Halogen Chemistry in CAM-CHEM & CCMVal

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NCAR

CAM-CHEM

Outline

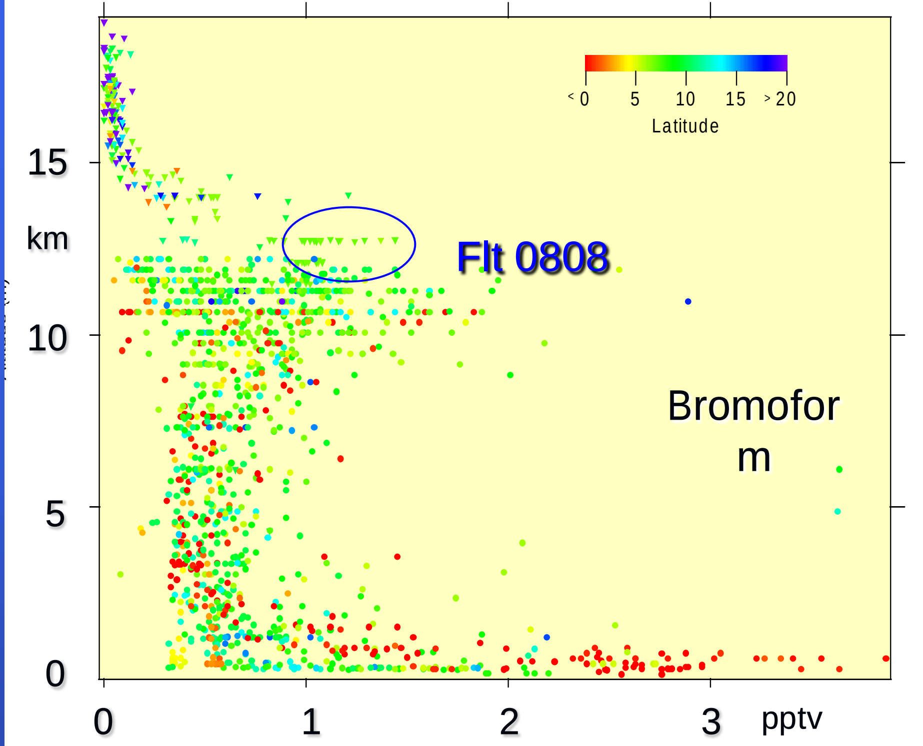
- VSL Halogens
- SPaRC CCMVal Chemistry-Climate Model Evaluation

VSL Halogen Scientific Questions

- Can observation of VSL halogens help constrain transport pathways into the tropical UTLS in a 3D CCM?
- What impact does VSL substances have on model derived Ozone trends?
- What is the Role that VSL organic bromine and iodine species have on the ozone budget in the tropical lower troposphere?
- What is the impact of VSL halogens on CH_4 lifetimes through amplification of OH
- What are the climatic impacts of VSL halogens?

Subset of the VSL Halogenated Substances currently being added the CAM-CHEM mechanism (~20 SG)

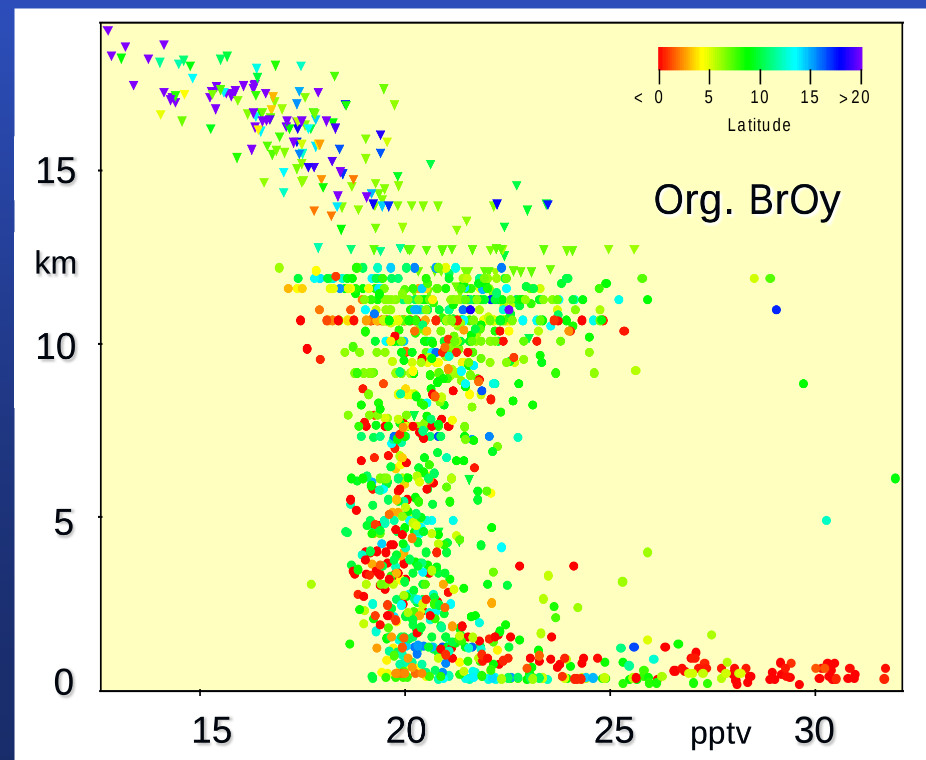
Source Gas	Formula	Local Lifetime (days)	Main Loss processes	WAS
Bromochloromethane	CH_2BrCl	150	OH	√
Trichloromethane (chloroform)	$CHCl_3$	150	OH	√
Methylene chloride	CH_2Cl_2	140	OH	√
Dibromomethane	CH_2Br_2	120	OH	√
Bromodichloromethane	$CHBrCl_2$	78	OH, hv	√
Dibromochloromethane	$CHBr_2Cl$	69	hv, OH	√
Tribromomethane (bromoform)	$CHBr_3$	26	hv	√
Methyl iodide	CH_3I	7	hv	√
Trifluoroiodomethane	CF_3I	4	hv	-



TC4, Whole Air Sampler, Schauffler, Atlas, et al., AGU, 2007

Good Profile Data!

- Convection lofting VSLS into the TTL.
- Influencing the total inorganic bromine abundance.
- Transported to ExTL?



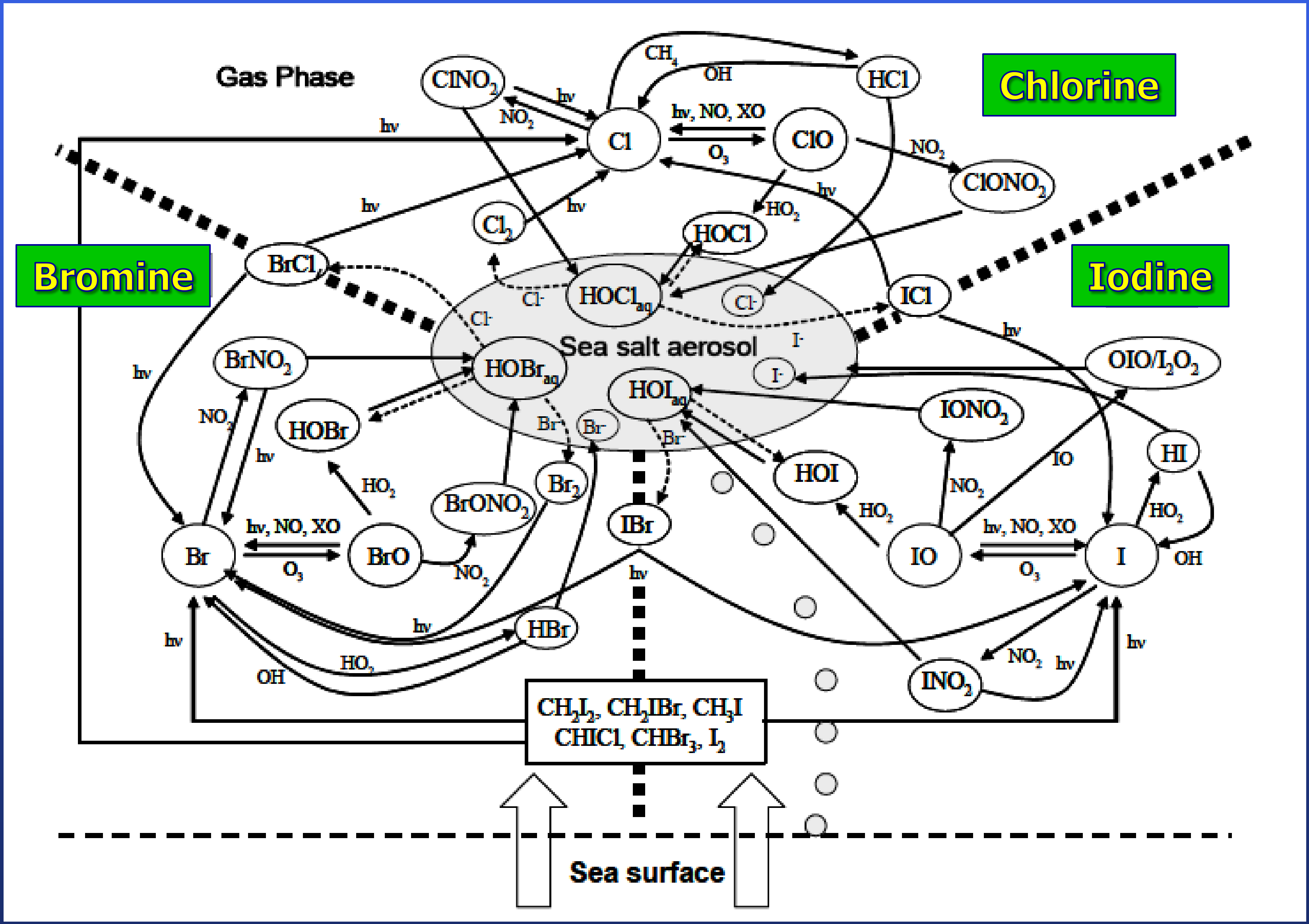
Modeling the Troposphere with VSLS

- Need a model with representation of Tropospheric O_3 chemistry (e.g., NMHCs; Emissions, etc…).

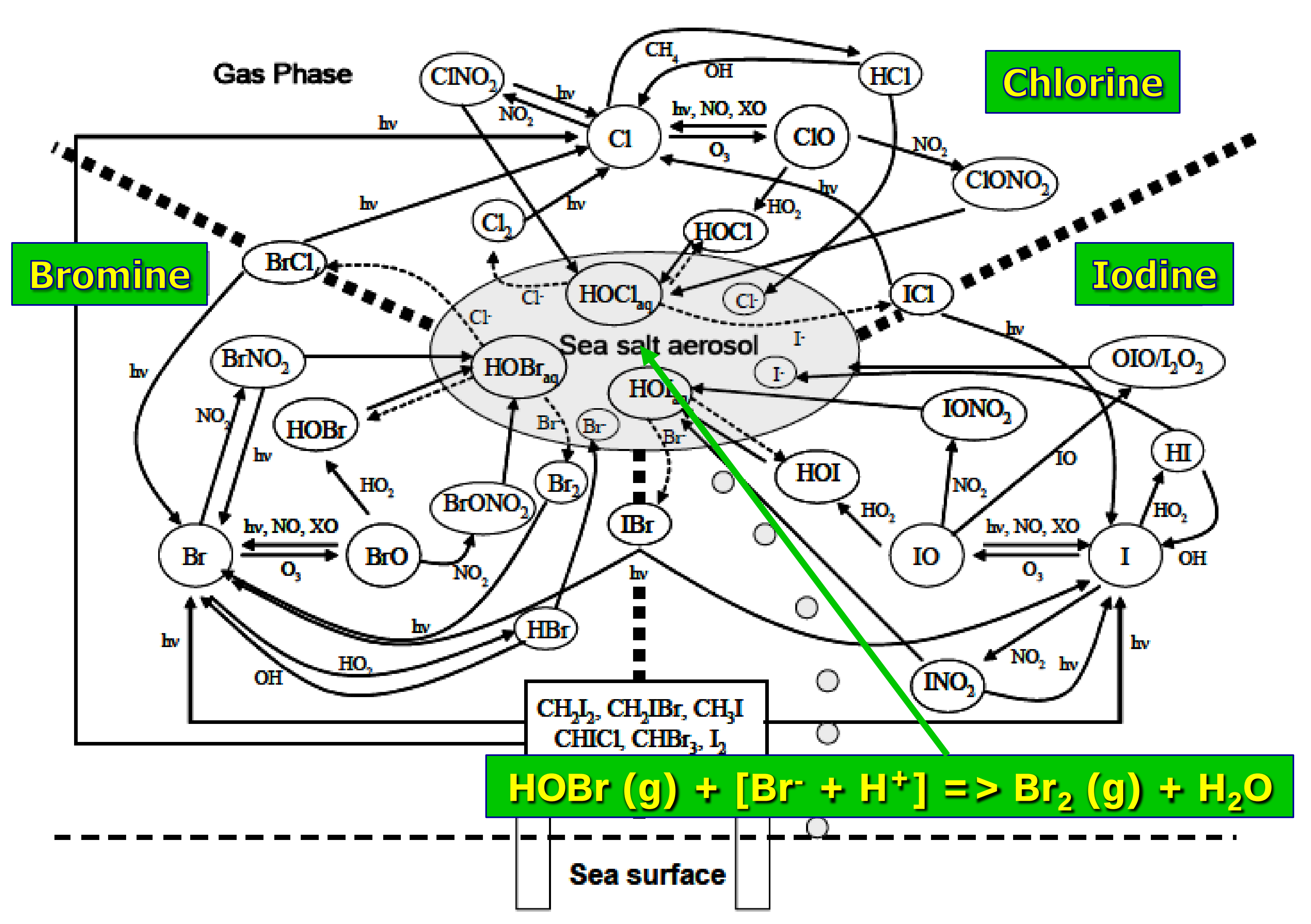
- Need a model that includes a VSL organic and inorganic mechanism.
  - Organic species: Adds ~18
  - Inorganic species: Adds ~20
  - Photolysis Rxns: Adds ~23
  - Sulfate Het. Rxns: Adds ~5
  - Sea Salt Aer. Rxns: Adds ~9

- Need Emissions – Observations suggest that the biogenic production seems to come from seaweed, phytoplankton, algae etcs… [we use Chlorophyll-A obs from SeaWIFS]

