Overview of Scavenging Studies

Alan Fried

Institute of Arctic & Alpine Research
University of Colorado

Many Other Contributors

DC3 Workshop Feb 26, 2013

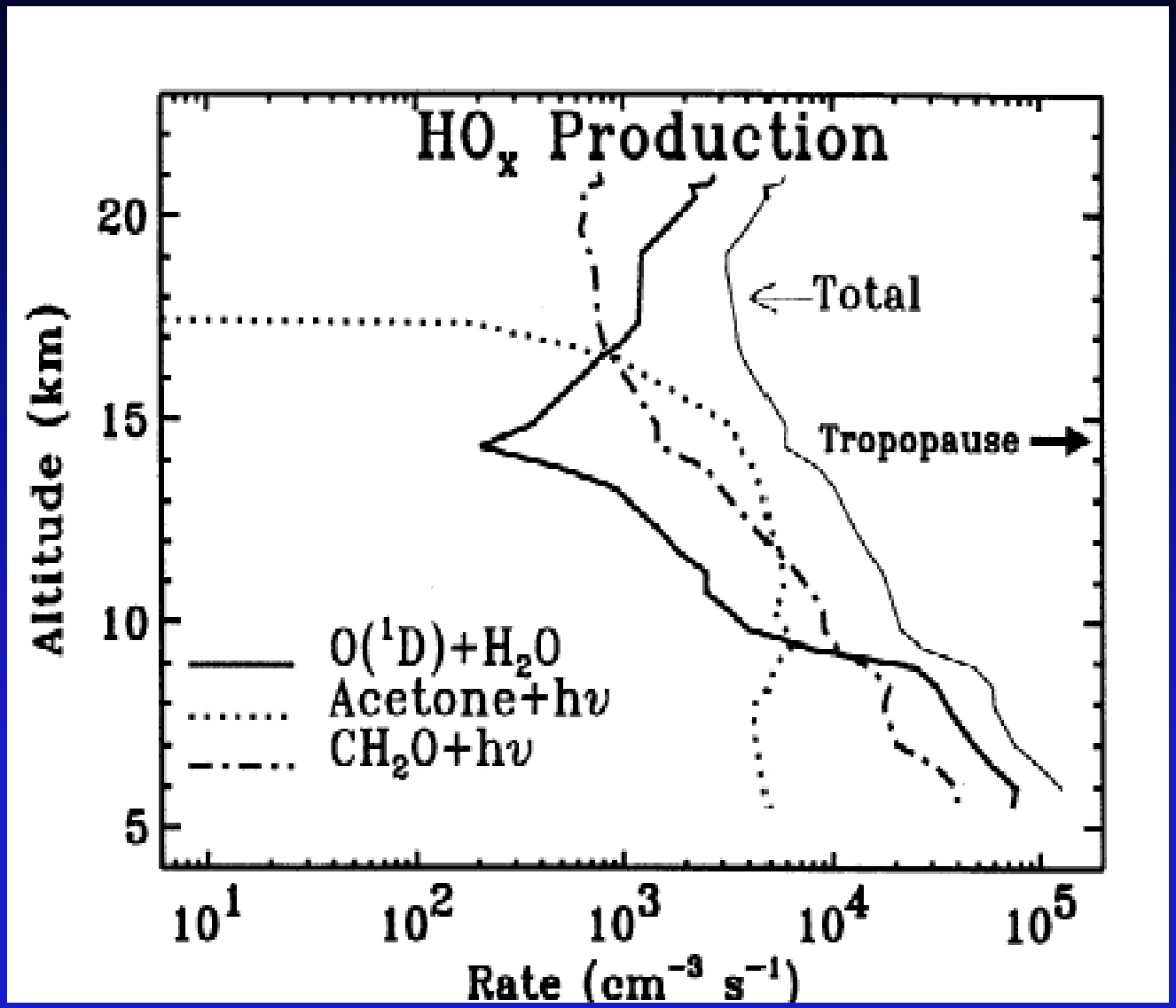
Many Soluble Trace Gases Convectively Transported to UT/LS Affect O_3

H_2O_2, CH_3OOH, CH_3OH, CH_2O, CH_3COCH_3 ……

Production (O_3) – Loss (O_3)

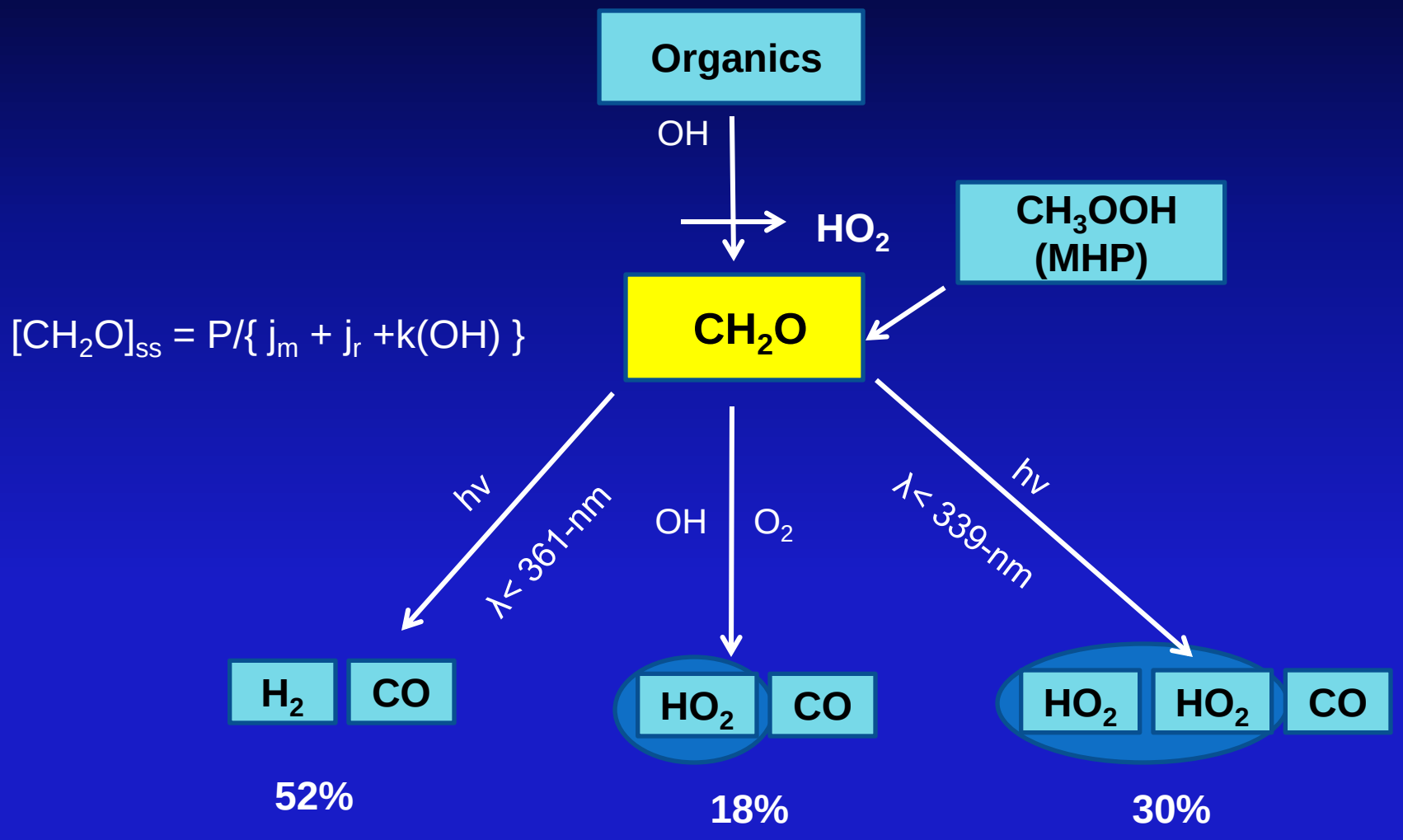
$$= k_1[NO][HO_2] - \{k_4[O(^1D)][H_2O] + k_6[HO_2][O_3] + k_5[OH][O_3]\}$$

