08-013-0011	S. Boulder Creek	0.088	07/09	0.086	07/02	0.085	07/01	0.085	07/20	0.085	07/31
08-031-0002	CAMP	0.064	07/21	0.058	07/01	0.057	07/09	0.057	07/29	0.056	06/23
08-031-0014	Carriage	0.081	07/09	0.079	07/21	0.077	07/31	0.076	06/29	0.075	07/20
08-035-0004	Chatfield State Park	0.086	07/31	0.085	08/25	0.083	07/09	0.082	07/21	0.080	07/02
08-041-0013	Colo. Spgs. - Academy	0.076	04/19	0.073	07/13	0.072	07/31	0.071	07/09	0.071	08/14
08-041-0016	Manitou Springs	0.079	04/19	0.075	07/13	0.074	07/09	0.072	03/28	0.072	05/13
08-059-0002	Arvada	0.084	07/09	0.080	07/31	0.079	07/02	0.078	07/20	0.076	06/30
08-059-0005	Welch	0.085	07/09	0.082	06/30	0.082	07/21	0.080	07/02	0.078	07/20
08-059-0006	Rocky Flats - N	0.098	07/09	0.095	08/25	0.094	07/31	0.090	06/30	0.088	07/02
08-059-0011	NREL	0.090	07/09	0.085	06/30	0.085	07/02	0.085	08/25	0.084	07/31
08-069-0011	Ft. Collins West	0.088	07/09	0.087	06/30	0.085	07/02	0.085	07/30	0.084	07/31
08-069-1004	Ft. Collins	0.073	06/30	0.073	07/09	0.071	07/01	0.069	06/24	0.069	07/02
08-123-0009	Greeley - Weld Tower	0.076	08/16	0.075	07/21	0.074	06/24	0.074	06/30	0.074	08/17