Tropospheric Halogen Chemistry

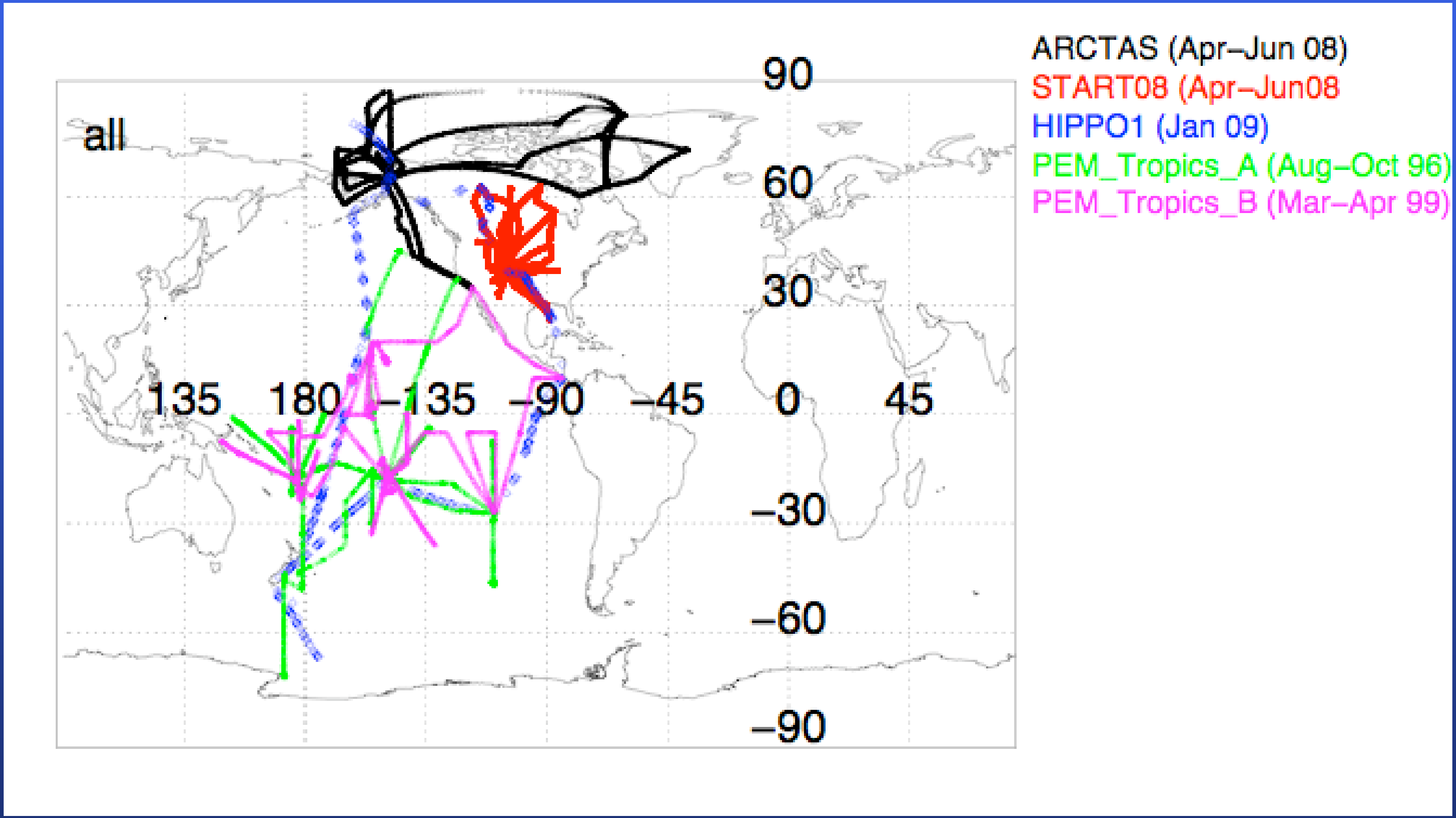


Tropospheric Halogen Chemistry



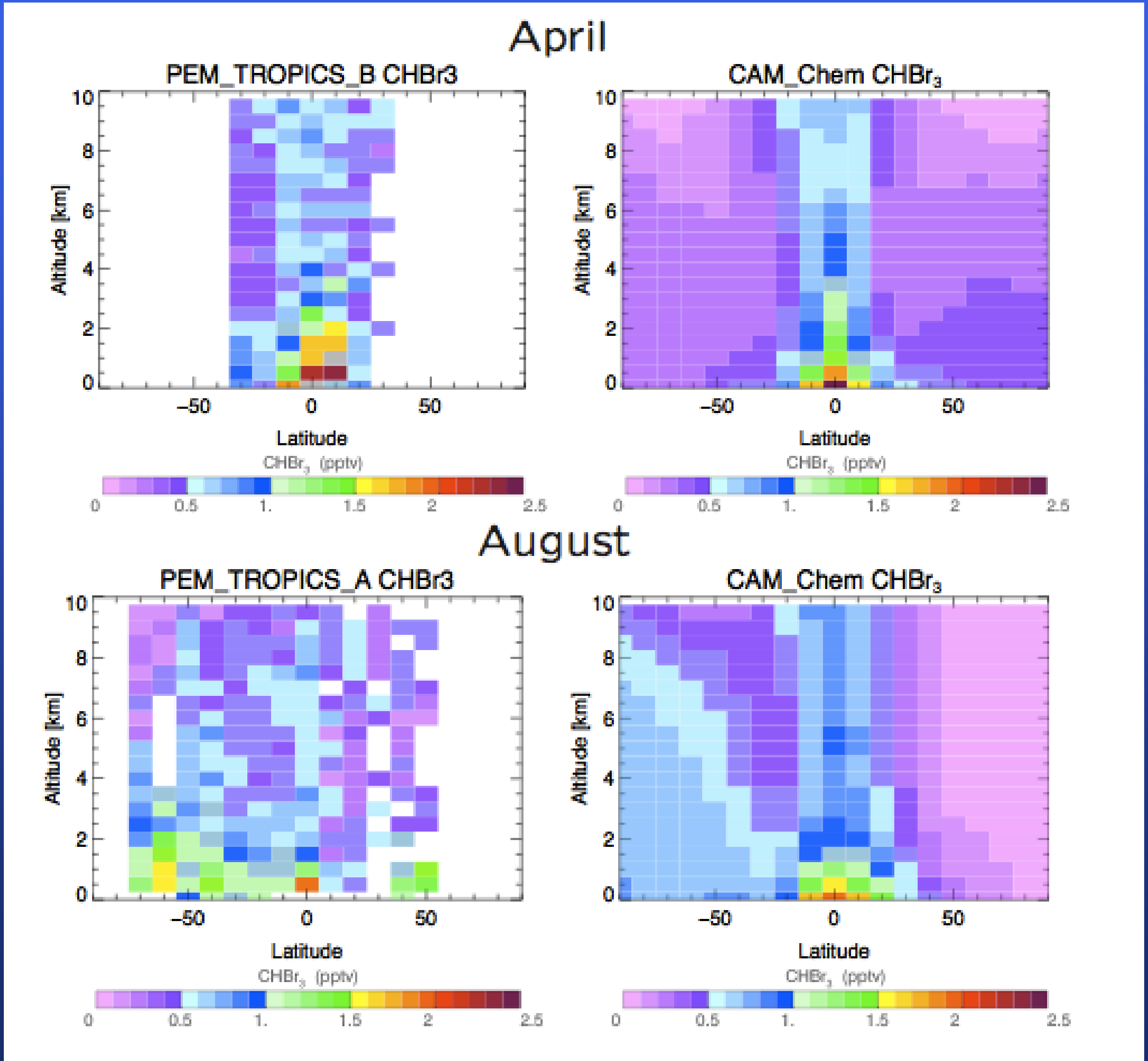
HOBr (g) + [Br$^-$ + H$^+$] => Br$_2$ (g) + H$_2$O

Aircraft Data for VSL Organics

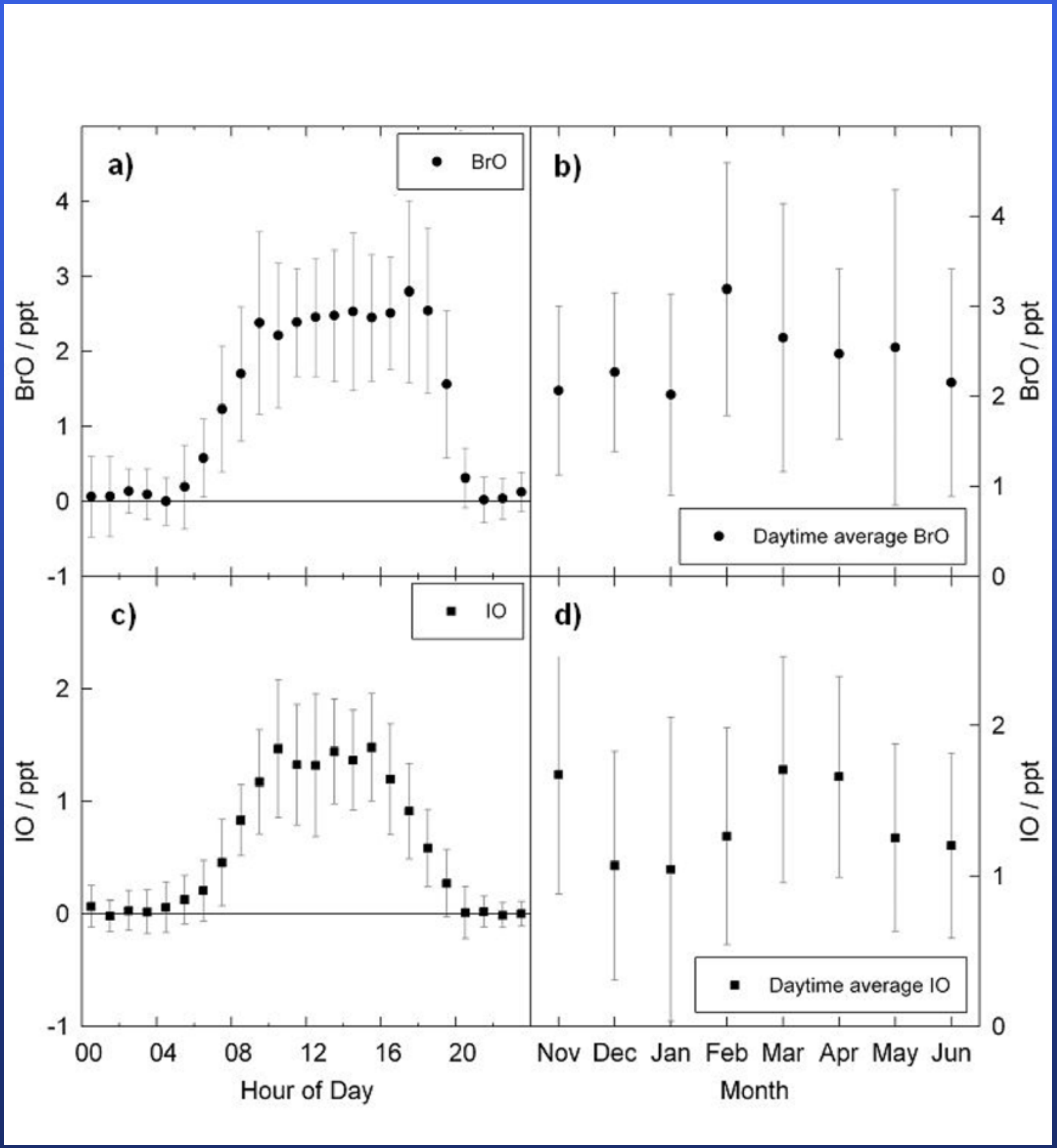


Courtesy of Simone Tilmes

$CHBr_3$ (Bromoform)