Diel Steady State HO_x Production During STRAT

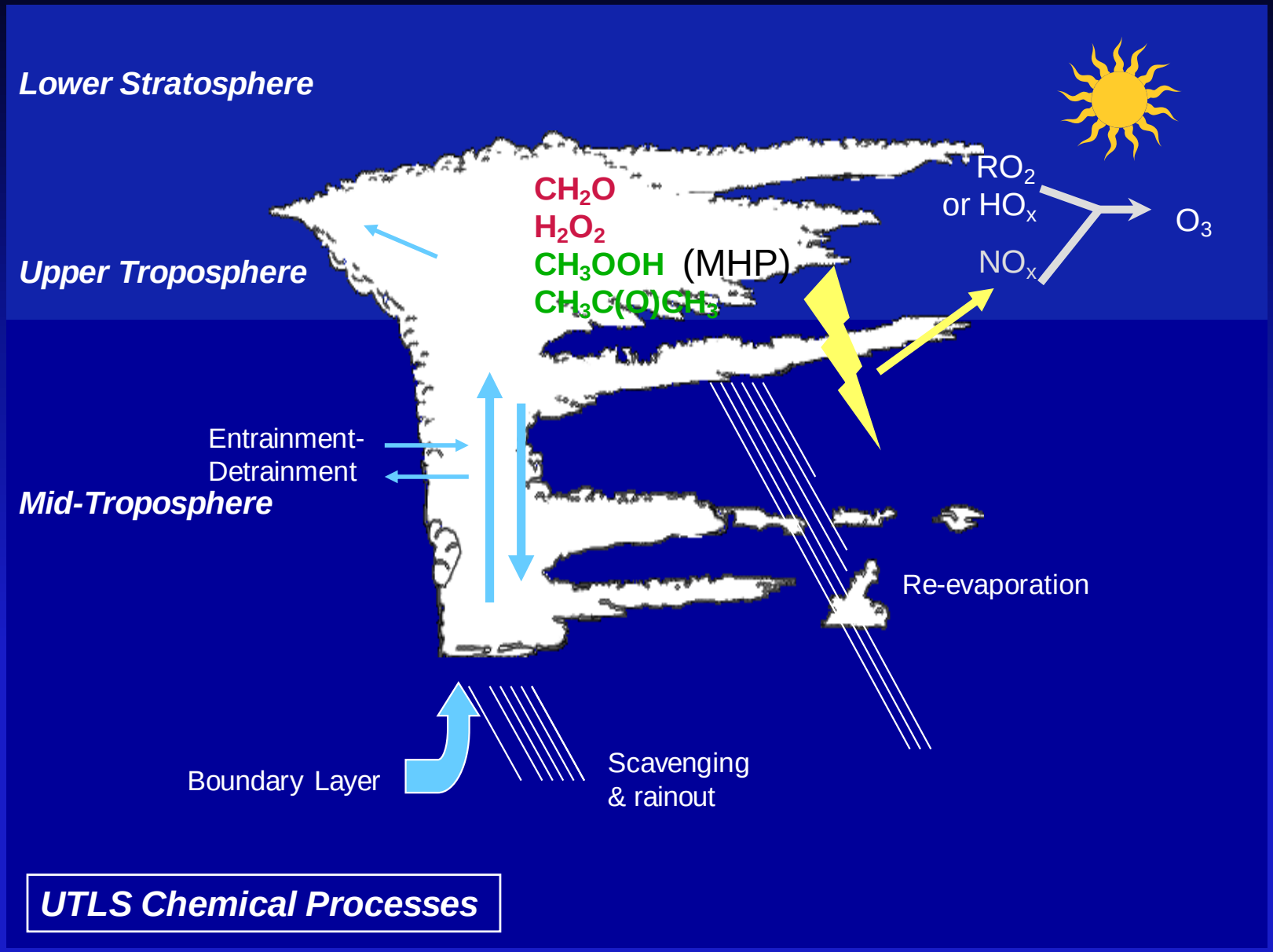


Jaegle et al., GRL 24, 3181, 1997

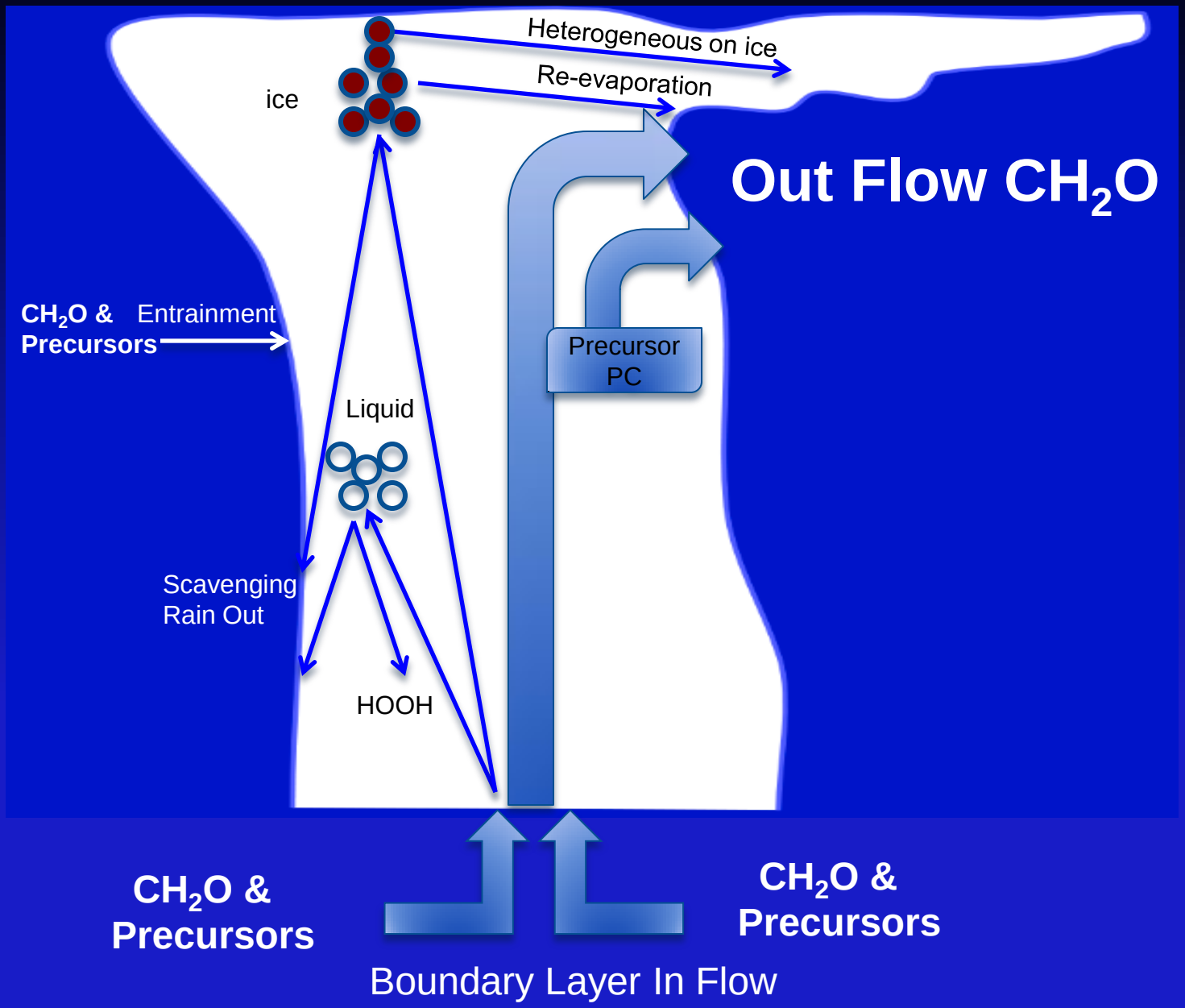
CH_2O Important Source of HO_2 Radicals in UT/LS



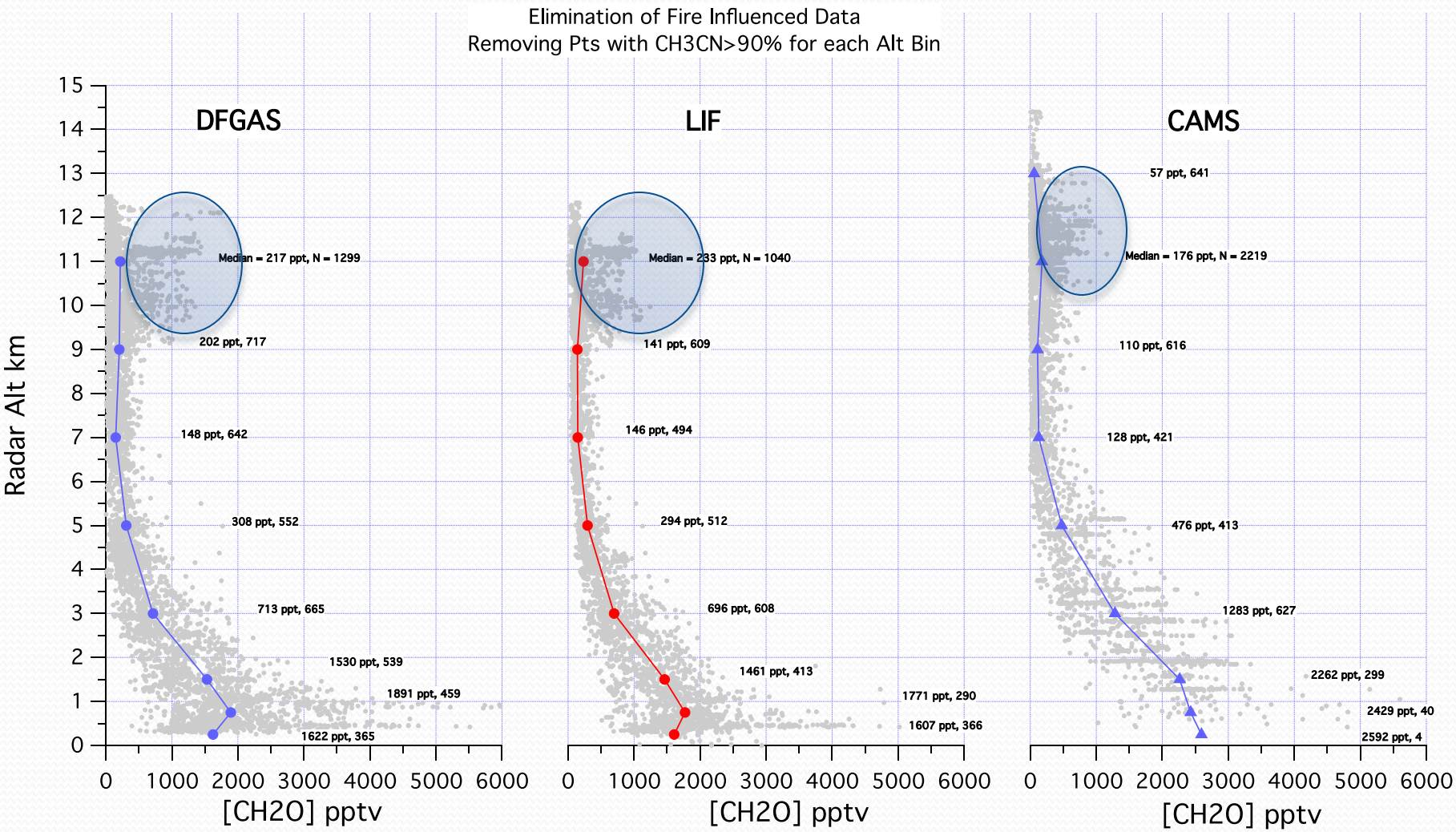
Convection of Important O_3 Precursors



Important Processes Involving CH_2O Convection



1-Minute Merged CH2O Data (Feb Merge) Eliminated Fire Influenced Points Reveals CH_2O UT Enhancements up to 1.5 ppbv



Determining CH_2O Scavenging Efficiencies (SE) Using a 3-Component Mixture Model
A. Borbon et al., JGR 2012

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 117, D12301, doi:10.1029/2011JD017121, 2012

Transport and chemistry of formaldehyde by mesoscale convective systems in West Africa during AMMA 2006

Agnès Borbon,[1] M. Ruiz,[1] J. Bechara,[1] B. Aumont,[1] M. Chong,[2] H. Huntrieser,[3] C. Mari,[2] C. E. Reeves,[4] Georges Scialom,[5] T. Hamburger,[3,6] H. Stark,[7,8,9] C. Afif,[1,10] C. Jambert,[2] G. Mills,[4] H. Schlager,[3] and P. E. Perros[1]

Determining CH_2O Scavenging Efficiencies (SE) Using a 3-Component Mixture Model
A. Borbon et al., JGR 2012

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 117, D12301, doi:10.1029/2011JD017121, 2012

Transport and chemistry of formaldehyde by mesoscale convective systems in West Africa during AMMA 2006

Agnès Borbon,[1] M. Ruiz,[1] J. Bechara,[1] B. Aumont,[1] M. Chong,[2] H. Huntrieser,[3] C. Mari,[2] C. E. Reeves,[4] Georges Scialom,[5] T. Hamburger,[3,6] H. Stark,[7,8,9] C. Afif,[1,10] C. Jambert,[2] G. Mills,[4] H. Schlager,[3] and P. E. Perros[1]

Interesting Approach, But Requires Lots of Verification

Non-Soluble Tracer(s) (X)

$$X_{CONV} = \beta X_{BL} + \alpha X_{FT} + (1-\beta-\alpha)X_{UT}$$

Mixing Ratios:

X_{CONV} = In Convective Outflow
X_{BL} = In Boundary Layer
X_{FT} = In Mid-Level Free Tropospheric Air
X_{UT} = In Background Upper Troposphere

Fractions

α = Fraction of Mid-Level Air Entrained in Cloud
β = Fraction of BL Air in Fresh Convection UT Air

Employ 2 or more Tracers to Determine α, β

Soluble Species (Y)

$$Y_{CONV} = (1-SE)\beta Y_{BL} + \alpha Y_{FT}(1-SE) + (1-\beta-\alpha)Y_{UT}$$

Scavenging Efficiency (SE)

$$SE = 1 - \frac{Y_{CONV} - (1-\beta-\alpha)Y_{UT}}{\beta Y_{BL} + \alpha Y_{FT}}$$

Determining CH_2O SE

- **Photochemical Production of CH_2O**

  - Enhanced Production From Lightning NO (causes non-uniform production vertically which dramatically affects PCH_2O, RO_2+ NO)

- **Assumption of Constant SE for BL and FT air**

- **Uncertainty in Some Terms**

  - What values to use peak, median (some cases big diff.)?