2007 Campaign Highlights: Haze

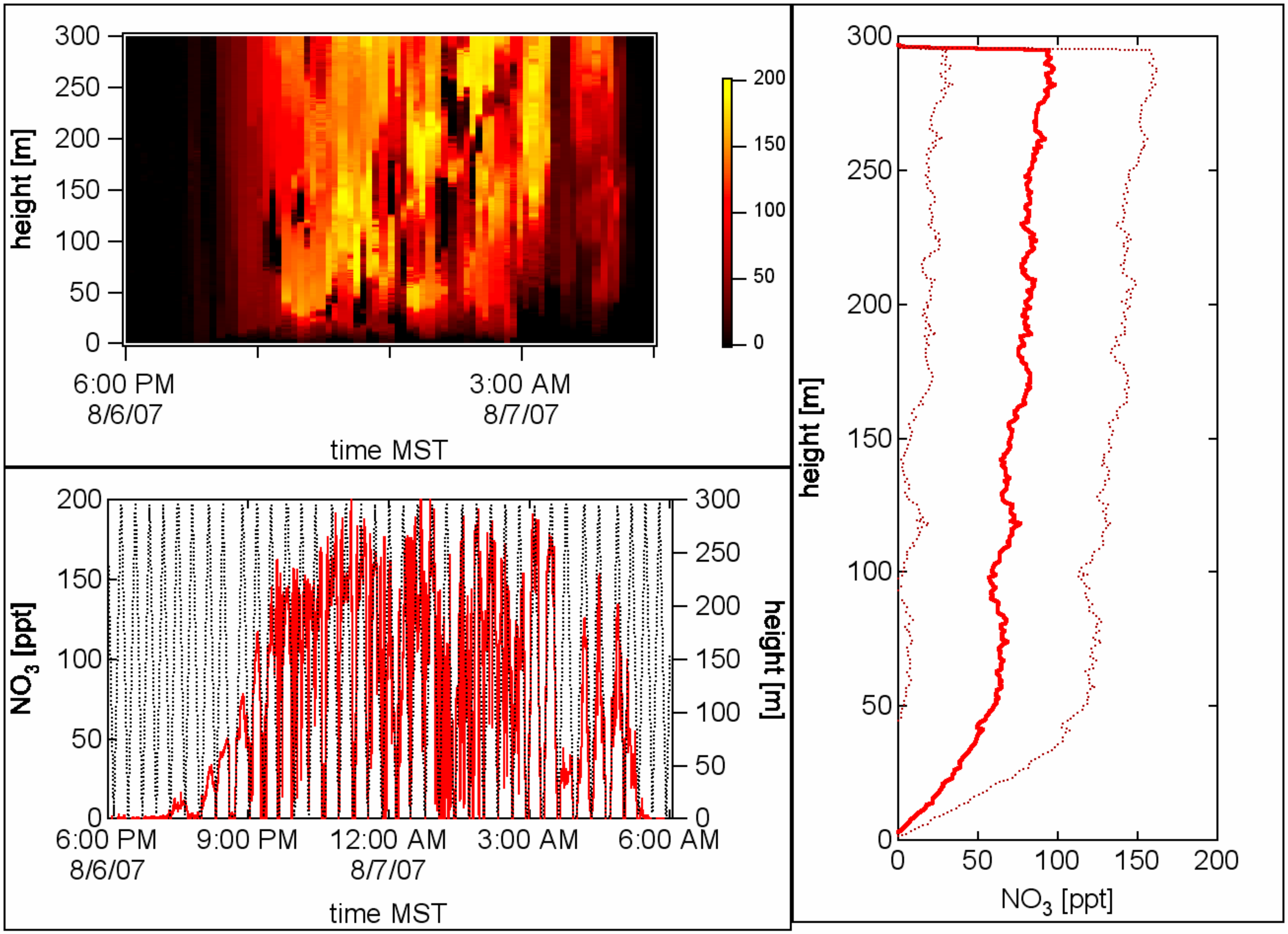




FLEXPART Boundary Layer CO



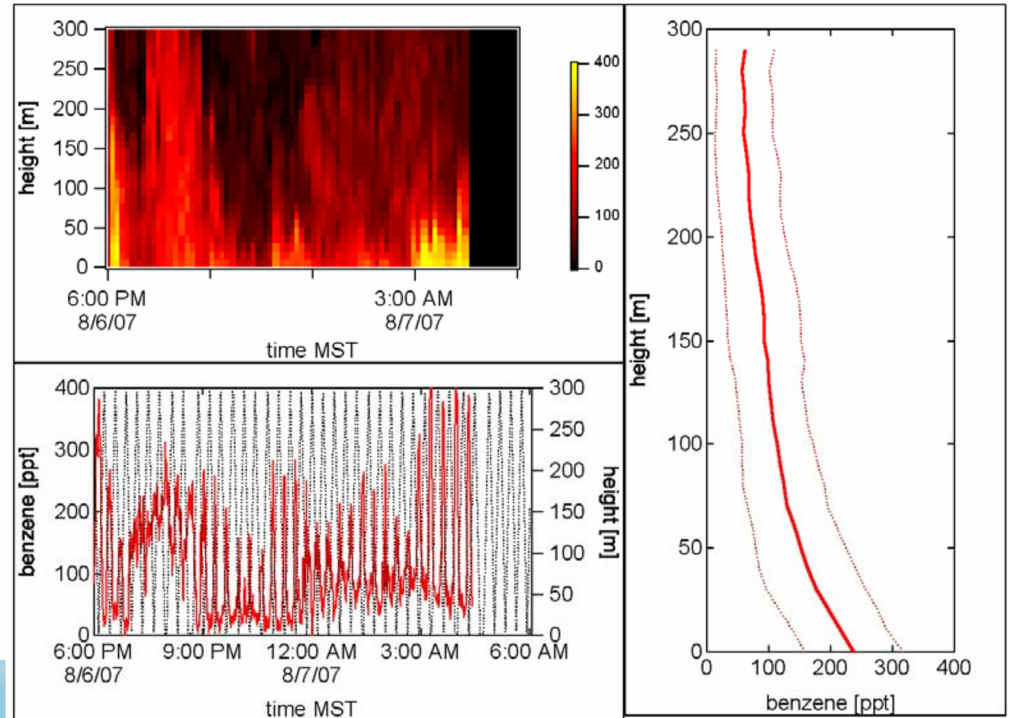
2007 Campaign Highlights: Nighttime Chemistry

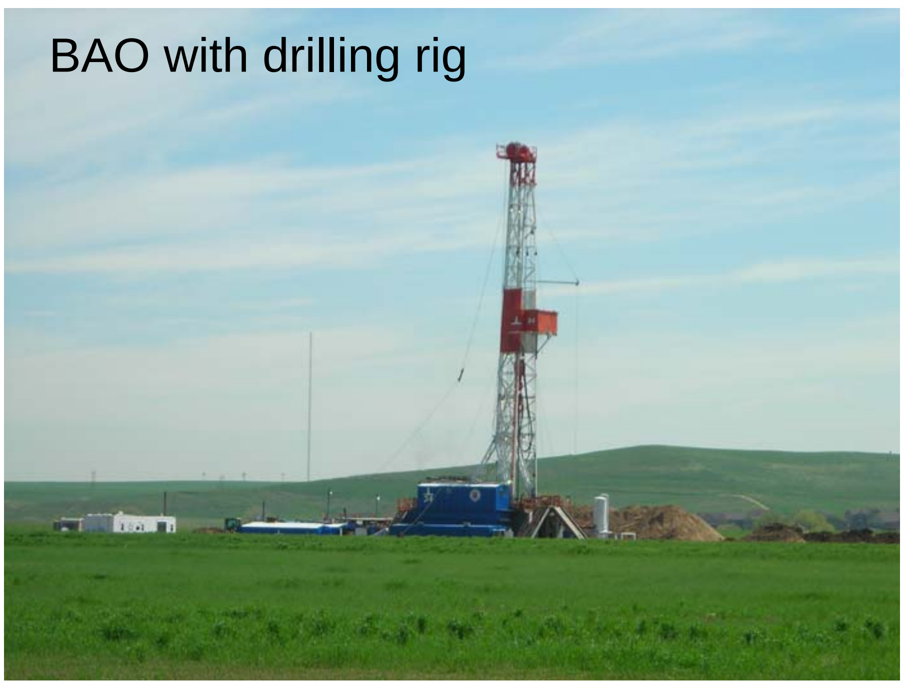


Substantial, but highly stratified, NO_x and oxidant levels at night

2007 Campaign Highlights: Front Range VOCs

Benzene as tracer for anthropogenic emissions →





← Alkanes as tracers for oil & gas development