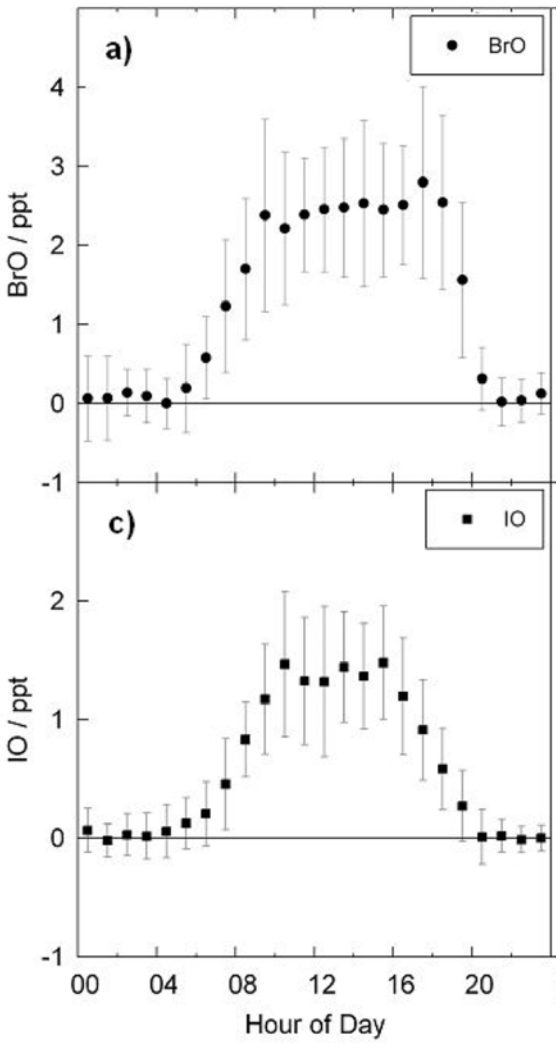
IO and BrO at Cape Verde

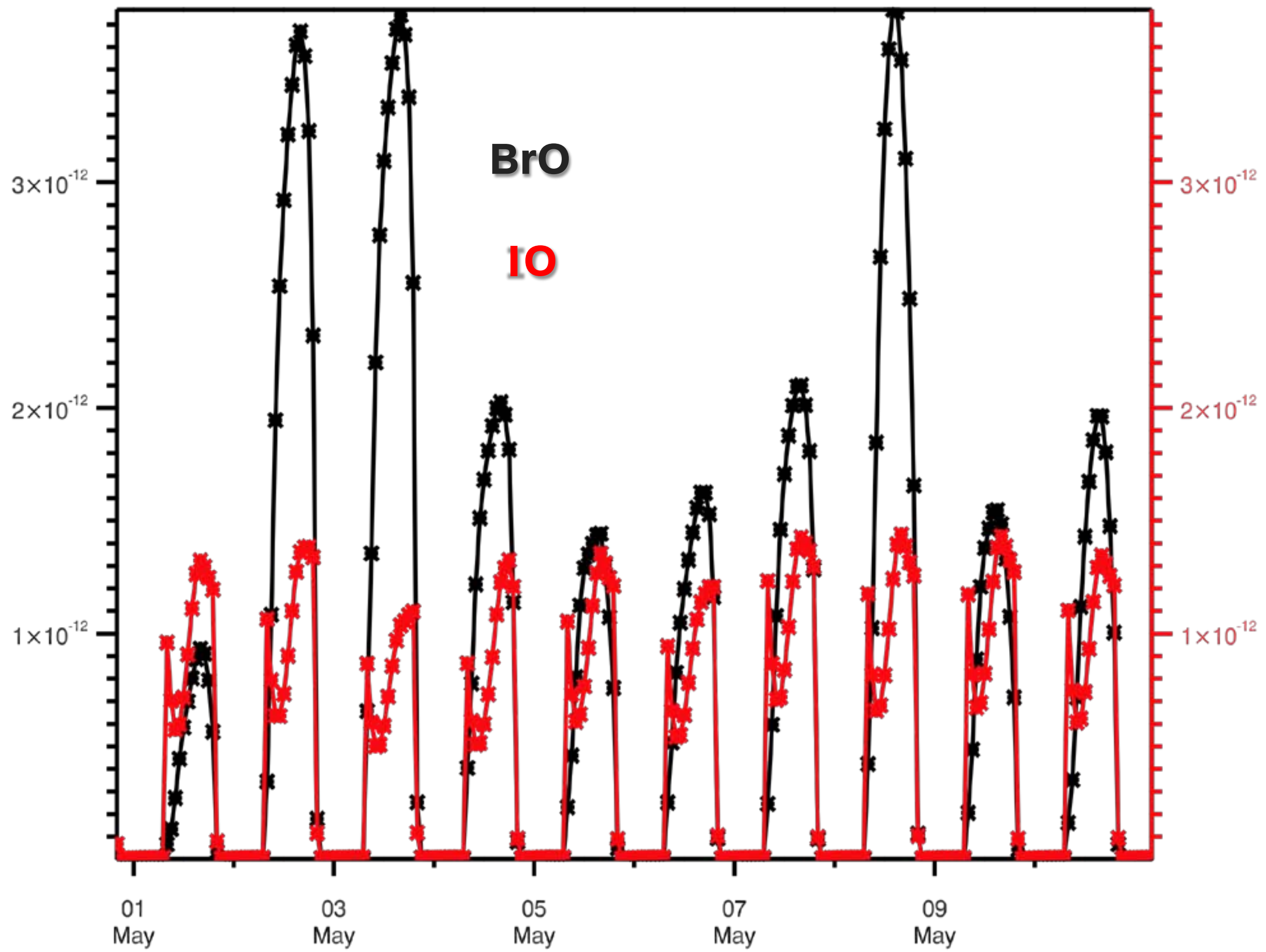


Read et al., Nature, 2008

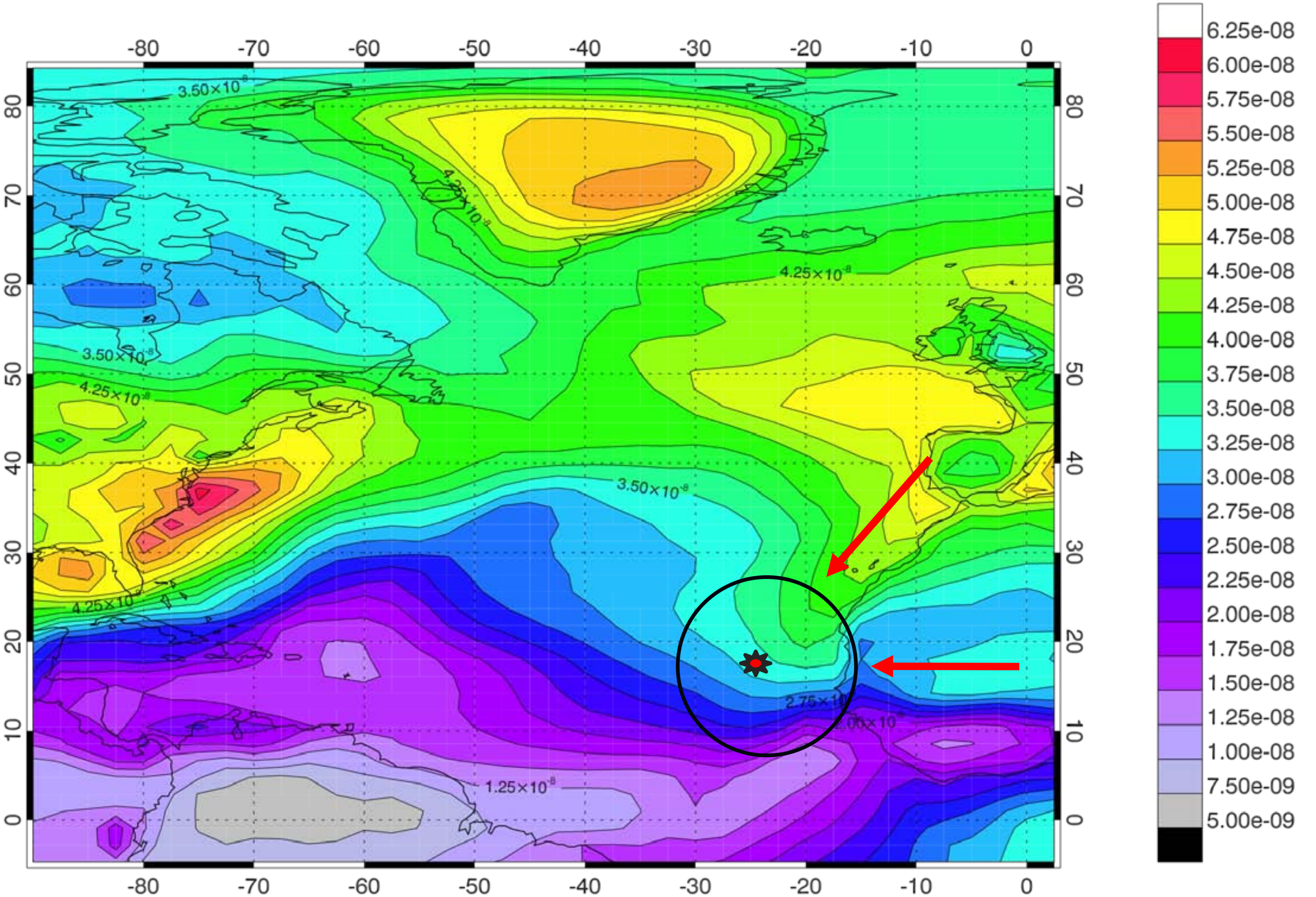
- Cape Verde [16.85N, 24.87W]
- DOAS measurements.

IO and BrO at Cape Verde (Diurnal)



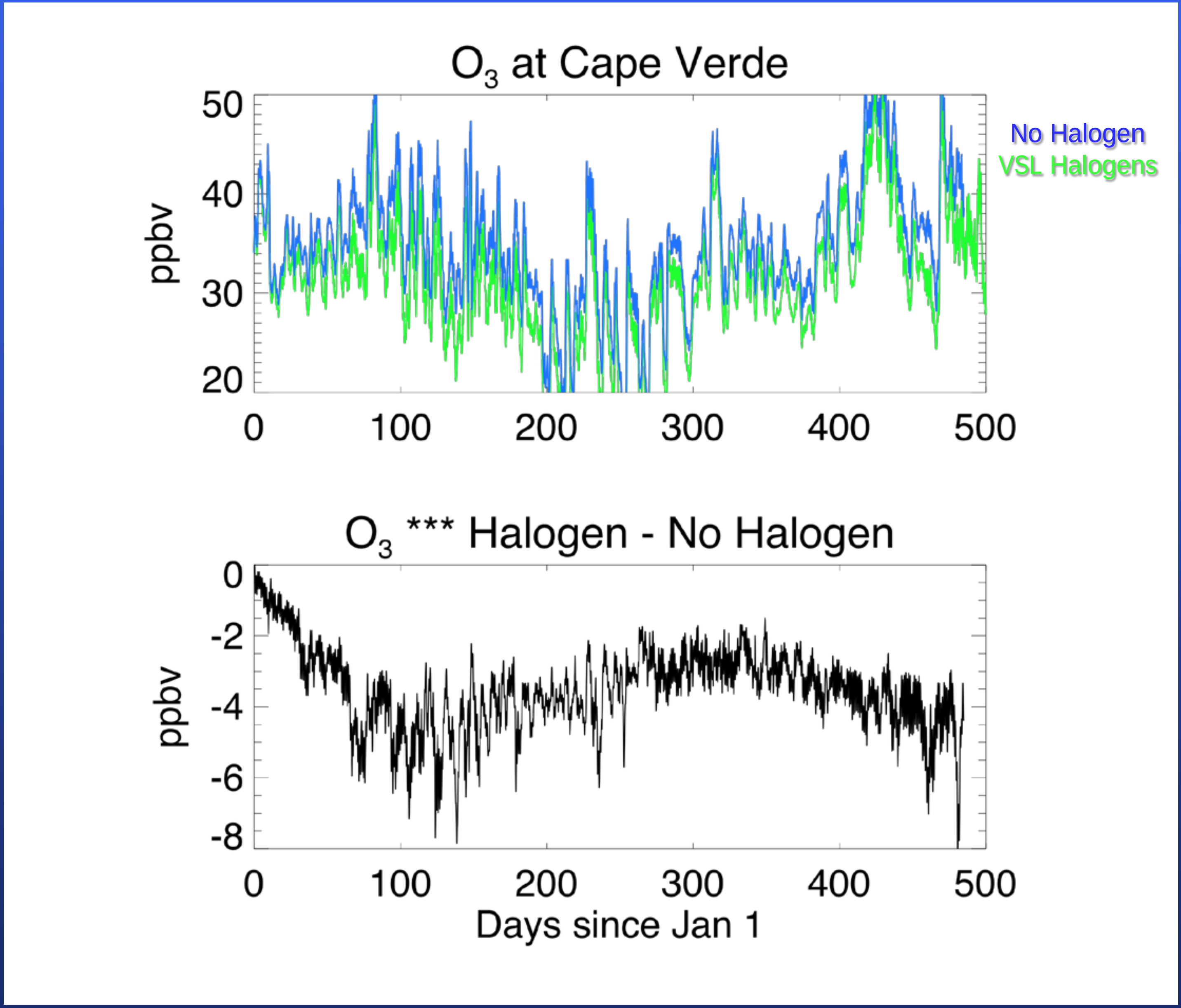


Ozone *** Surface *** May

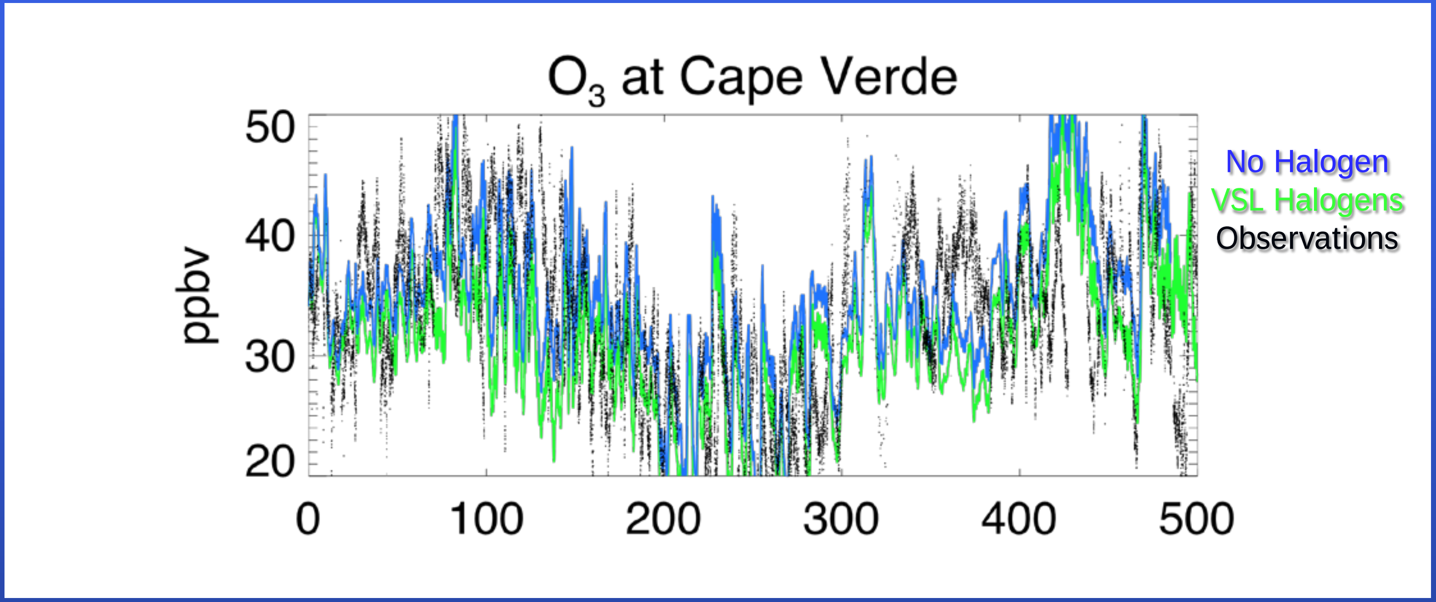


Cape Verde, 16.9N, 24.9W

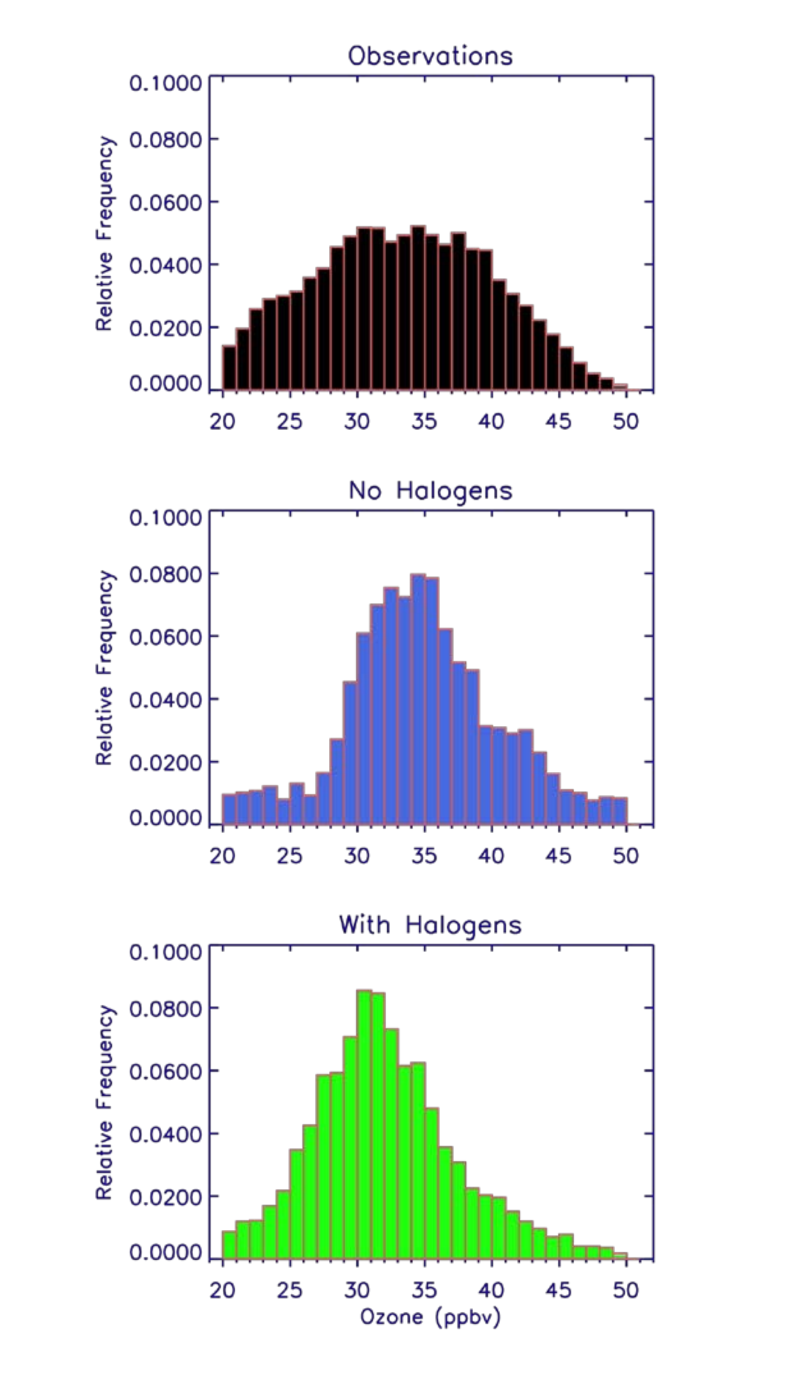
Ozone at Cape Verde (16.9° N, 24° W)