- **Ambiguities Properly Connecting In Flow & Out Flow Regions**

- **Employing SS-Box Model (Need Lagrangian Model)**

- **Complications From Fire Plumes**

Cannot Ignore Photochemical Production of CH_2O

JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 113, D17306, doi:10.1029/2007JD009760, 2008

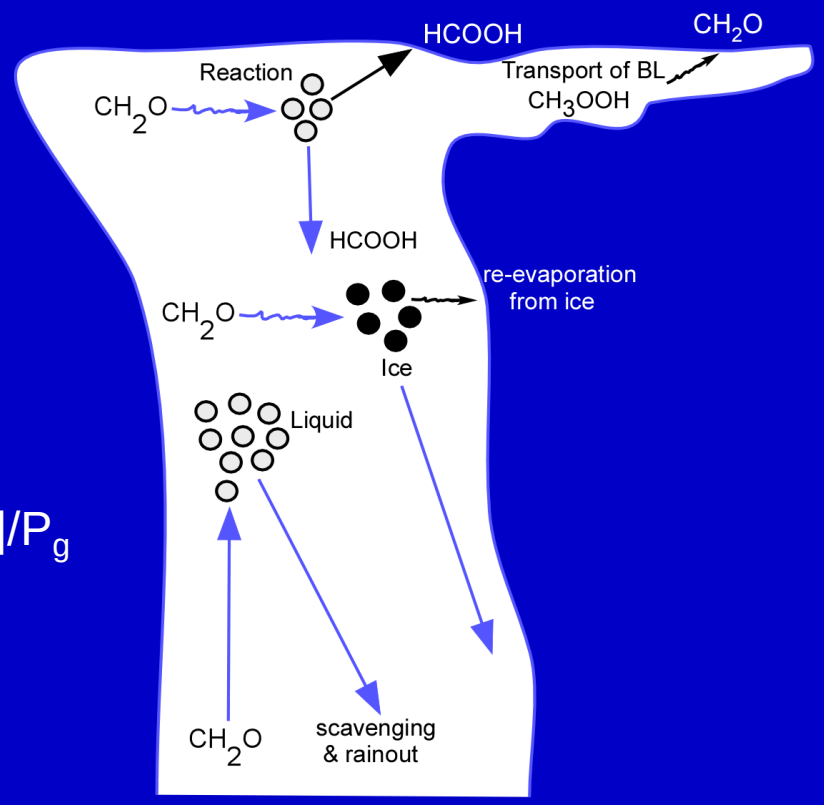
Click Here for Full Article

Role of convection in redistributing formaldehyde to the upper troposphere over North America and the North Atlantic during the summer 2004 INTEX campaign

Fried et al. JGR 2008

- **At least 70% of elevated UT CH_2O observations arise from convection of precursors rather than direct transport of BL CH_2O**
- **Transport of lower solubility precursors like MHP, methanol, ethene can affect UT CH_2O levels**

Relative Solubility of Trace Gases

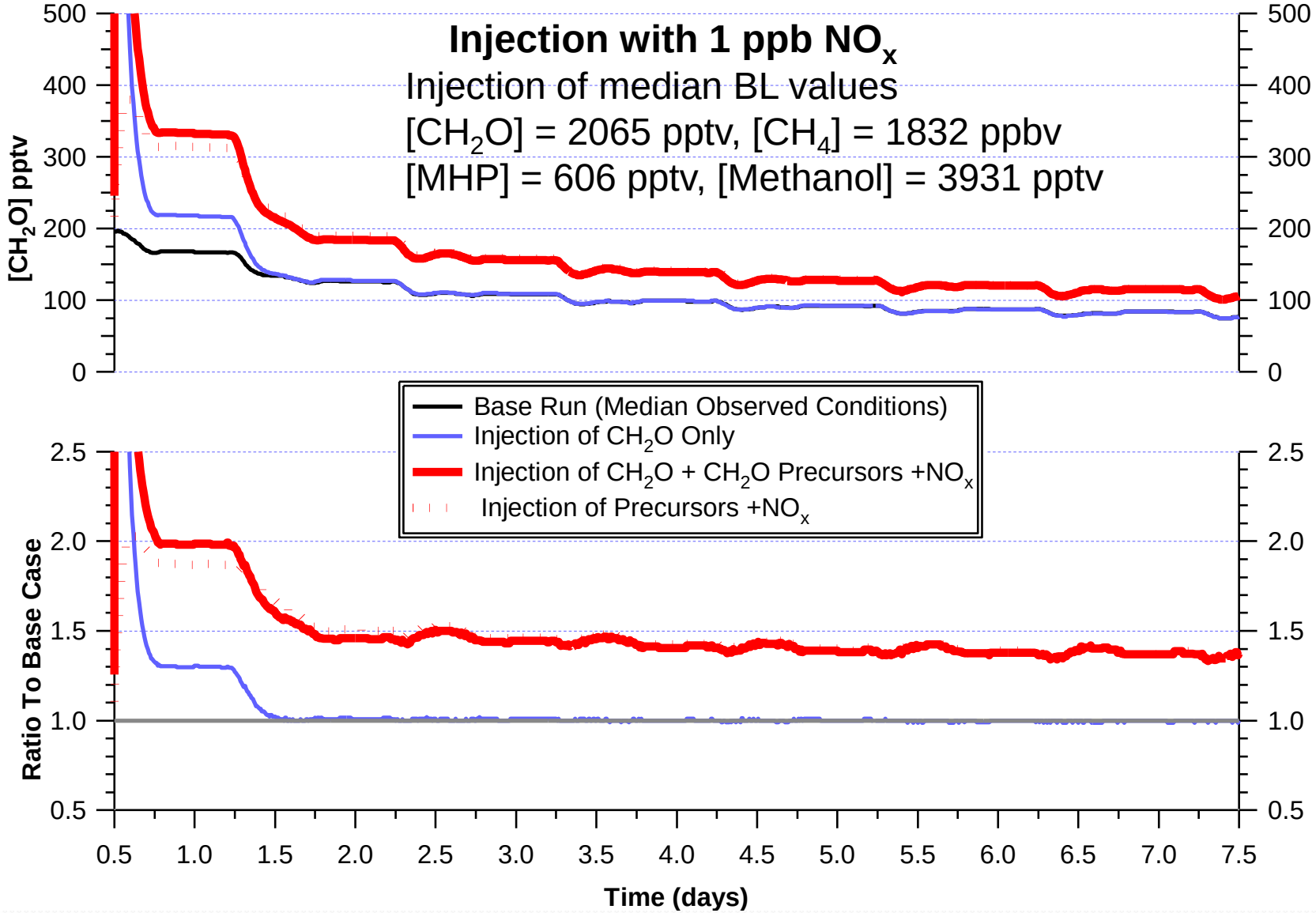


$H = [C_L]/P_g$

$H_{298\ K}$ (M/atm.)

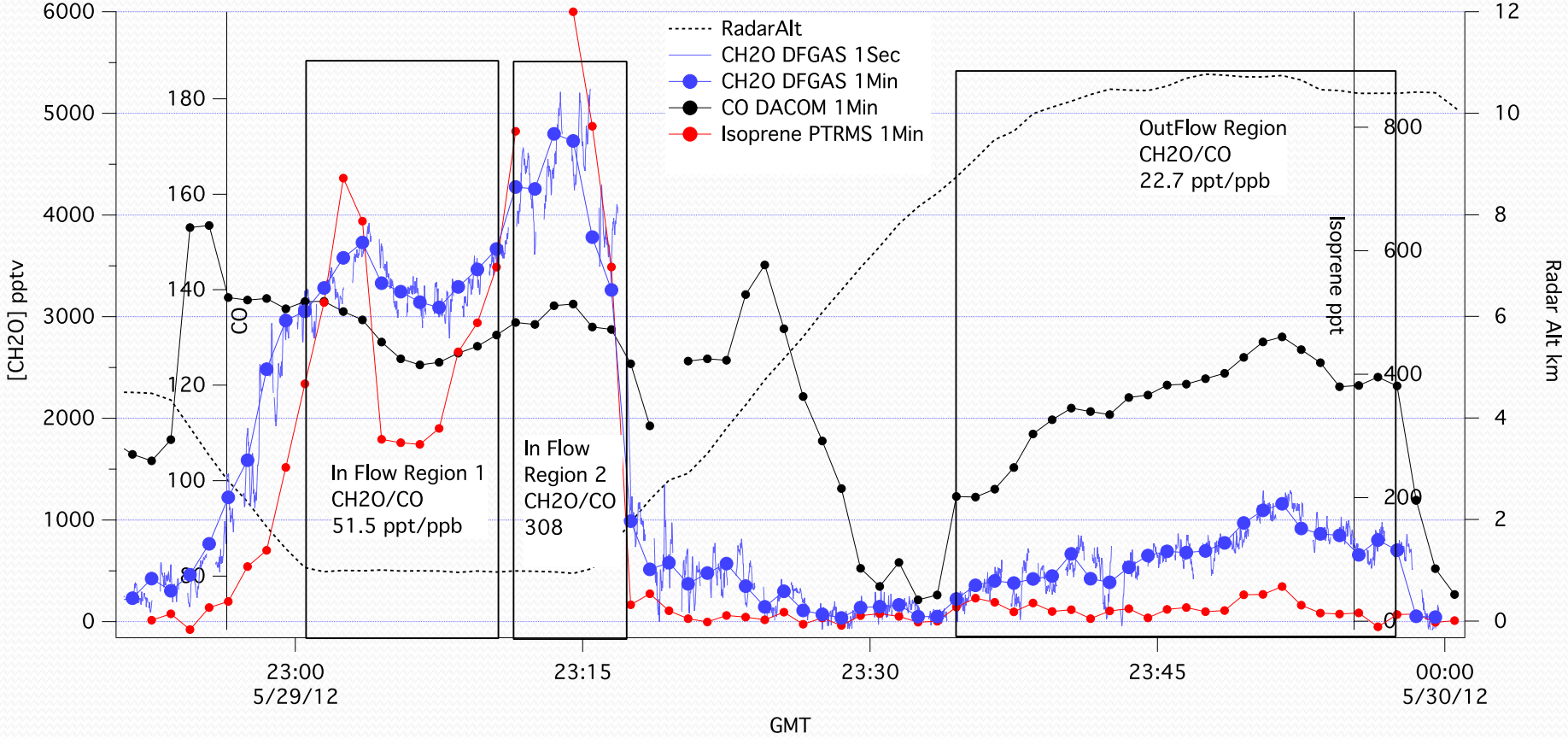
CH_3OH	CH_3OOH	CH_2O	H_2O_2	HNO_3
220	311	6.3×10^3	8.3×10^4	2.1×10^5

Direct CH_2O Injection at 9 km versus Injection of its Precursors During INTEX-NA