Ozone at Cape Verde (16.9° N, 24° W)

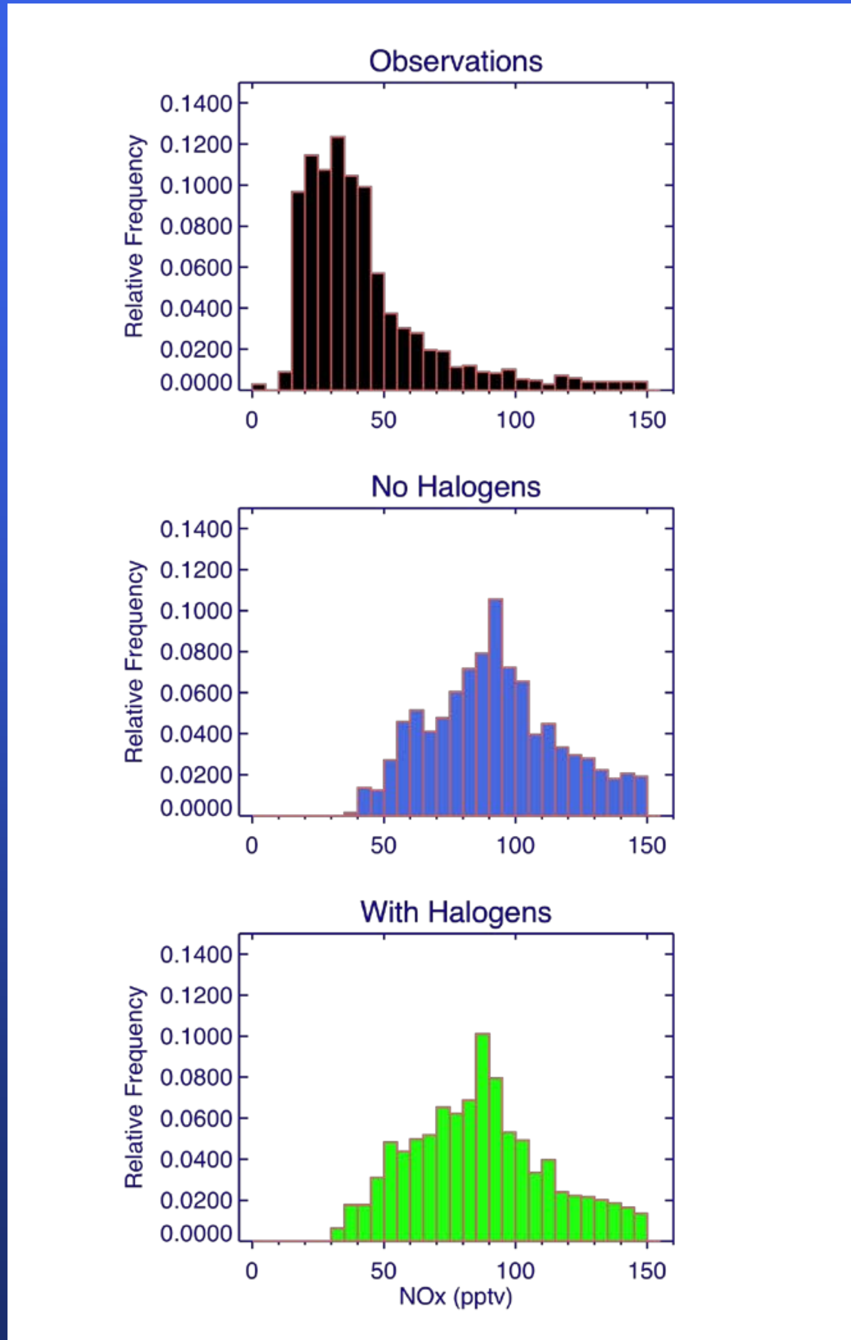


- **Seasonal cycle is well represented.**



Ozone Distribution

- Model without halogen is OK (in for the mean).
- Observations have a broader distribution (more variablity)?

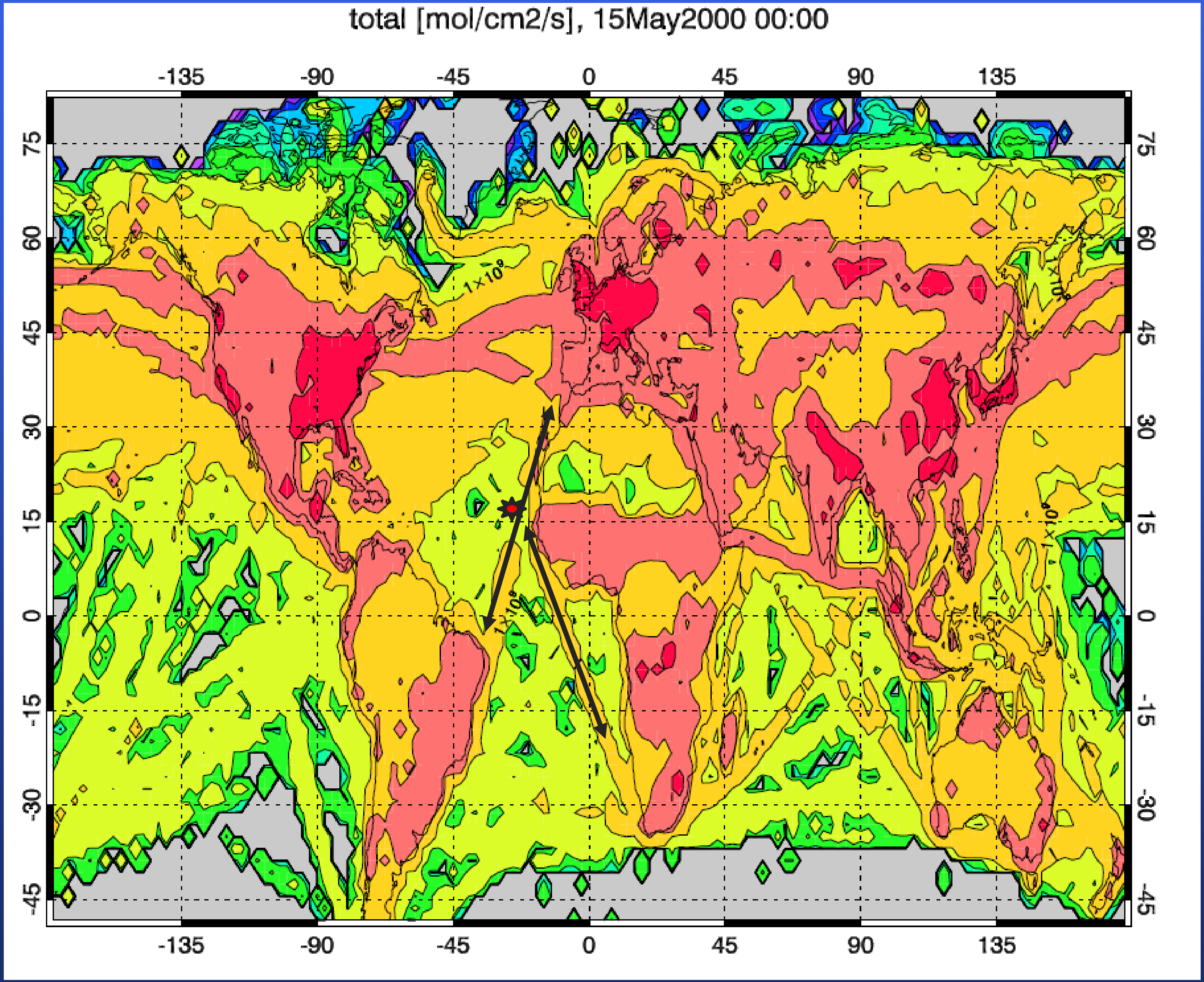


NOx Distribution

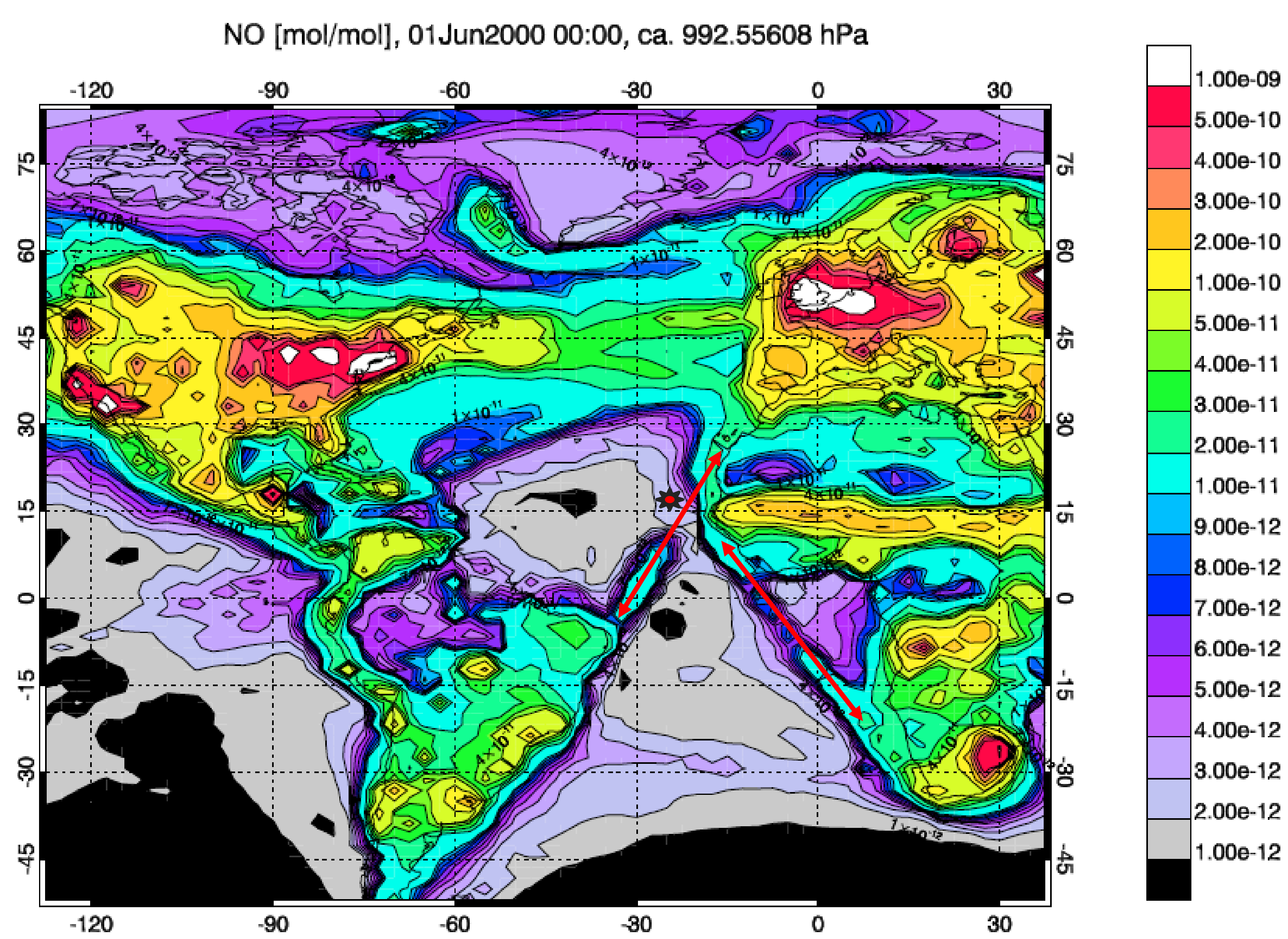
- Model is too high
- Emissions need to be improved?
- Model resolution?

Also have CO distributions

NOx Emissions



NO (vmr) – Baseline Simulation



Outline

- VSL Halogens
- SPaRC CCMVal Chemistry-Climate Model Evaluation
  - Chemistry evaluation [Chapter 6].
  - Results will be published in 2010.

Process	Diagnostic	Variables	Observations	References
1. Photolysis Rates	Offline profiles of key O_3 controlling photolysis rates.	Photolysis rates	Benchmark reference model (Bian and Prather, 2002).	Prather and Remsberg, [1993]
2. Photochemical mechanisms and short timescale chemical processes	Offline box model profile comparisons of fast chemistry constituents (~ ≤ one week)	Full chemical constituents [Reservoir and radical species]	HO_x: balloon, shuttle, aircraft NO_x: satellite, shuttle, balloon, aircraft ClO_x: satellite, shuttle, balloon, aircraft; BrO_x: aircraft	Gao *et al*., [2001] Salawitch *et al.*, [1994a].
	Partitioning of chemical species within the families	Species from families (ClO_x, NO_x, HO_x, BrO_x, Cl_y, NO_y, Br_y) temperature, PV from wind fields	Save as above.	Pierson *et al*., [2000]; Park *et al.*, [1999].
3. Long timescale chemical processes	Comparison of abundance of reservoirs and radical precursors	Instantaneous output of all chemical constituents and temperature (one per month)	Satellite measurements of reservoirs and precursors.	Millard *et al*., [2002], Salawitch *et al.*, [2002], Sen *et al.*, [1998].
	Tracer-tracer relations	O_3, NO_y, CH_4, H_2O, N_2O		Chang *et al*., [1996], Fahey *et al.*, [1996], Müller *et al*., [1996]
4. Polar processes in winter / spring	Chemical Ozone Loss versus PSC activity	O_3, Sulfate SAD, N_2O, T, U, V, PV (derive Eqlat / θ)	Satellite observations of N_2O and O_3; meteorological data products.	Rex *et al*., [2004], Tilmes *et al*., [2004]
	Denitrification/ Dehydration	H_2O, HNO_3, T, U, V, PV (derive Eqlat / θ)	Aura MLS observation of H_2O and HNO_3.	Manney *et al.* [2007], Santee *et al.* [2007], Lambert *et al.* [2007].
	Chlorine Activation	HCl, T, U, V, PV (derive Eqlat / θ)	Aura MLS observation of HCl.	Manney *et al.* [2007], Froidevaux *et al.* [2008].
	NAT/ICE Surface Area Density	T, U, V, PV (derive Eqlat / θ)	No Observation; model/model comparison.	

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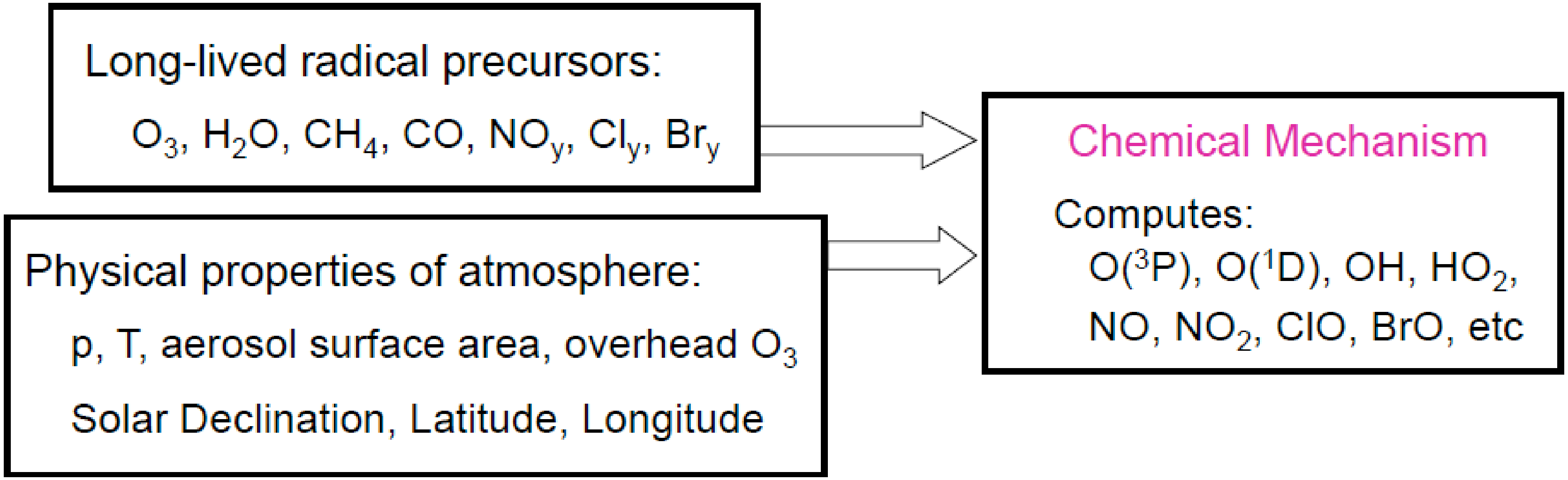
Photochemical Steady State Approach

Chemical Mechanism



Contend:

If all models are using "JPL 2006" kinetics, which defines their **chemical mechanism**, then all models should compute the same values of $O(^3P)$, OH, NO, ClO, BrO, etc for the same specification of long-lived radical precursors & physical properties

Salawitch, Canty, Kinnison, and Chipperfield.

Grading the Models

- We then use σ_{PSS} and σ_{CCM} in the computation of g, which is shown for each panel of each plot (this took a fair amount of effort to setup and formulate ☺):

$$g = \frac{1}{N} \sum_{0}^{N} 1 - \left(\frac{\text{abs}(\text{Mixing Ratio}_{CCM} - \text{Mixing Ratio}_{PSS})}{3 \cdot (\sigma_{CCM} + \sigma_{PSS})} \right)$$

where we have:

a) floored g at 0 for each altitude (i.e., g is not allowed to go negative)

b) evaluated g between: the tropopause (which we determine) and 1 hPa for all species except BrO/Br_y, the tropopause (which we determine) and 5 hPa for all BrO/Br_y (there seem to be issues with model representation of BrO at high altitude, where it simply does not matter, for BrO we focus on only the altitudes that matter ☺

c) evaluated g for JPL 2002 kinetics and JPL 2006 kinetics for $O(^1D)$ and BrO/Br_y, and propagate the higher value of g (many CCMs clearly did not add the O+BrONO2 reaction, new for JPL 2006, into their chemical mechanism; since we can account for this nuance, we will show the best value of g, but will indicate on the metric summary which kinetic set was used)

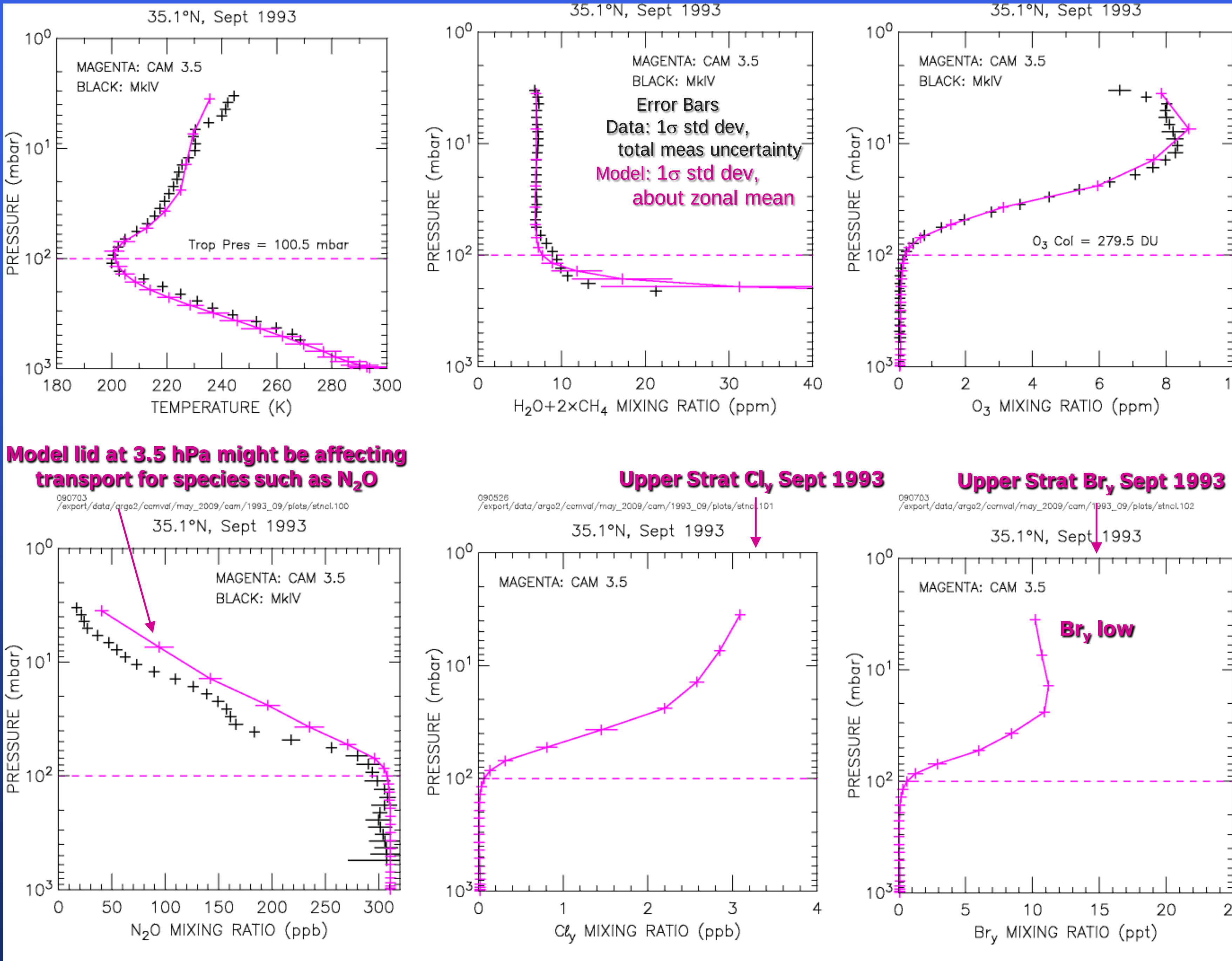
(again, this builds on the work of Waugh & Eyring, ACP, 2008)

σ_{obs} = is the uncertainly in the observations

σ_{ccm} = average value of the std dev about the zonal mean

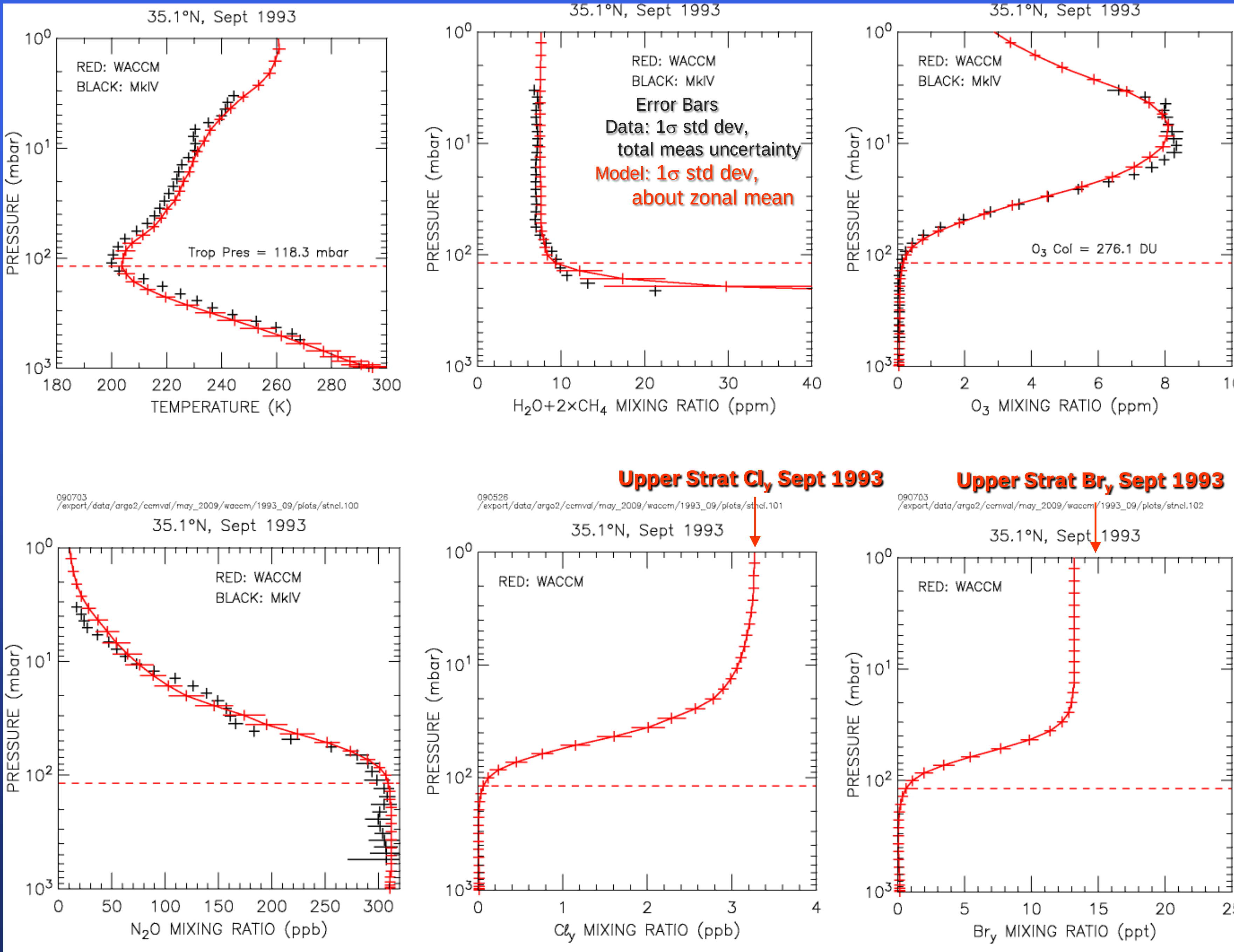
Salawitch, Canty, Kinnison, and Chipperfield.

CAM 3.5



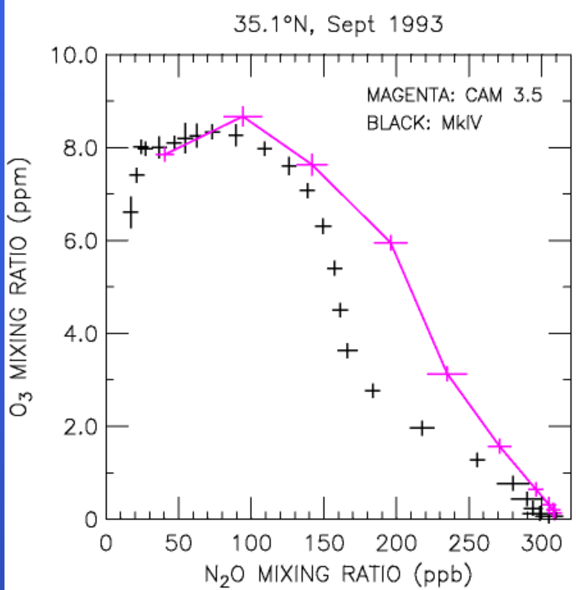
35.1°N, Sept 1993
MAGENTA: CAM 3.5
BLACK: MkIV
Trop Pres = 100.5 mbar
PRESSURE (mbar)
TEMPERATURE (K)
35.1°N, Sept 1993
MAGENTA: CAM 3.5
BLACK: MkIV
Error Bars
Data: 1σ std dev, total meas uncertainty
Model: 1σ std dev, about zonal mean
PRESSURE (mbar)
H2O+2×CH4 MIXING RATIO (ppm)
35.1°N, Sept 1993
MAGENTA: CAM 3.5
BLACK: MkIV
O3 Col = 279.5 DU
PRESSURE (mbar)
O3 MIXING RATIO (ppm)
Model lid at 3.5 hPa might be affecting transport for species such as N2O
Upper Strat Cly Sept 1993
Upper Strat Bry Sept 1993
090703
/export/data/argo2/ccmval/may_2009/cam/1993_09/plots/stncl.100
35.1°N, Sept 1993
MAGENTA: CAM 3.5
BLACK: MkIV
PRESSURE (mbar)
N2O MIXING RATIO (ppb)
090526
/export/data/argo2/ccmval/may_2009/cam/1993_09/plots/stncl.101
35.1°N, Sept 1993
MAGENTA: CAM 3.5
PRESSURE (mbar)
Cly MIXING RATIO (ppb)
090703
/export/data/argo2/ccmval/may_2009/cam/1993_09/plots/stncl.102
35.1°N, Sept 1993
MAGENTA: CAM 3.5
Bry low
PRESSURE (mbar)
Bry MIXING RATIO (ppt)