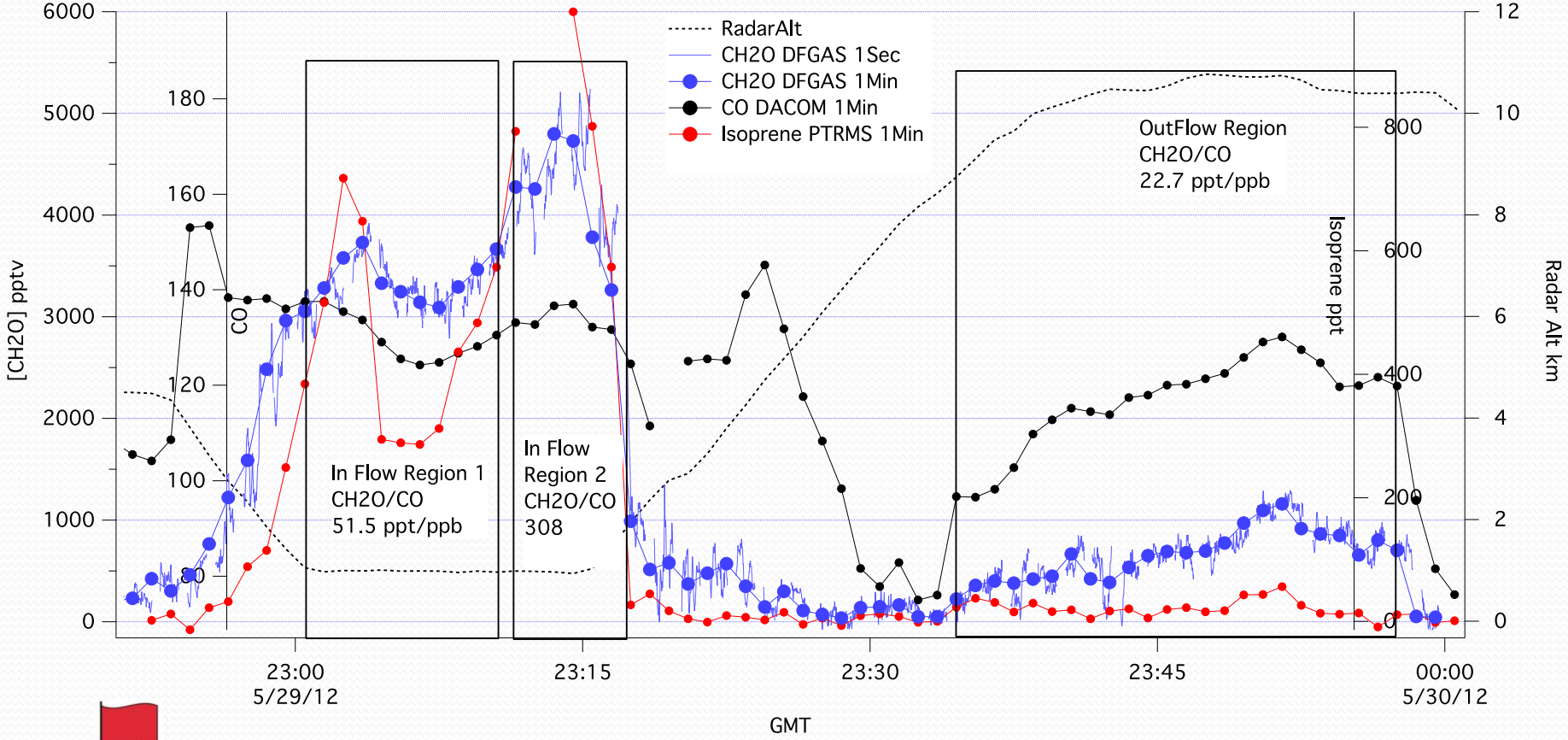


Provide Examples of Two Storms May 29 & May 19, One of Which Determine SE by Borbon Model

May 29 DC-8 In Flow & Out Flow Over Oklahoma

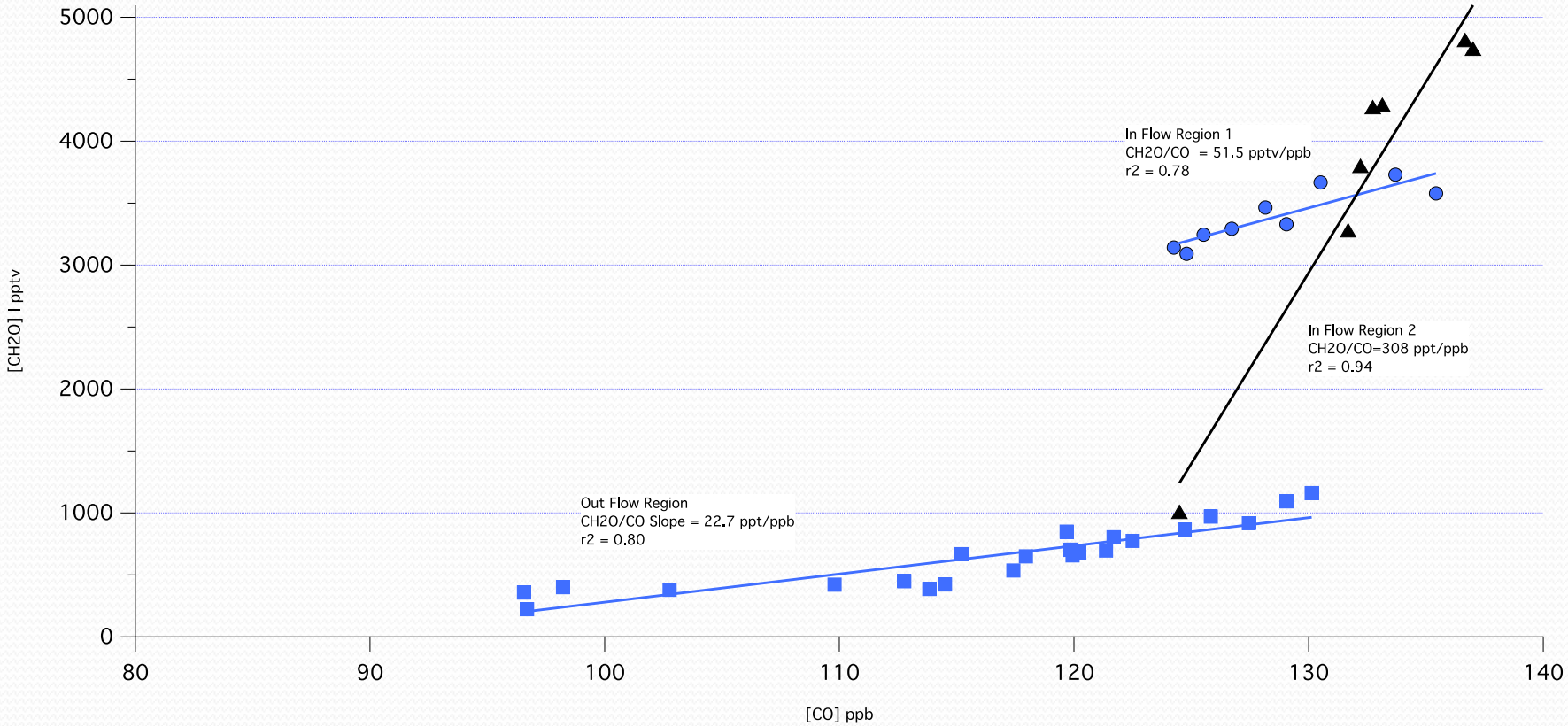


May 29 DC-8 In Flow & Out Flow Over Oklahoma



Different BL [Isoprene] dramatically affects CH2O
Raises questions regarding simple picture of a single BL In Flow tied to OF
Which BL mixture if any is tied to the observed OF ?

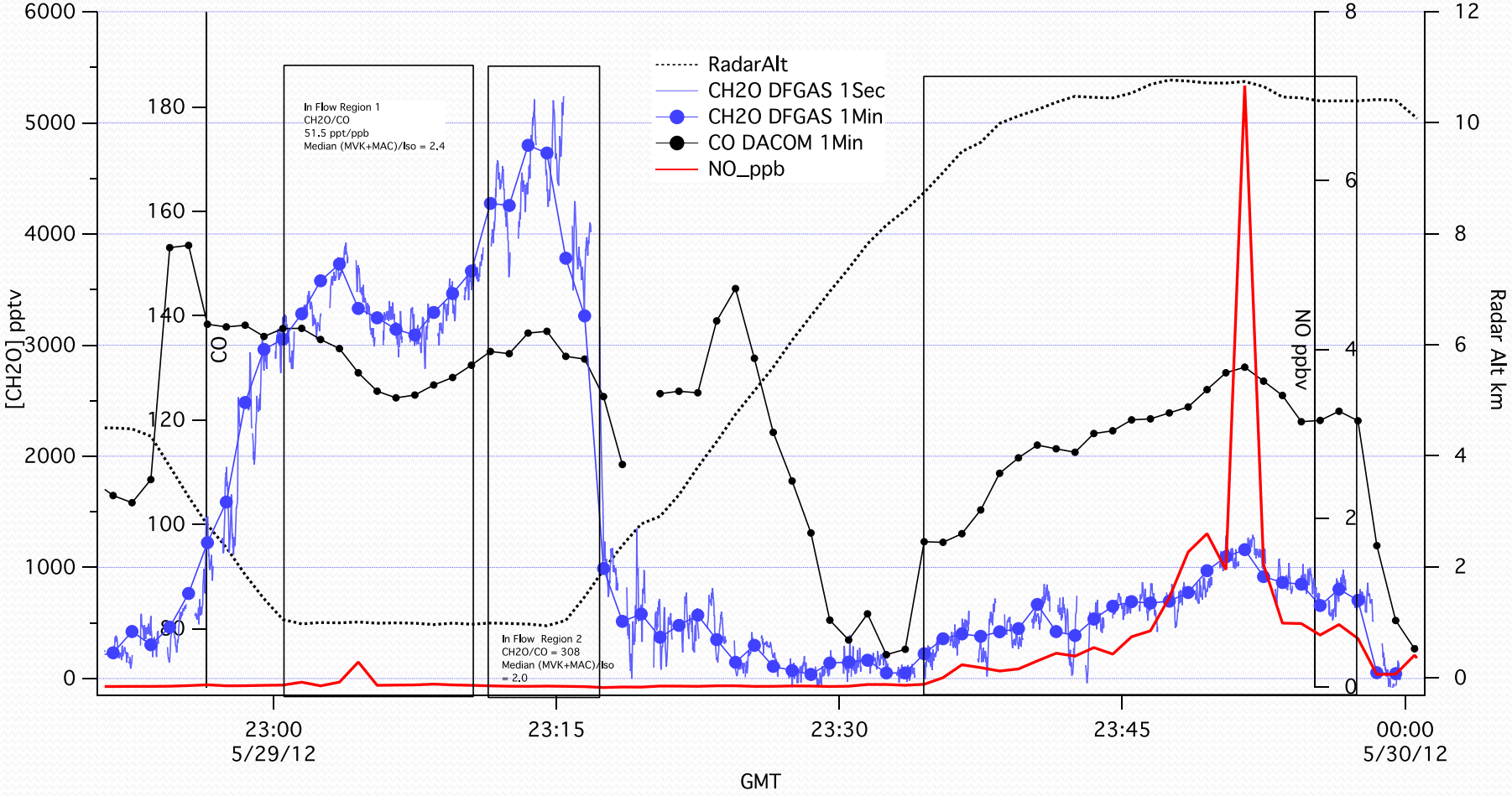
May 29 DC-8 In Flow & Out Flow CH2O-CO Slopes



Which IF Profile Should the OF be Compared to?