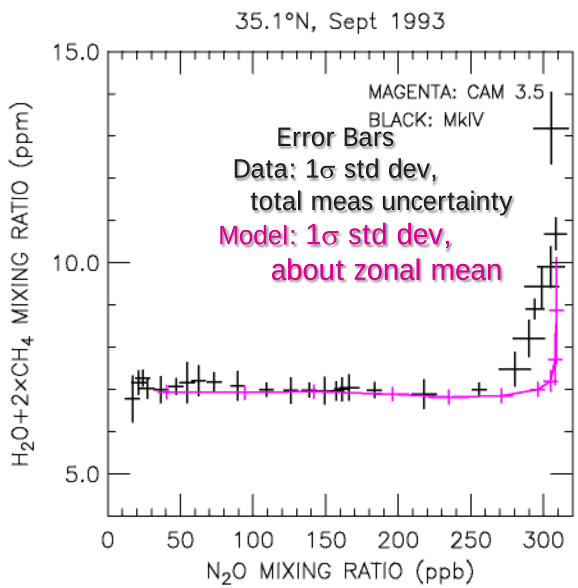
WACCM

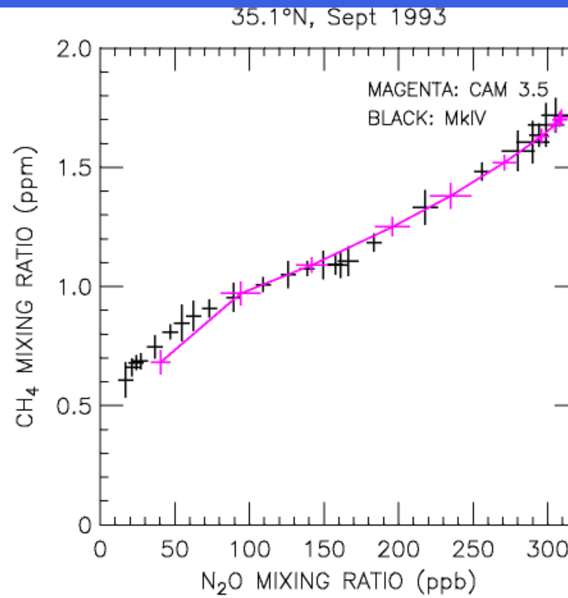


35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
Trop Pres = 118.3 mbar
PRESSURE (mbar)
TEMPERATURE (K)
35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
Error Bars
Data: 1σ std dev,
total meas uncertainty
Model: 1σ std dev,
about zonal mean
PRESSURE (mbar)
H2O+2×CH4 MIXING RATIO (ppm)
35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
O3 Col = 276.1 DU
PRESSURE (mbar)
O3 MIXING RATIO (ppm)
Upper Strat Cly Sept 1993
Upper Strat Bry Sept 1993
090703
/export/data/argo2/ccmval/may_2009/waccm/1993_09/plots/stncl.100
35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
PRESSURE (mbar)
N2O MIXING RATIO (ppb)
090526
/export/data/argo2/ccmval/may_2009/waccm/1993_09/plots/stncl.101
35.1°N, Sept 1993
RED: WACCM
PRESSURE (mbar)
Cly MIXING RATIO (ppb)
090703
/export/data/argo2/ccmval/may_2009/waccm/1993_09/plots/stncl.102
35.1°N, Sept 1993
RED: WACCM
PRESSURE (mbar)
Bry MIXING RATIO (ppt)

CAM 3.5

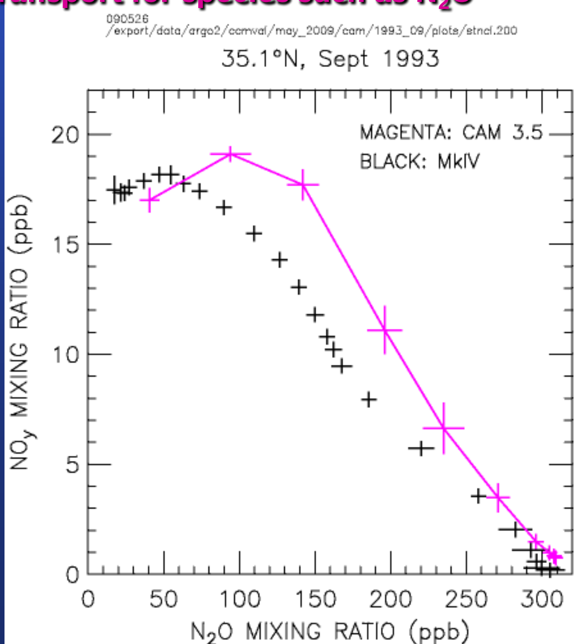


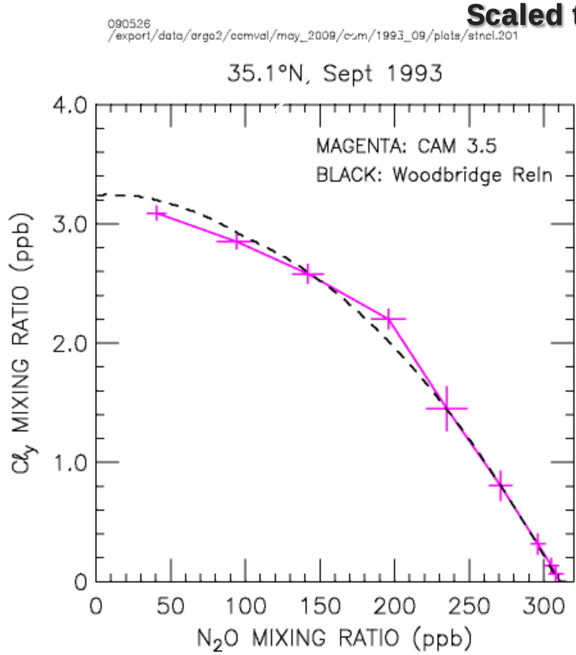


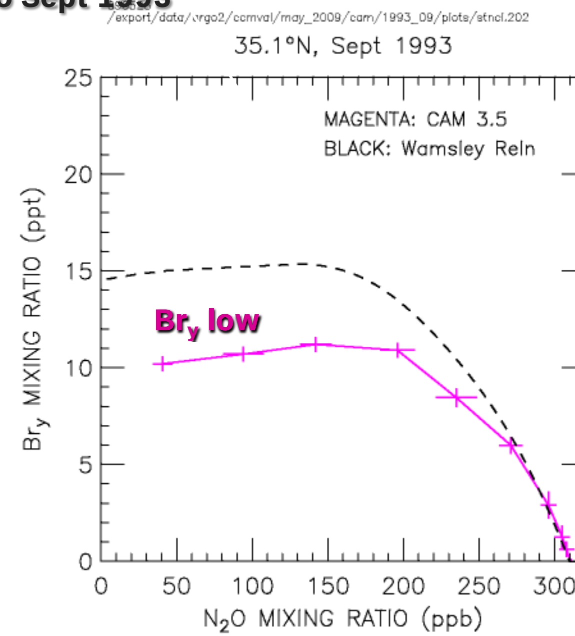


Model lid at 3.5 hPa might be affecting transport for species such as N_2O

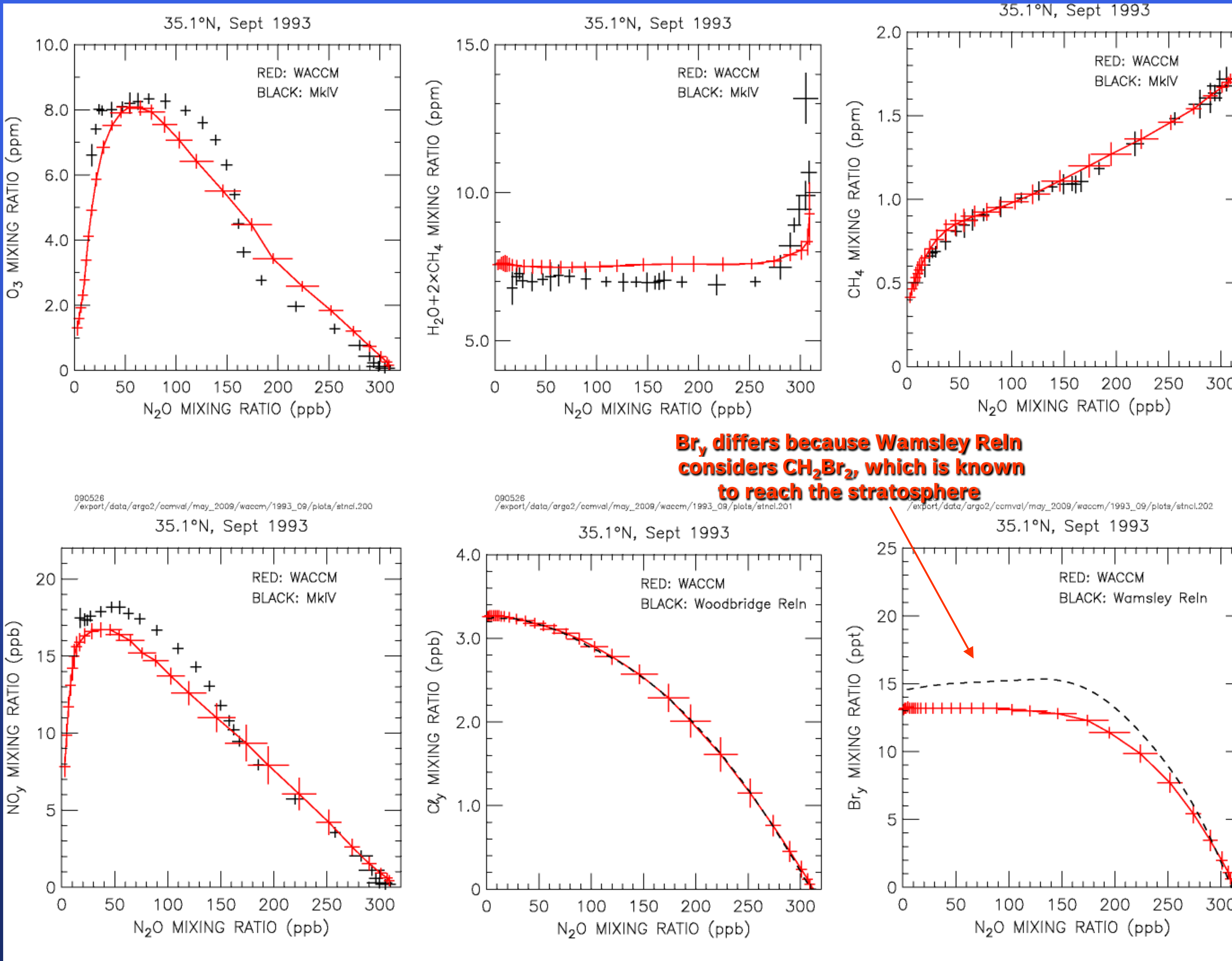
Woodbridge and Wamsley Relns Scaled to Sept 1993





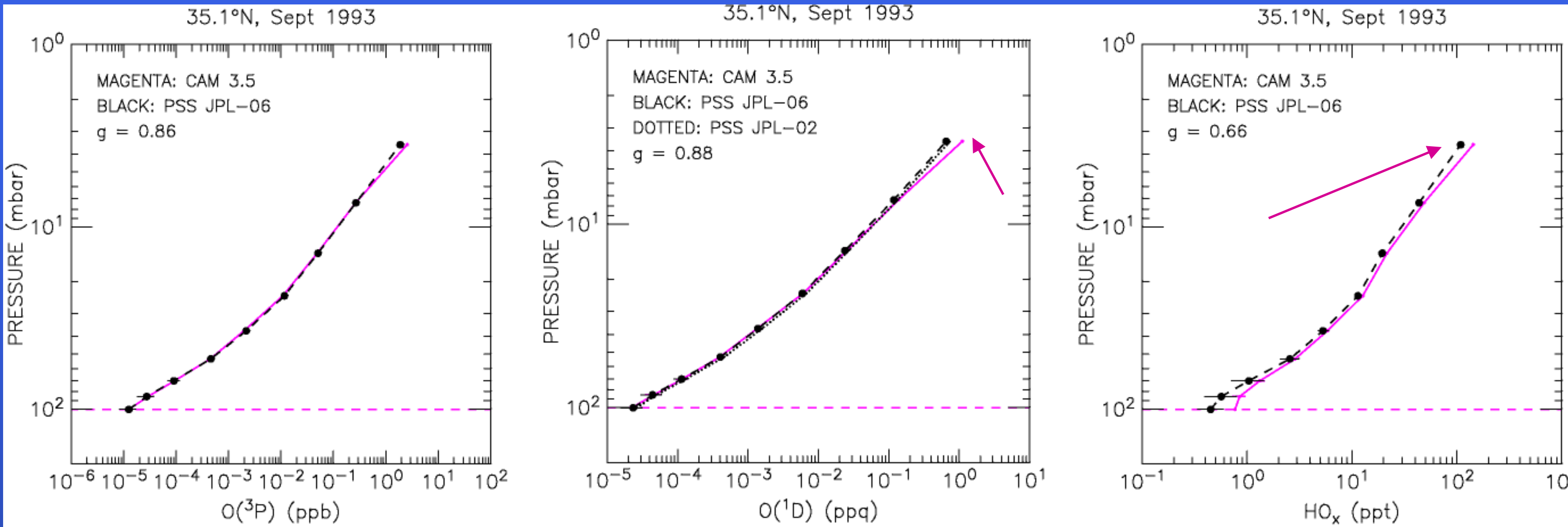


WACCM

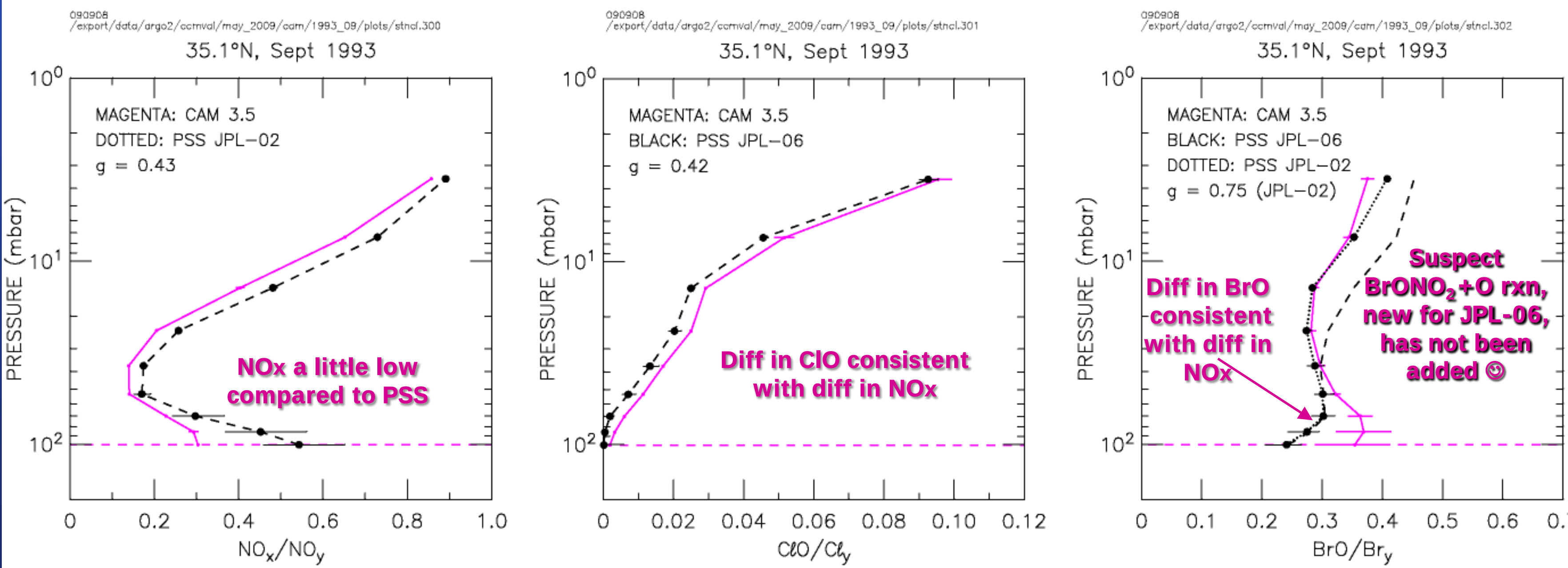


35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
O_3 MIXING RATIO (ppm)
N_2O MIXING RATIO (ppb)
35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
$H_2O+2\times CH_4$ MIXING RATIO (ppm)
N_2O MIXING RATIO (ppb)
35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
CH_4 MIXING RATIO (ppm)
N_2O MIXING RATIO (ppb)
Br_y differs because Wamsley Reln considers CH_2Br_2, which is known to reach the stratosphere
090526 /export/data/argo2/ccmval/may_2009/waccm/1993_09/plots/stncl.200
35.1°N, Sept 1993
RED: WACCM
BLACK: MkIV
NO_y MIXING RATIO (ppb)
N_2O MIXING RATIO (ppb)
090526 /export/data/argo2/ccmval/may_2009/waccm/1993_09/plots/stncl.201
35.1°N, Sept 1993
RED: WACCM
BLACK: Woodbridge Reln
Cl_y MIXING RATIO (ppb)
N_2O MIXING RATIO (ppb)
/export/data/argo2/ccmval/may_2009/waccm/1993_09/plots/stncl.202
35.1°N, Sept 1993
RED: WACCM
BLACK: Wamsley Reln
Br_y MIXING RATIO (ppt)
N_2O MIXING RATIO (ppb)

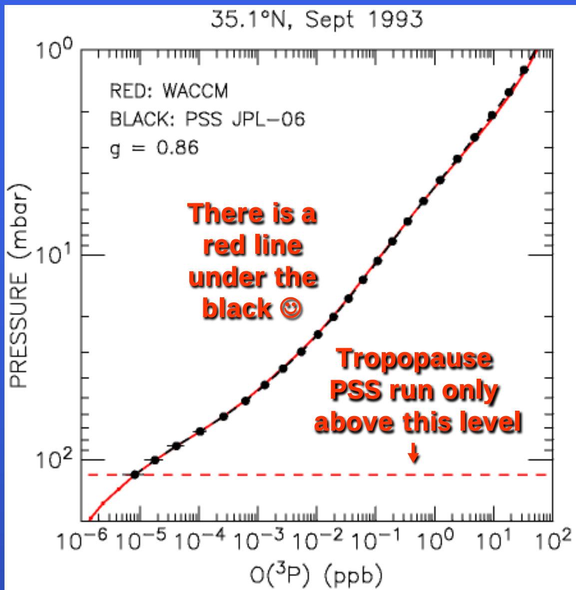
CAM 3.5

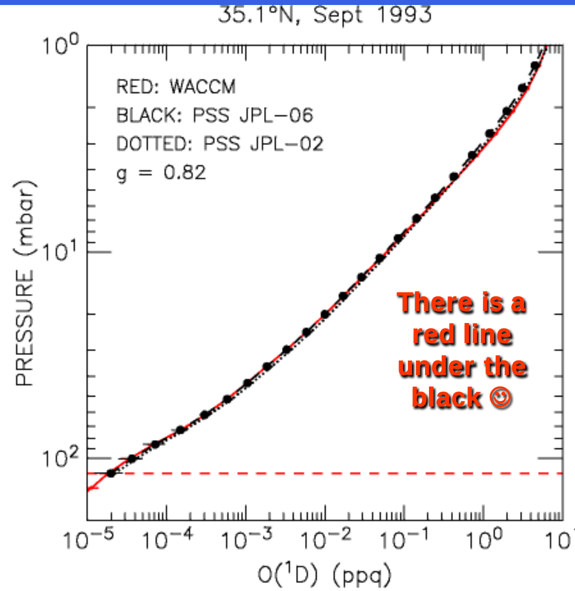


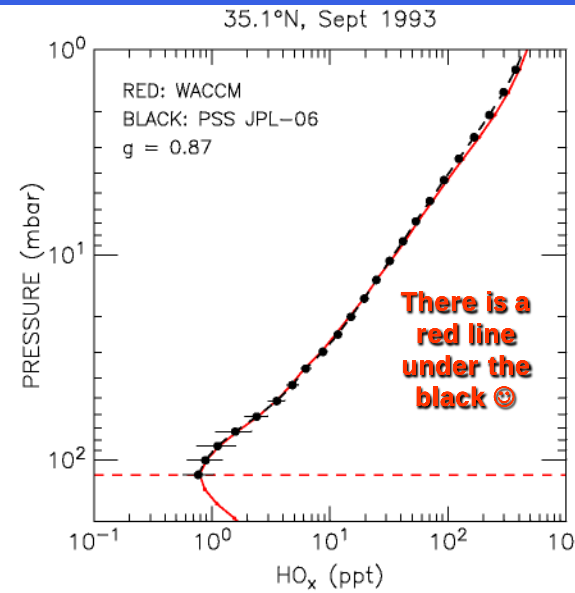
Looks good. NOx a little low. $BrONO_2$+O rxn was not included in thist model



WACCM

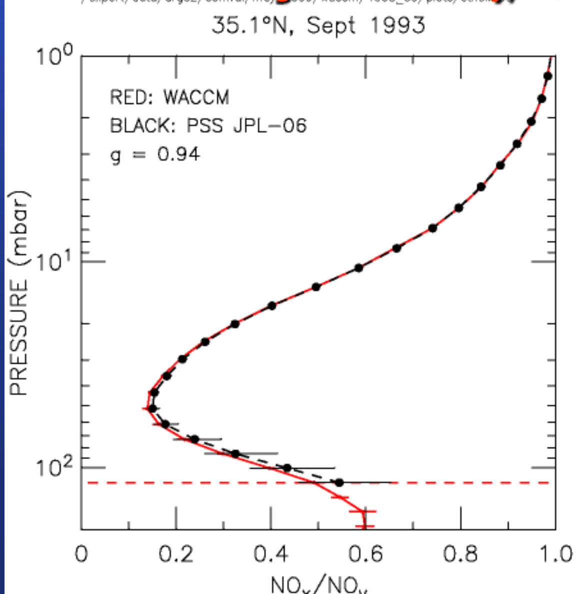


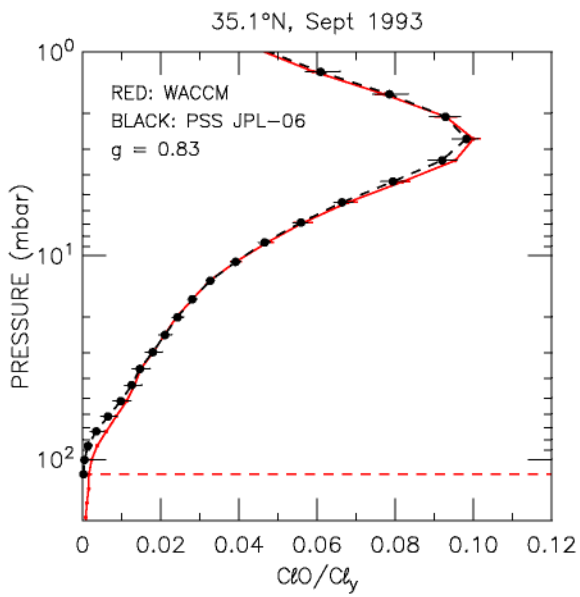


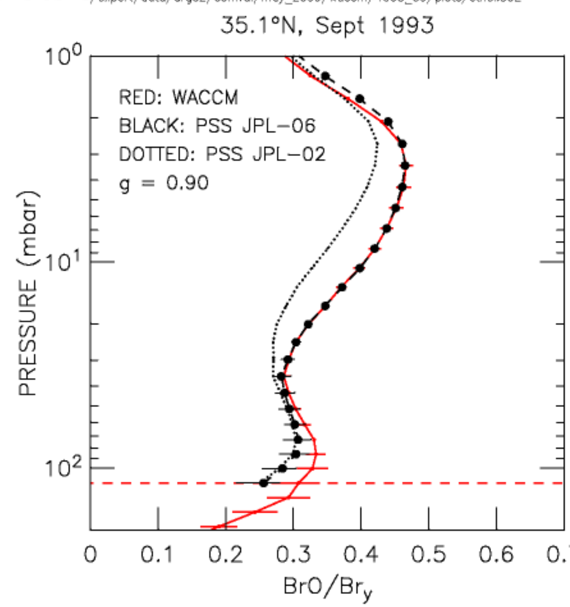


As good as it gets ! If we are actually solving the same set of chemical reactions, as we aspire, then all comparisons should look nearly this good ☺

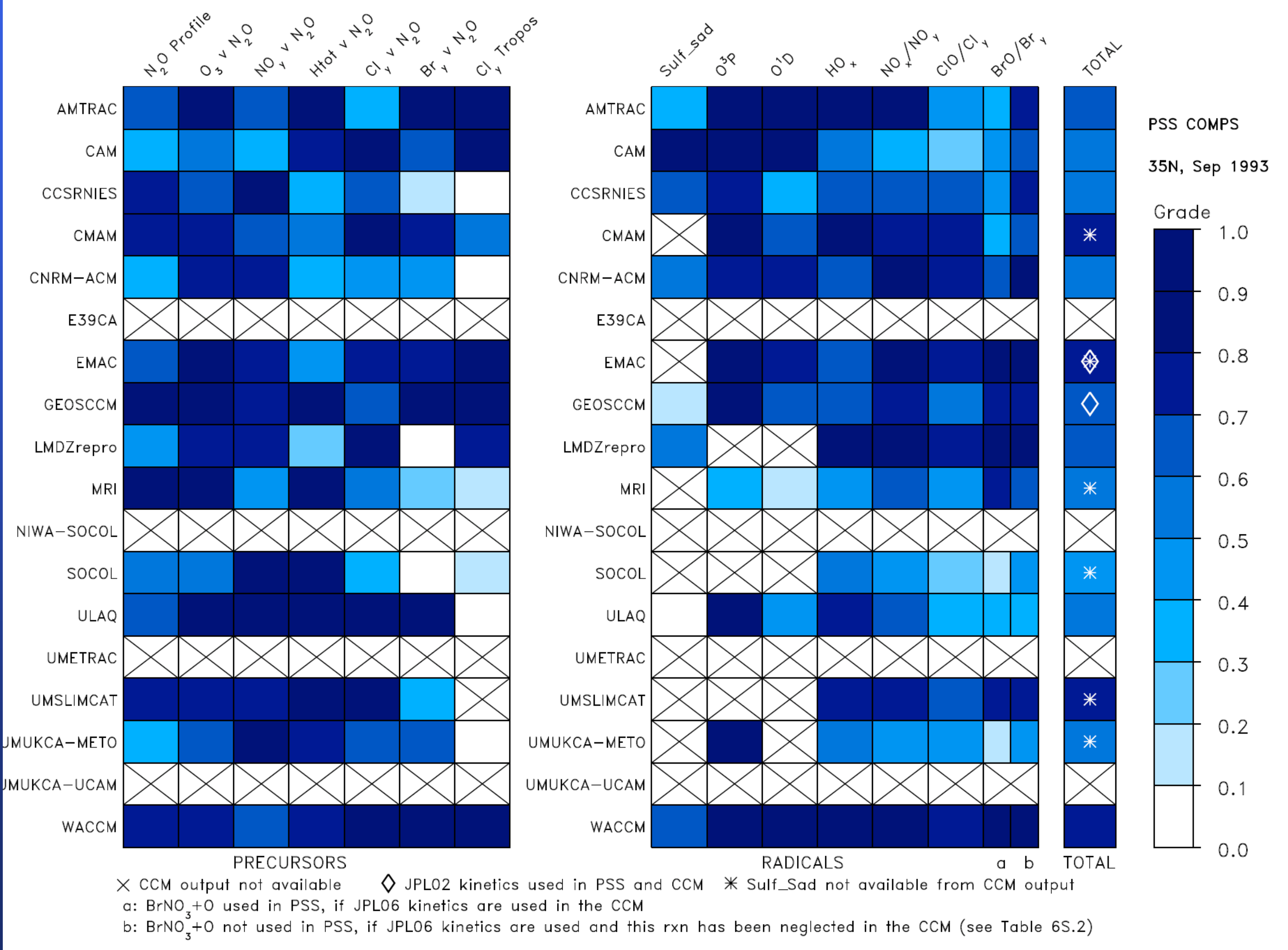
Values of g are not unity, however, because the multi-decadal log plots obscure small differences