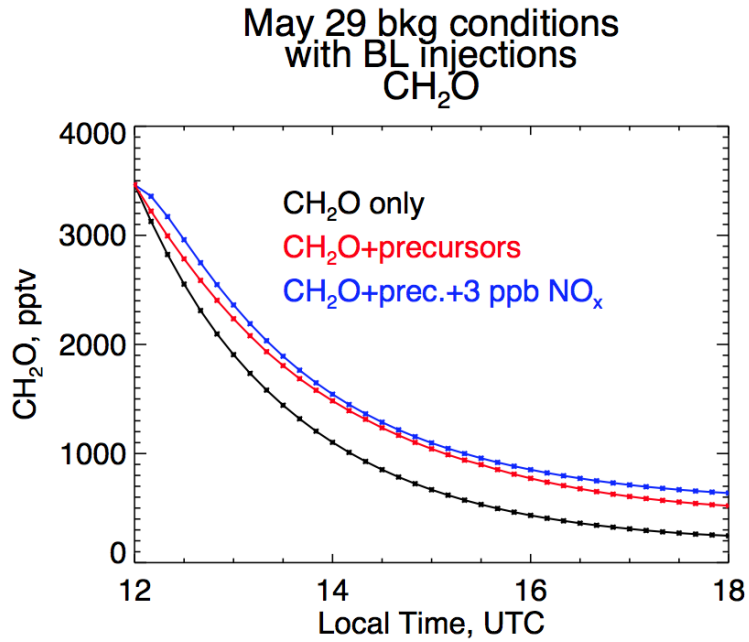
Nevertheless the OF CH_2O/CO Slope is Comparable to Slopes in BL Under Polluted Conditions, Suggesting PC of CH_2O

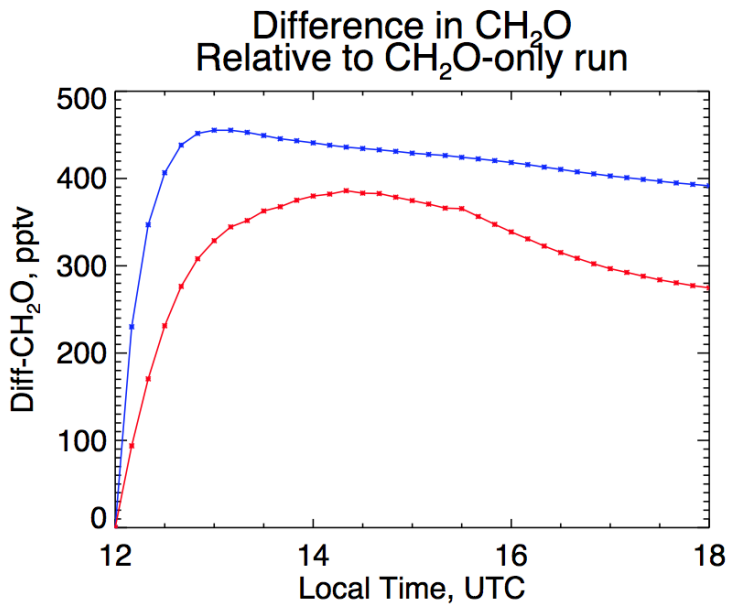
May 29 DC-8 In Flow & Out Flow Over Oklahoma



Lightning NO Enhances $P(CH_2O)$

Olson, Crawford, et al. - Lagrangian Runs for May 29

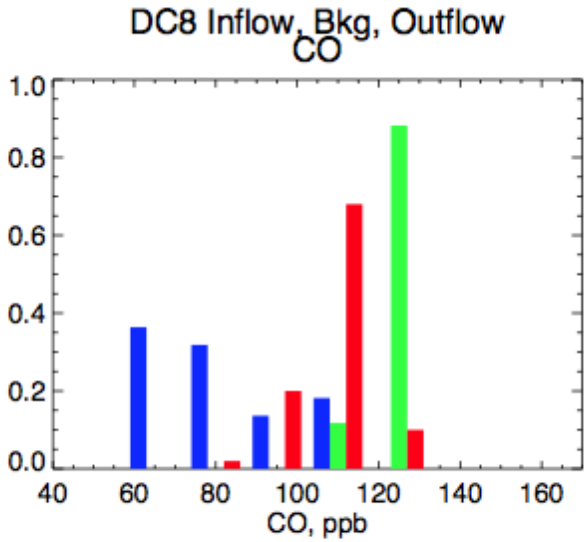


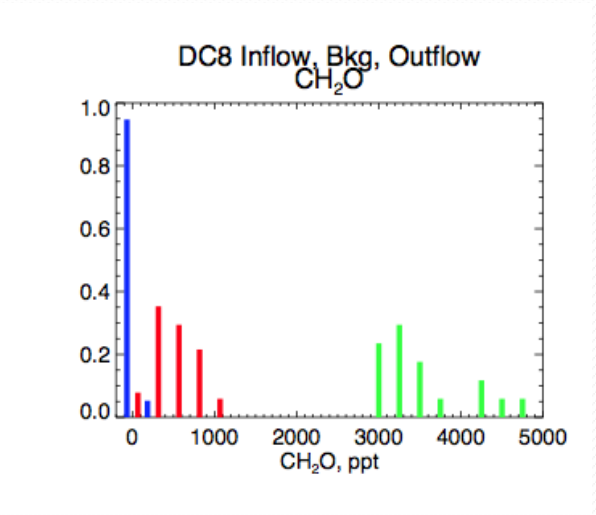


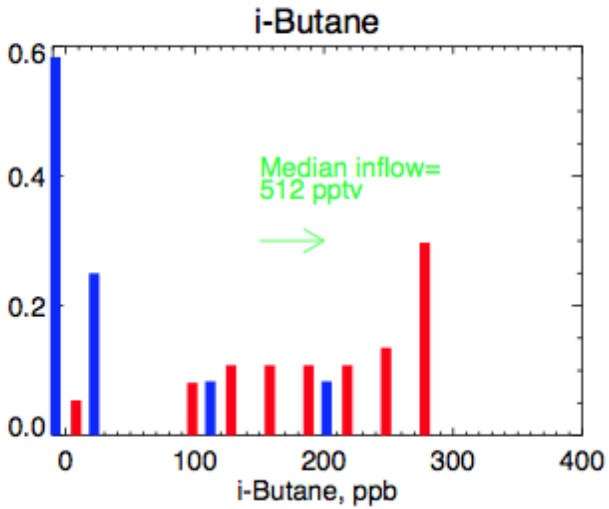
Shows PC Production of CH_2O can be ~ 20 to 40% of Direct Convection Term From 0.5h to Several Hours After Convection

Photochemical Production of CH_2O Needs to be Included in SE Calculations!

Olson Histogram Plots Used in Determining Mixing Ratios for 3-Level Model







Red – Convective Out Flow
Green – In Flow
Blue - UT Background

Mid Trop. Levels for Entrainment
23:18 – 23:34 2 to 8km

Mixing Ratios Determined from Both DC-8 and GV Histograms

CO (DACOM, Campos)

X_{CONV} = 110.8 ± 3.0 ppbv
$X_{In\ Flow}$ = 123.2 ppbv
X_{UT} = 77.3 ± 1.1 ppbv
X_{FT} = 109.9 ppbv

Iso-Butane (Blake, Apel Groups)

204.5 ± 8.4 pptv
512 pptv
4.7 ± 5.2 pptv
12 pptv

CH_2O (DFGAS & CAMS)

Y_{CONV} = 456 ± 55.0 pptv (accounts for Photochemical Production)
Y_{CONV} (max) = 1160 (affected by lightning NO)
$Y_{in\ Flow}$ = 3564 pptv
Y_{UT} = 53 pptv
Y_{FT} = 165 pptv

Results

May 29 Preliminary Results

$\alpha = 0.48$, $\beta = 0.39$

Borbon (Benzene, Toluene, CO)

$\alpha = 0.41$ $\beta = 0.50$

Borbon (3D Cloud Resolving Model)

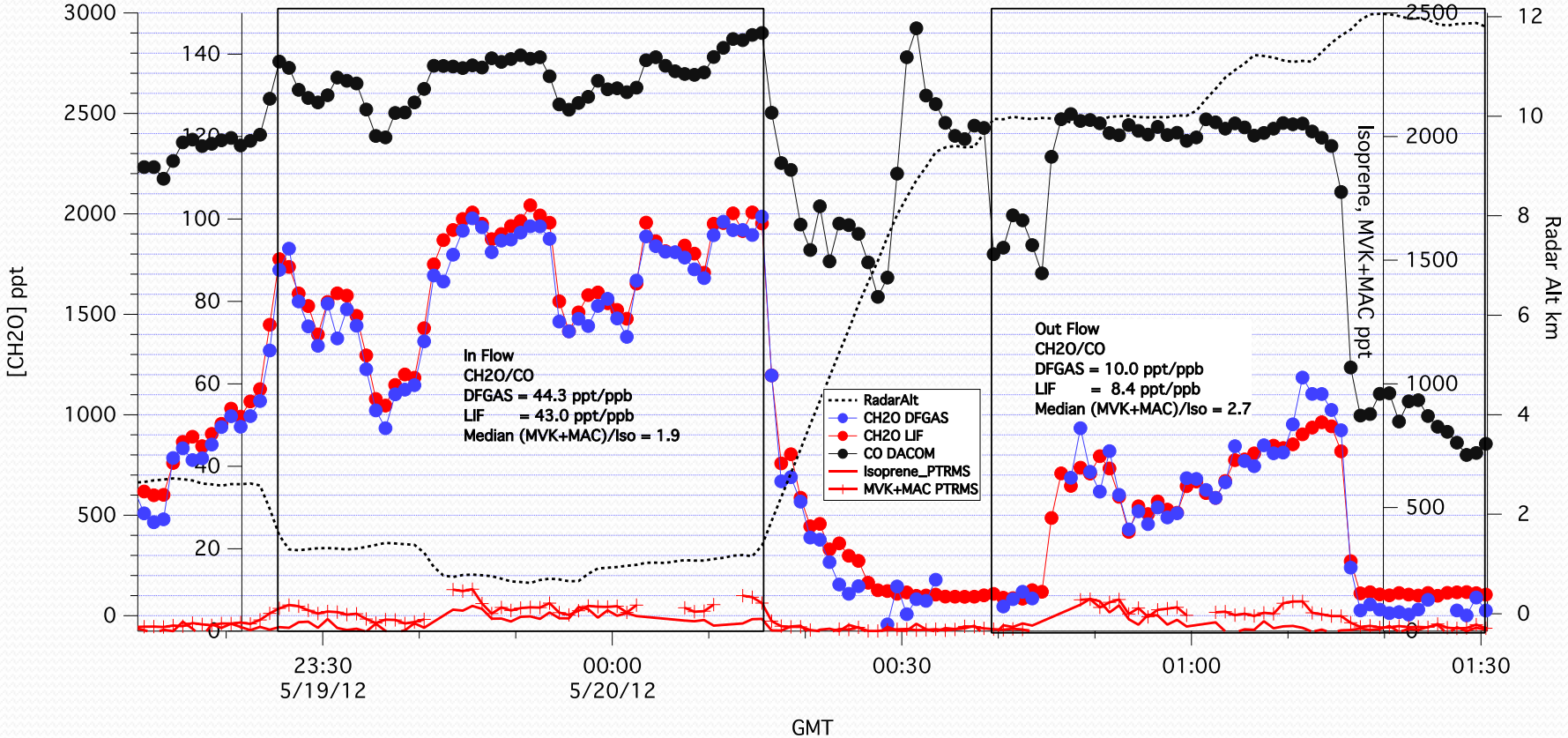
$\alpha = 0.45$ $\beta = 0.35$

Would be Highly Desirable to Employ 3D Cloud Resolving Model to Verify Tracer Determined α and β values