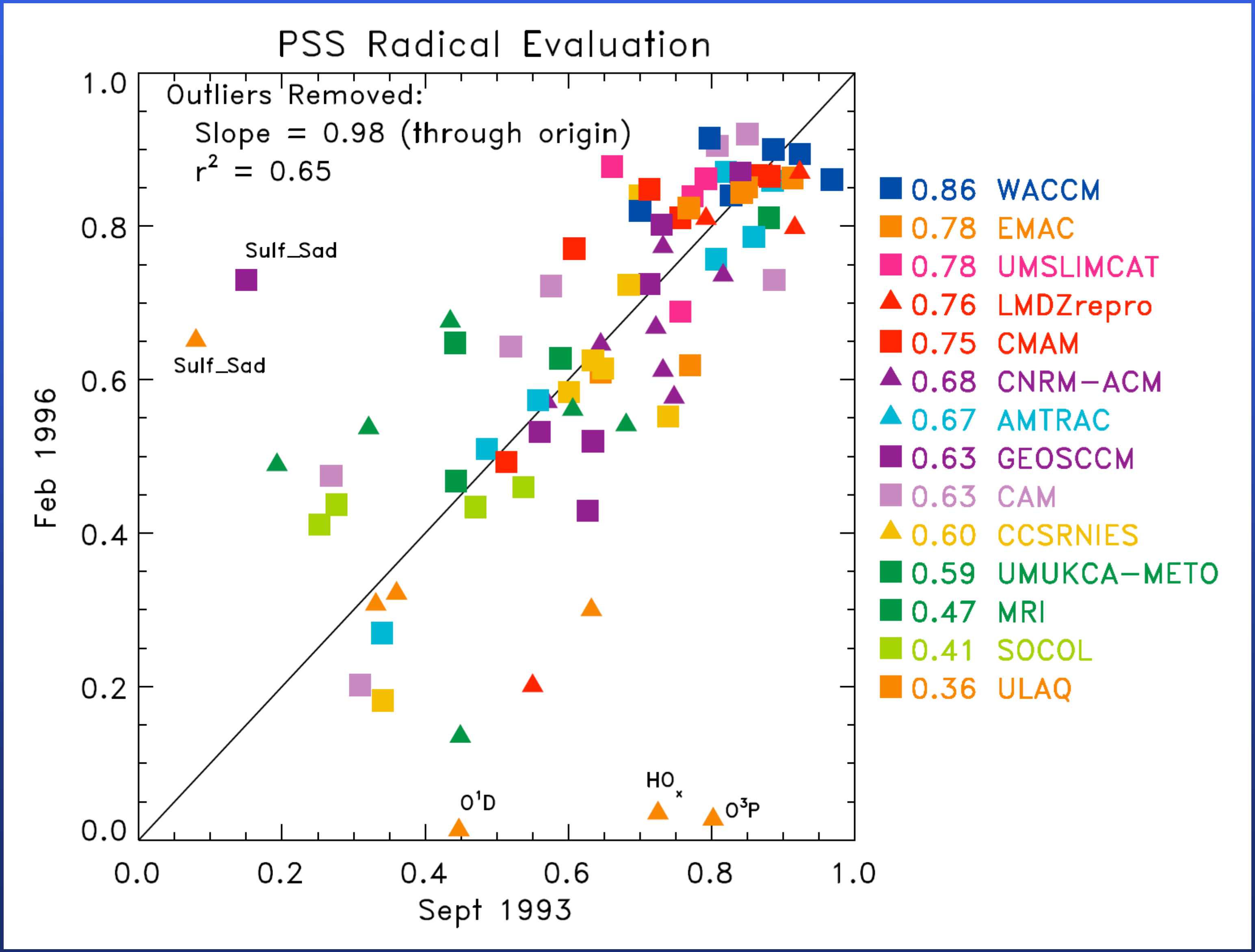




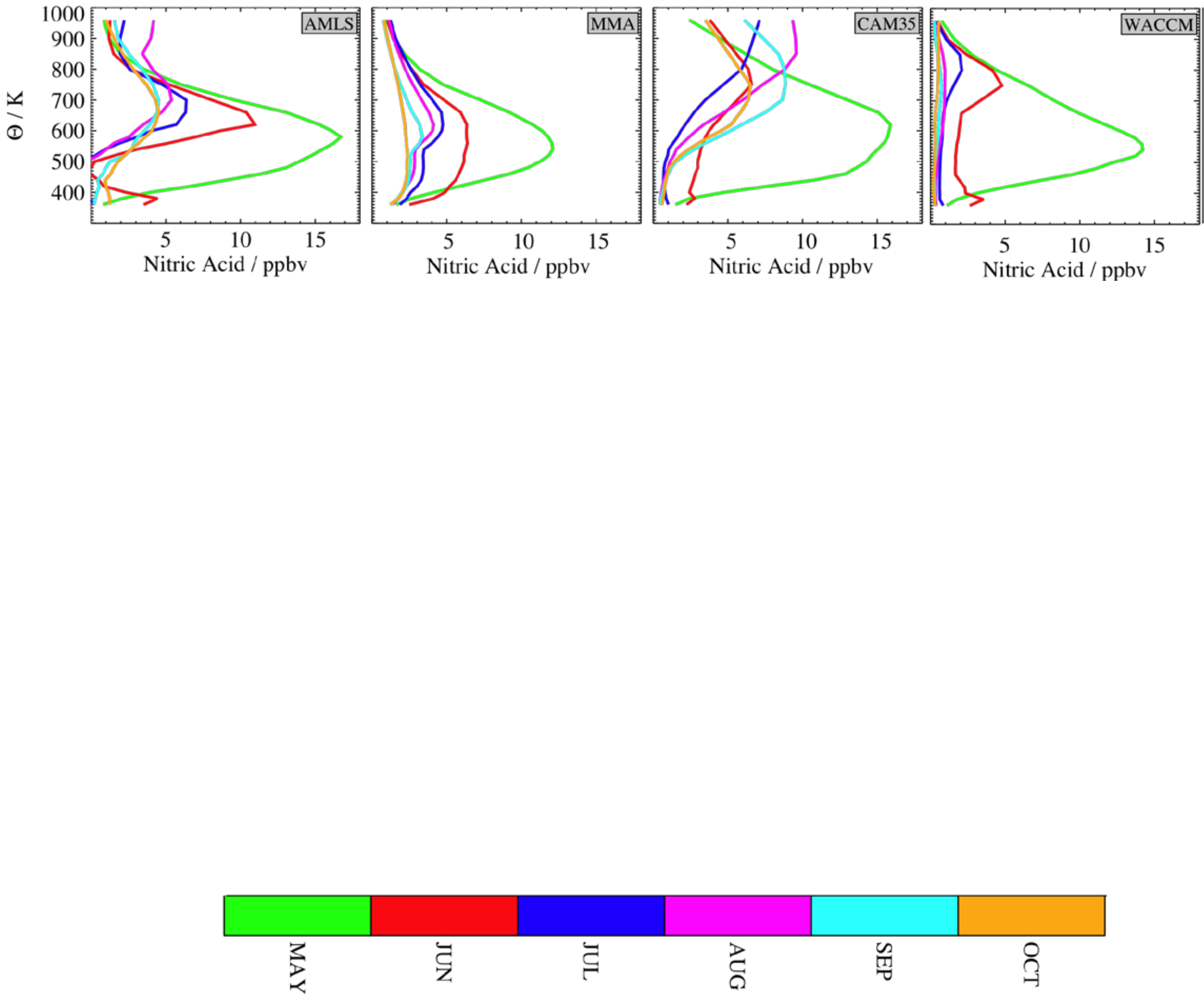
PSS Grading Table



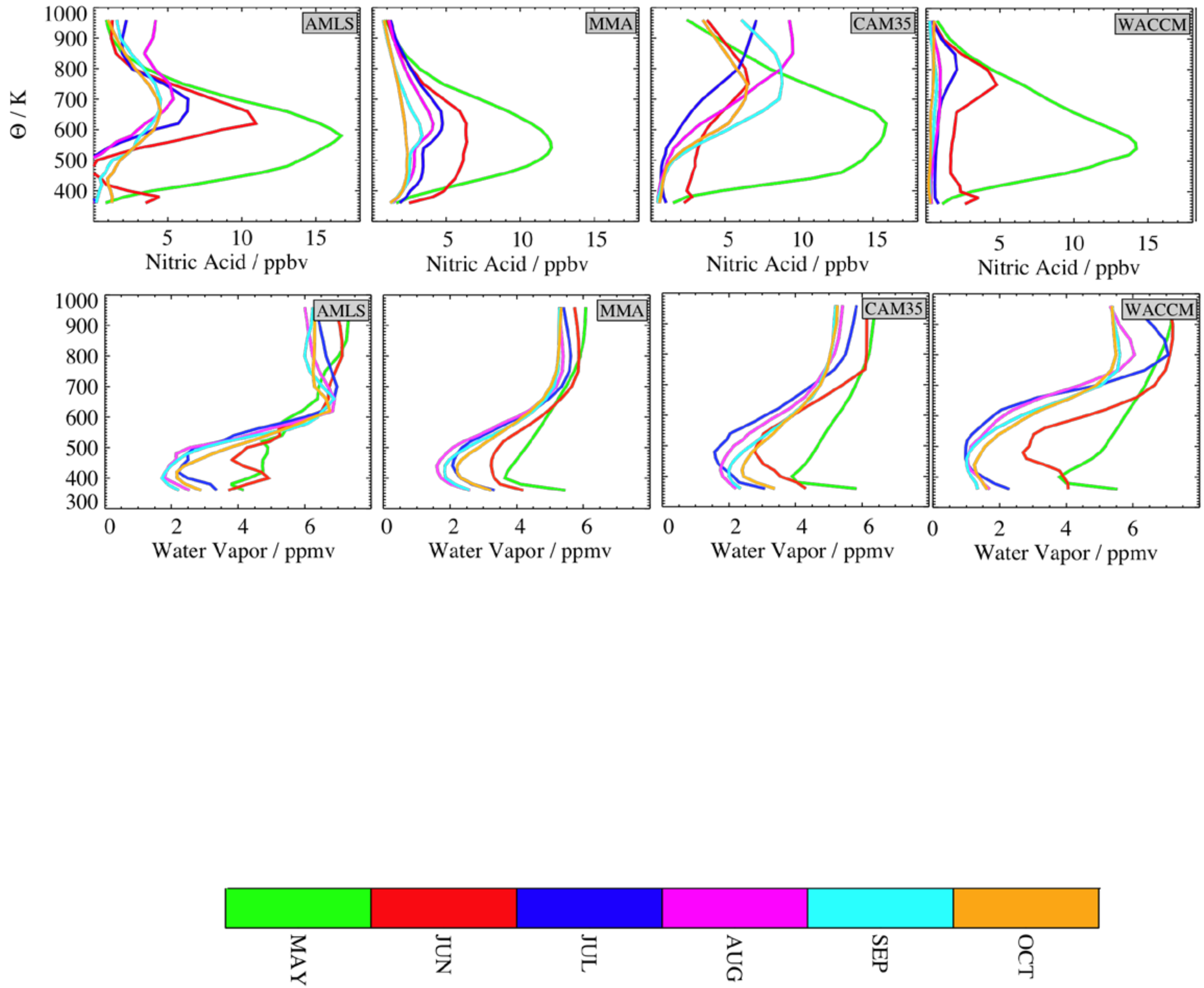
Correlation low vs high SAD



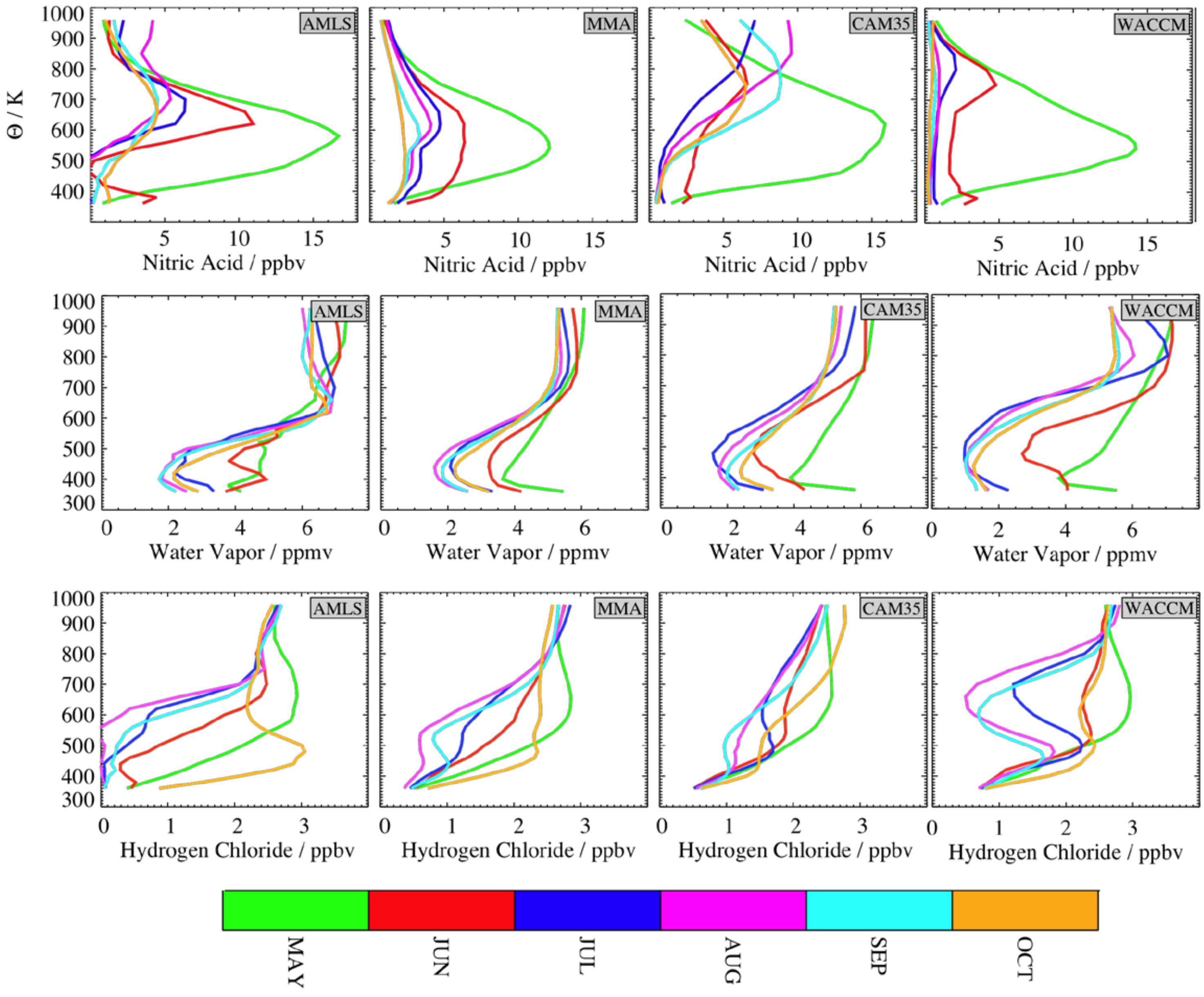
Equivalent Latitude 89°S-79°S and Θ



Equivalent Latitude 89°S-79°S and Θ



Equivalent Latitude 89°S-79°S and Θ



Summary of Chemistry Evaluation

- Overall, CAM-CHEM graded out high in the Photocomp and Long-lived sections (not shown).
- Comparison in the fast chemistry section was also generally good; with the exceptions that the NOx/NO_Y and Clx / Cl_Y were graded lower!?
- The ozone hole was not as deep as observations; which is probably due to a warm bias. More work is needed here (i.e., validate the polar chemistry).

The End!