SE (removing PC of CH_2O) ~ 0.69 (31% of Convective CH_2O in UT is from Direct BL Convection+ Ice Degassing)

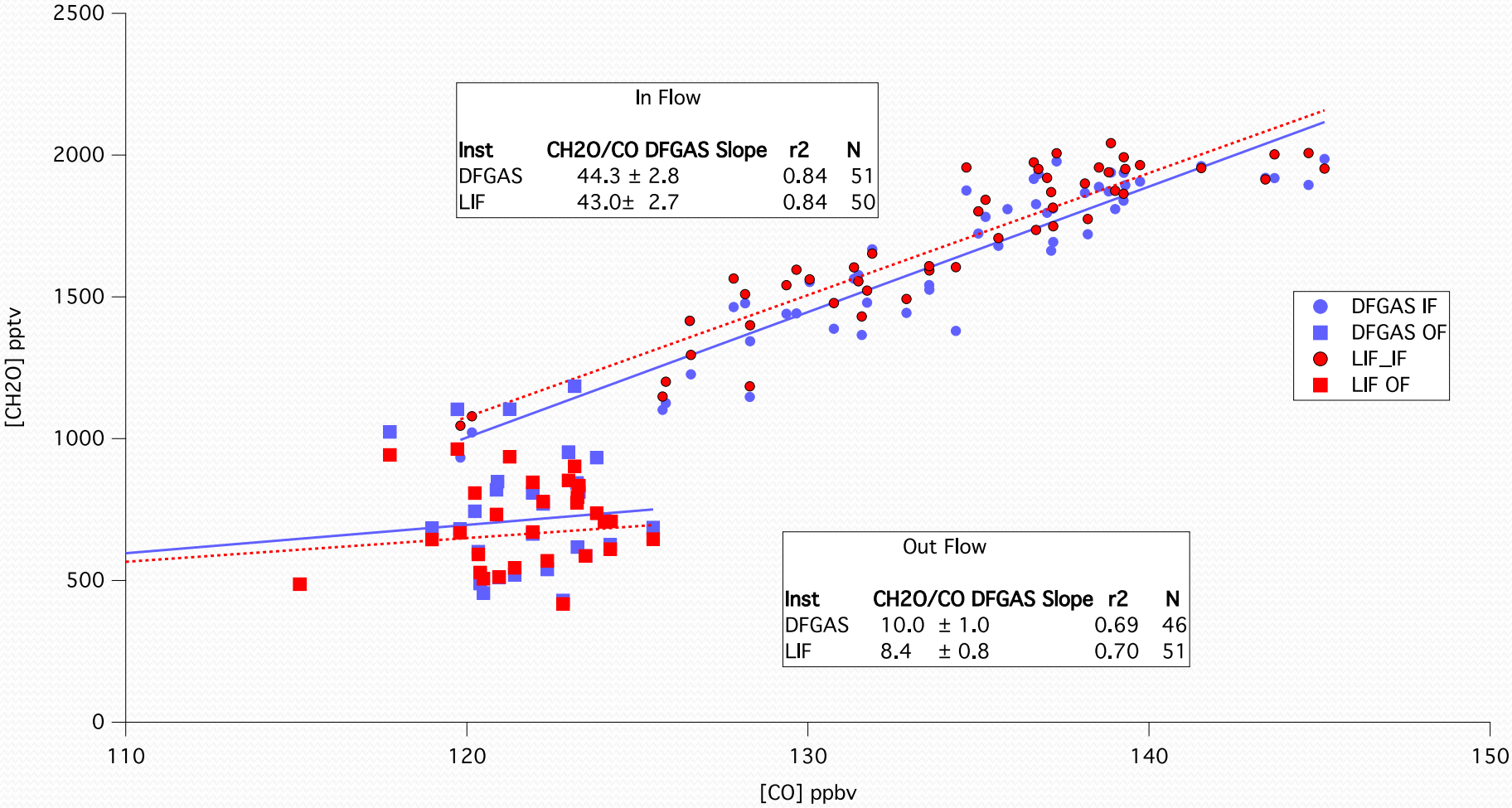
SE (don't remove PC of CH_2O) ~ 0.62 (38% from BL Convection)

May 19 DC-8 In Flow & Out Flow Over Oklahoma

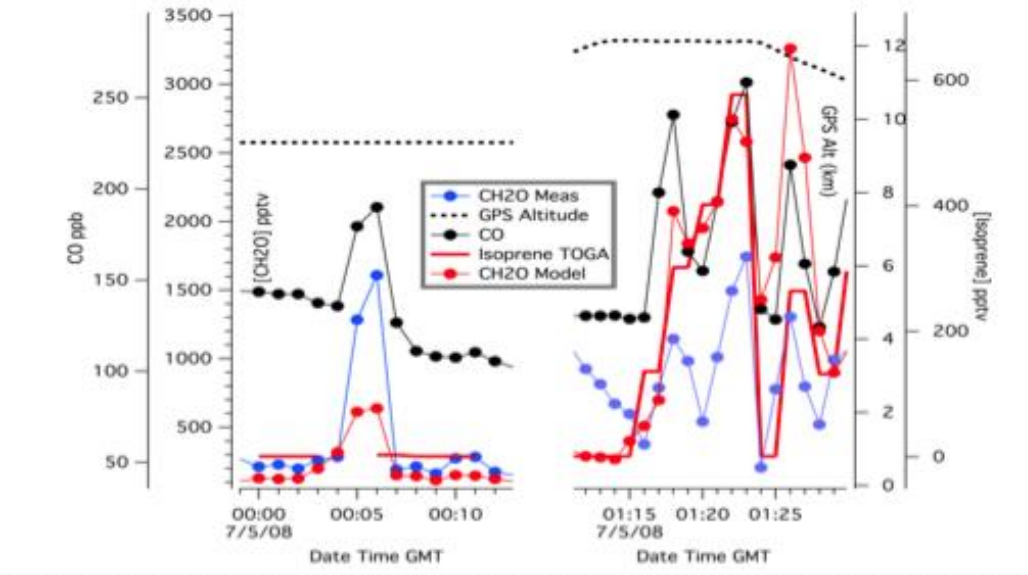


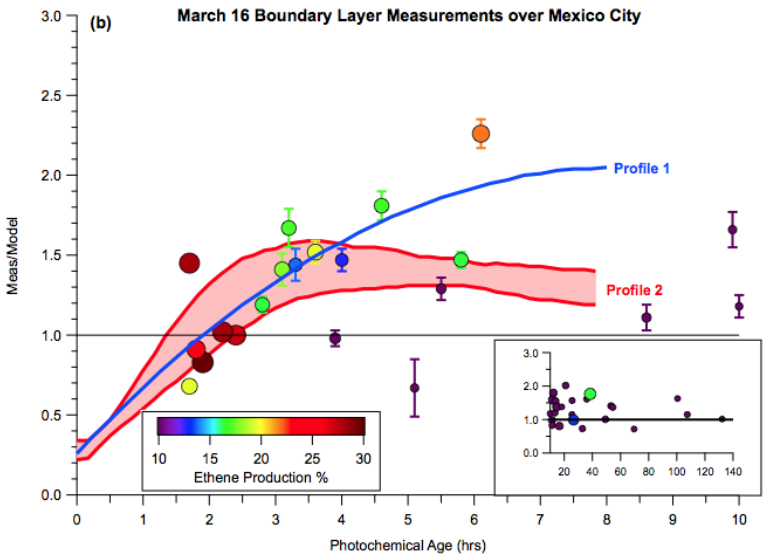
Unlike May 29, Isoprene & MVK+MAC Levels Are Low (Elim. BL Flag of May 29)
DFGAS & LIF Yield CH2O/CO Out Flow Slopes ~ ½ of May 29 (Less PC?)

May 19 DC-8 In Flow & Out Flow



Why SS Box Model Should Be Used Carefully



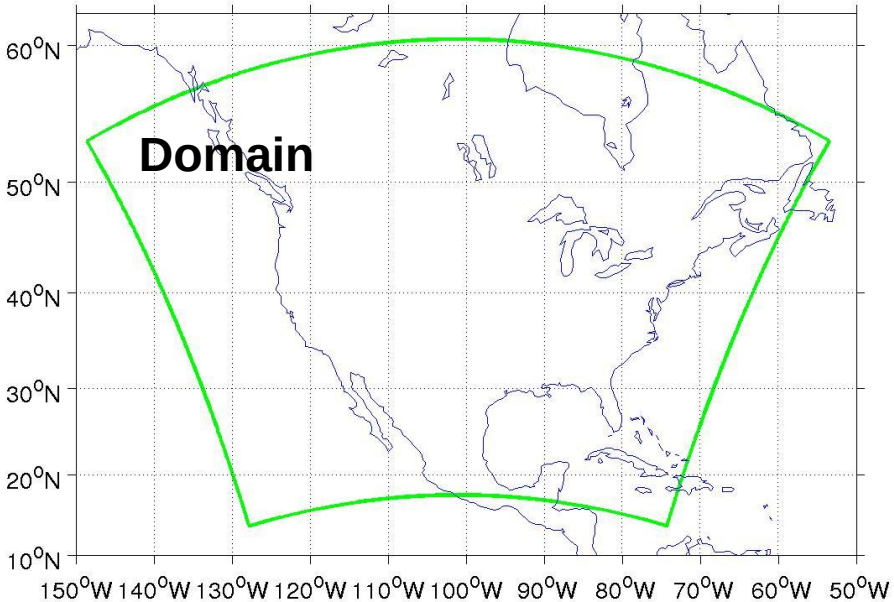


Box Model Large Over-estimations in Pyro-convective Plume during ARCTAS. SS is not achieved during convection.

Large SS Box Model Over-estimates In BL Plumes Close to Large Ethene Sources Over Mexico City. The red Lagrangian Profiles Show Same Behavior (Fried et al. ACP 2011)

Steady State is Not Achieved in These Cases

WRF-Chem 15km May 29 OK Storm Simulation (Bela, Barth)



Grid spacing: dx = 15 km, 40 vertical levels to 50 hPa (~650 m in UT)

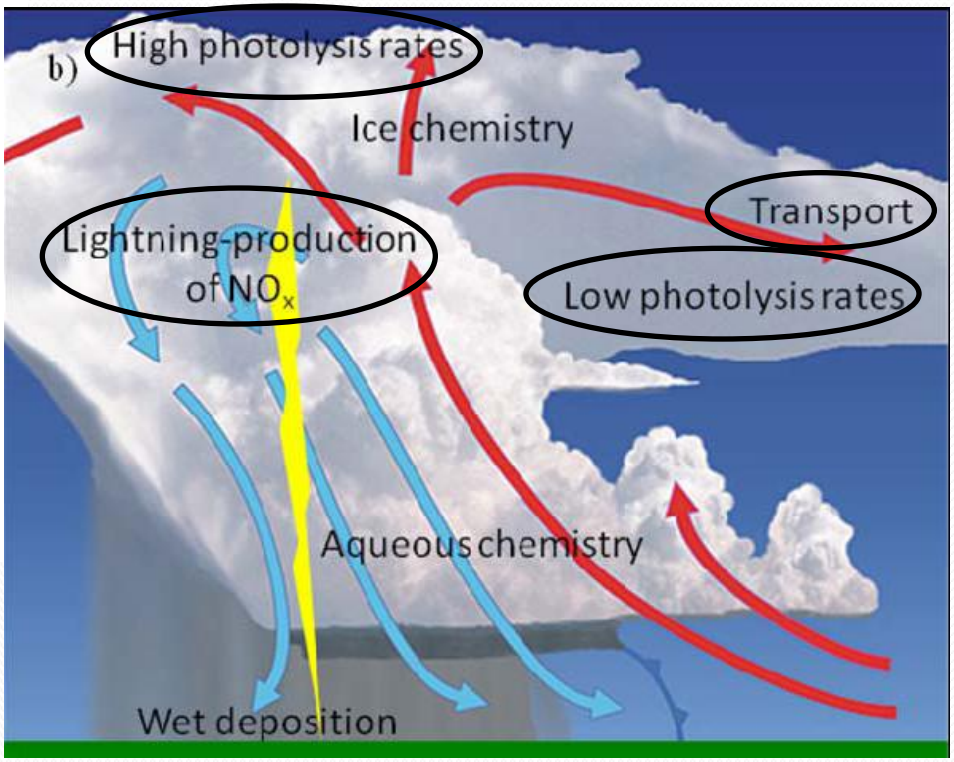
Initial/Boundary Conditions: DART (met), MOZART (chem)

Physics: Grell 3D convection, Morrison cloud microphysics, MYJ PBL

Chemistry: MOZART gas chemistry mechanism; GOCART aerosol scheme

Emissions: EPA NEI 2005 anthropogenic (2012 NO/NO2 based on OMI NO2), aircraft from Baughcum (1999), MEGAN v2.0.4 biogenic, FINN fire

Included processes:



https://www2.acd.ucar.edu/sites/default/files/dc3/thunderstorm-airmass_squall-line.jpg

Lightning-NOx : FR = $3.44 \times 10^{-5}\ z_{top}^{4.9}$

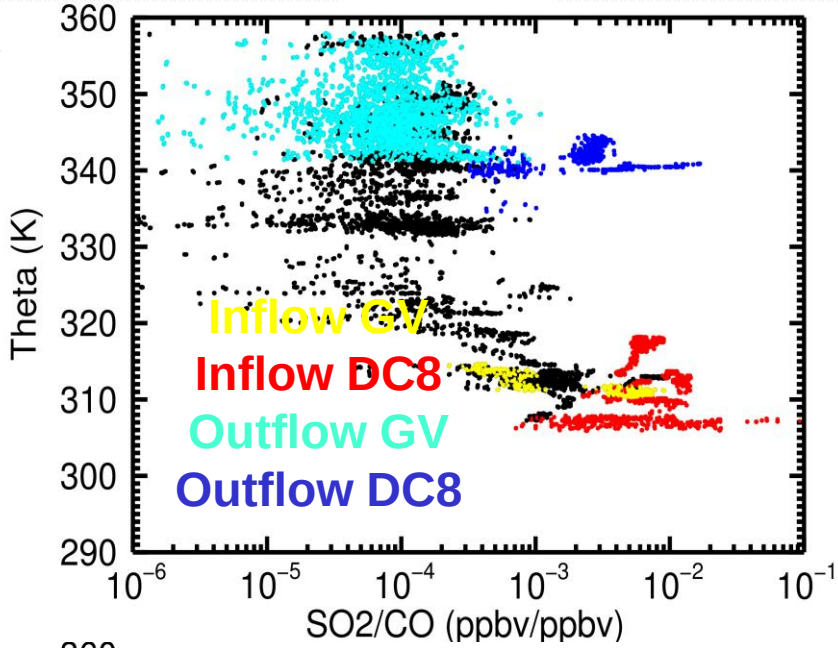
z_{top} = cloud top height = level neutral buoyancy – 2 km (Wong et al., 2012)

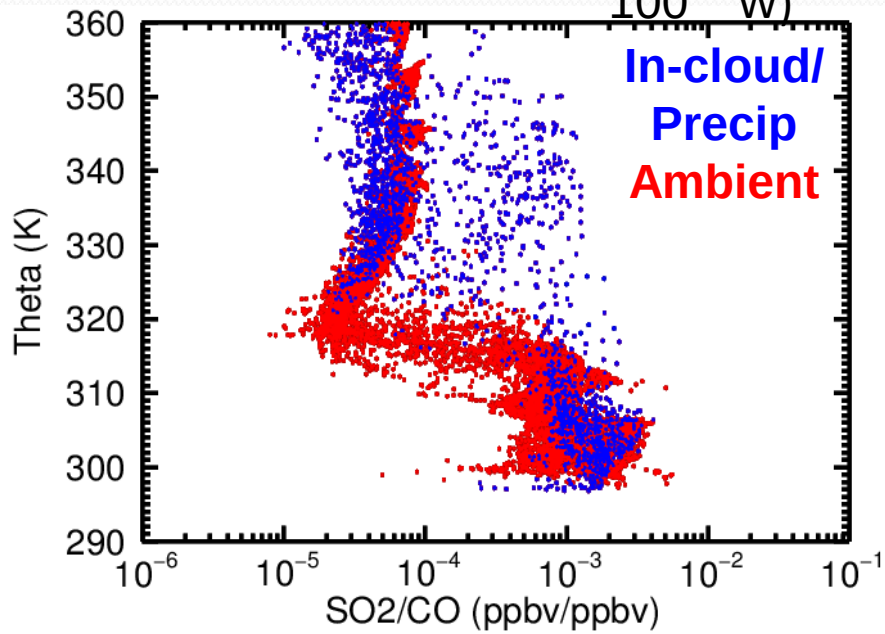
500 moles NO/flash placed vertically following Ott et al. (2010) curves

WRF-Chem values of SO2 and CH2O are higher than observed, indicating that wet scavenging (not included in WRF-Chem) is important for these species

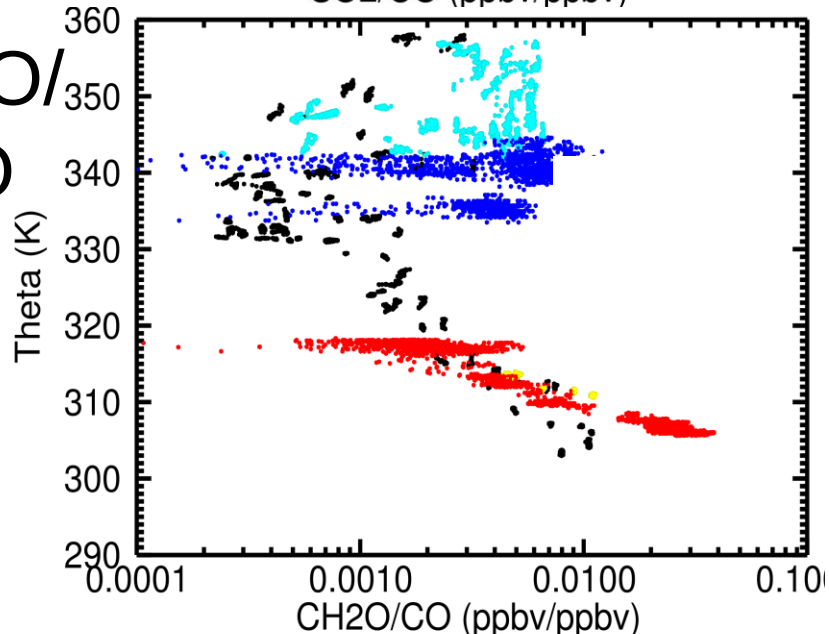
May 29 22Z – May 30 01Z OBS WRF-Chem (35-40° N, 95-100° W)

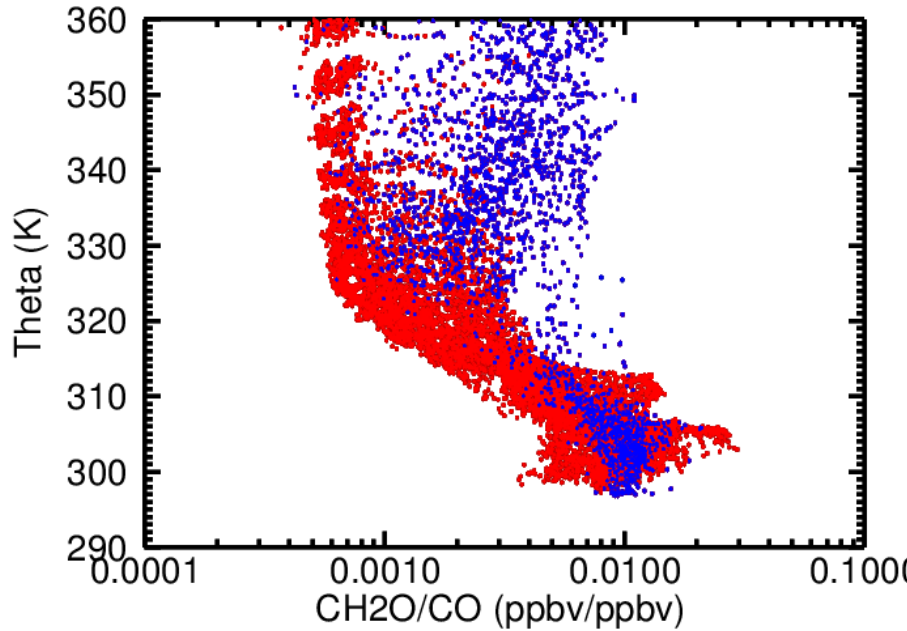
SO2/CO





CH2O/CO

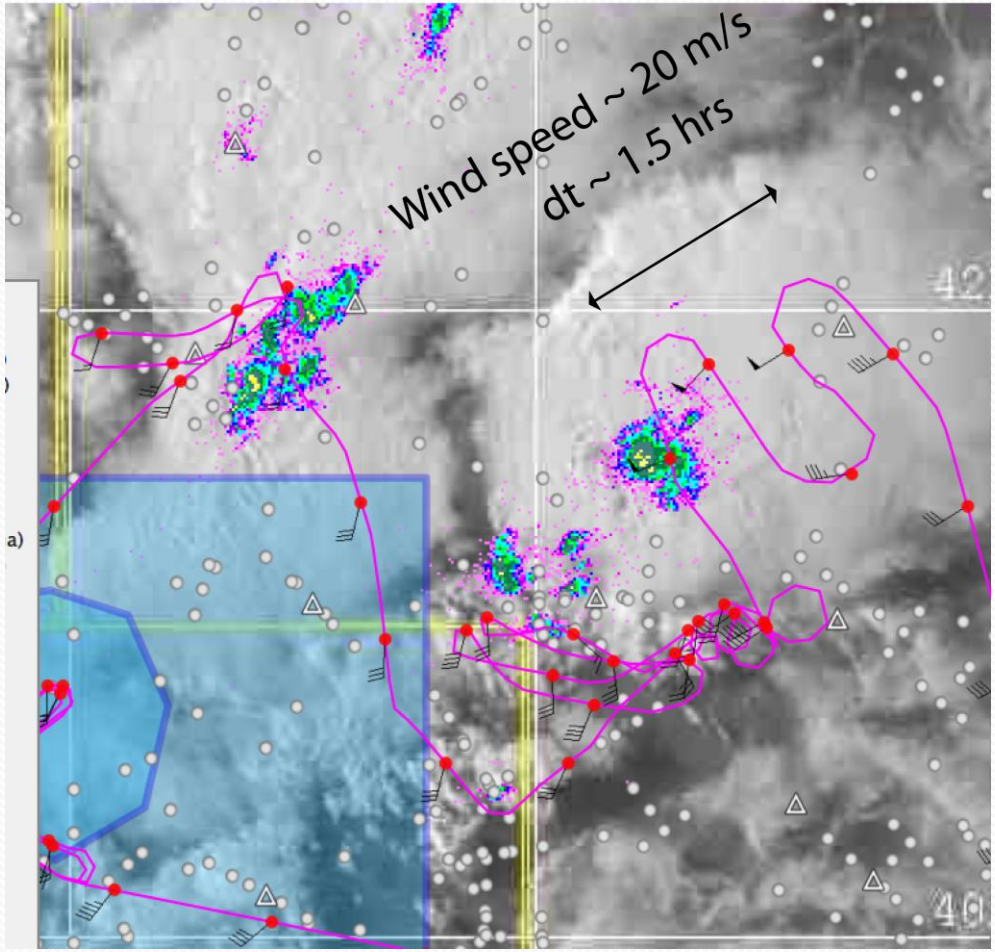




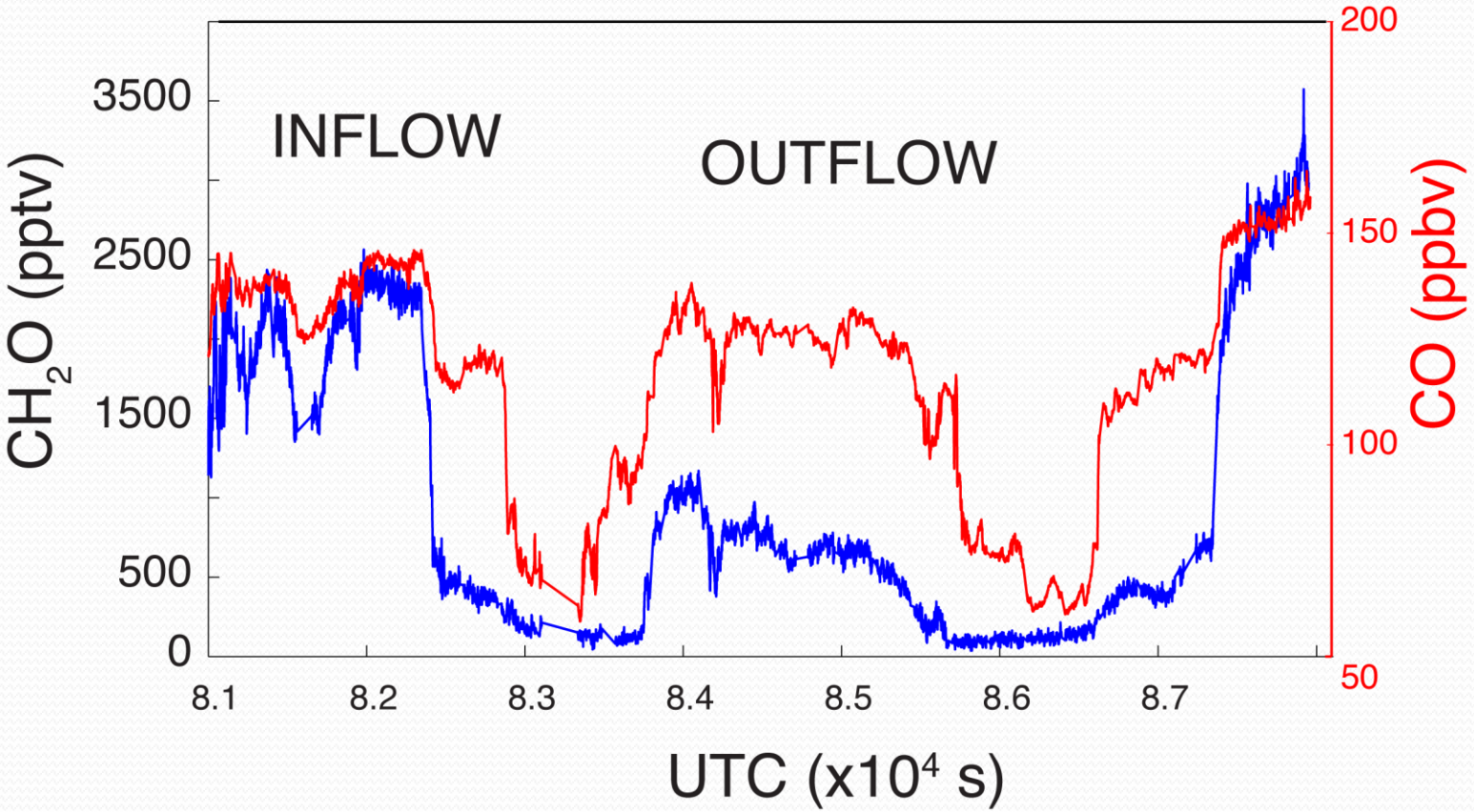
Vertical Transport of Formaldehyde by Thunderstorms

Thomas F. Hanisco (GSFC), Heather L. Arkinson (UMD), Maria D. Cazorla (USF de Quito), Glenn M. Wolfe (UMBC), Glenn S. Diskin (LaRC), Glen W. Sachse (LaRC), Samuel R. Hall (NCAR).

20120518 NE Colorado/SW Nebraska Flight pattern and IR image



Estimate Entrainment/Dilution Effects with CO

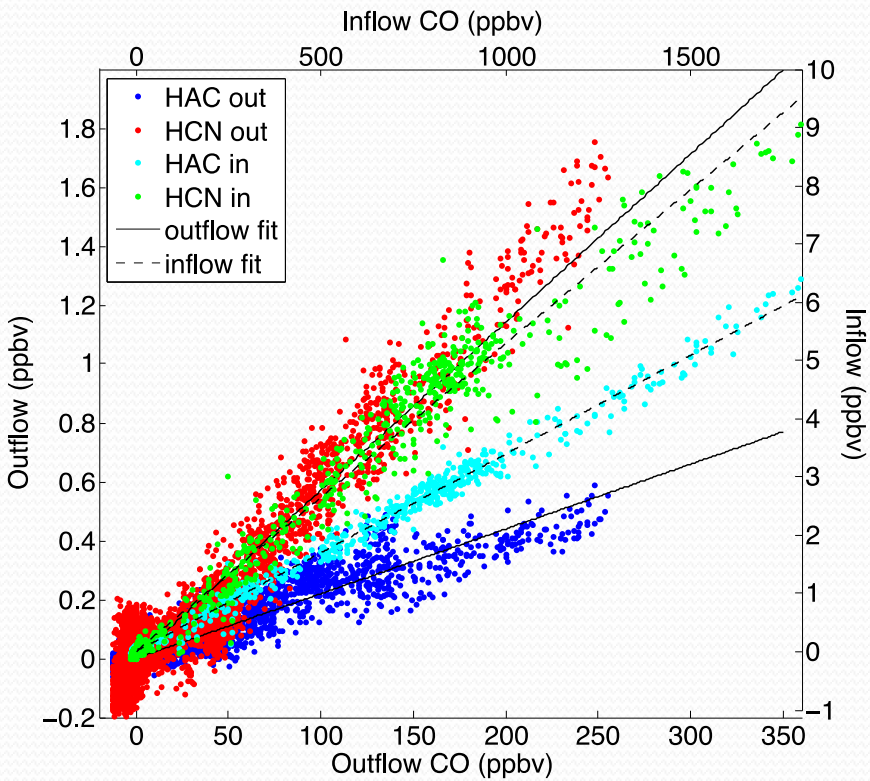


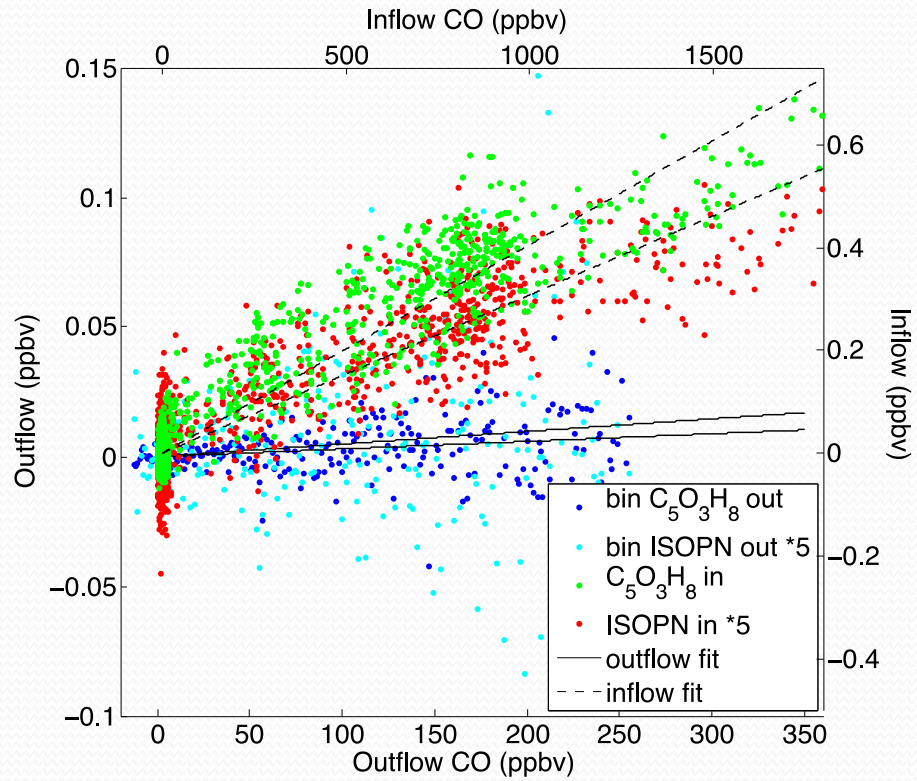
- CH_2O outflow is roughly 40% of the inflow.
- CO shows ~15% dilution in the anvil plume relative to the BL.
- Note “old” outflow indicated by CO

Conclusions Hanisco et al.

- Formaldehyde is transported efficiently in Thunderstorms.
- Formaldehyde Observations are well described by photochemistry
- Only ~20% of formaldehyde is removed by rainout or other process for the May 18 2012 Storm

Cloud processing of fire emissions: 2012 June 22 By Caltech-CIMS





•Species measured by the Caltech-CIMS show varied levels of removal by cloud processing, as predicted by their different Henry's Law coefficients.

Jason St. Clair, John Crounse, Paul Wennberg

Discussion Topics for Breakout Session

- Ambiguities Connecting In Flow & Out Flow Regions
- Additional Passive Tracers to Employ
- Dynamical Methods to Verify α and β Determinations
- Lagrangian Photochemical Production of CH_2O
  - Enhanced production from Lightning NO
- Assumption of Constant SE for BL and FT air
- Uncertainty in Some Terms
  - What values to use peak, median
- Photochemical Clocks (time since BL convection, time since sampled UT convection (H. Fuelberg))
- Degassing from Ice vs Liquid Water