1-D Modeling Analysis of HOx chemistry during PASE

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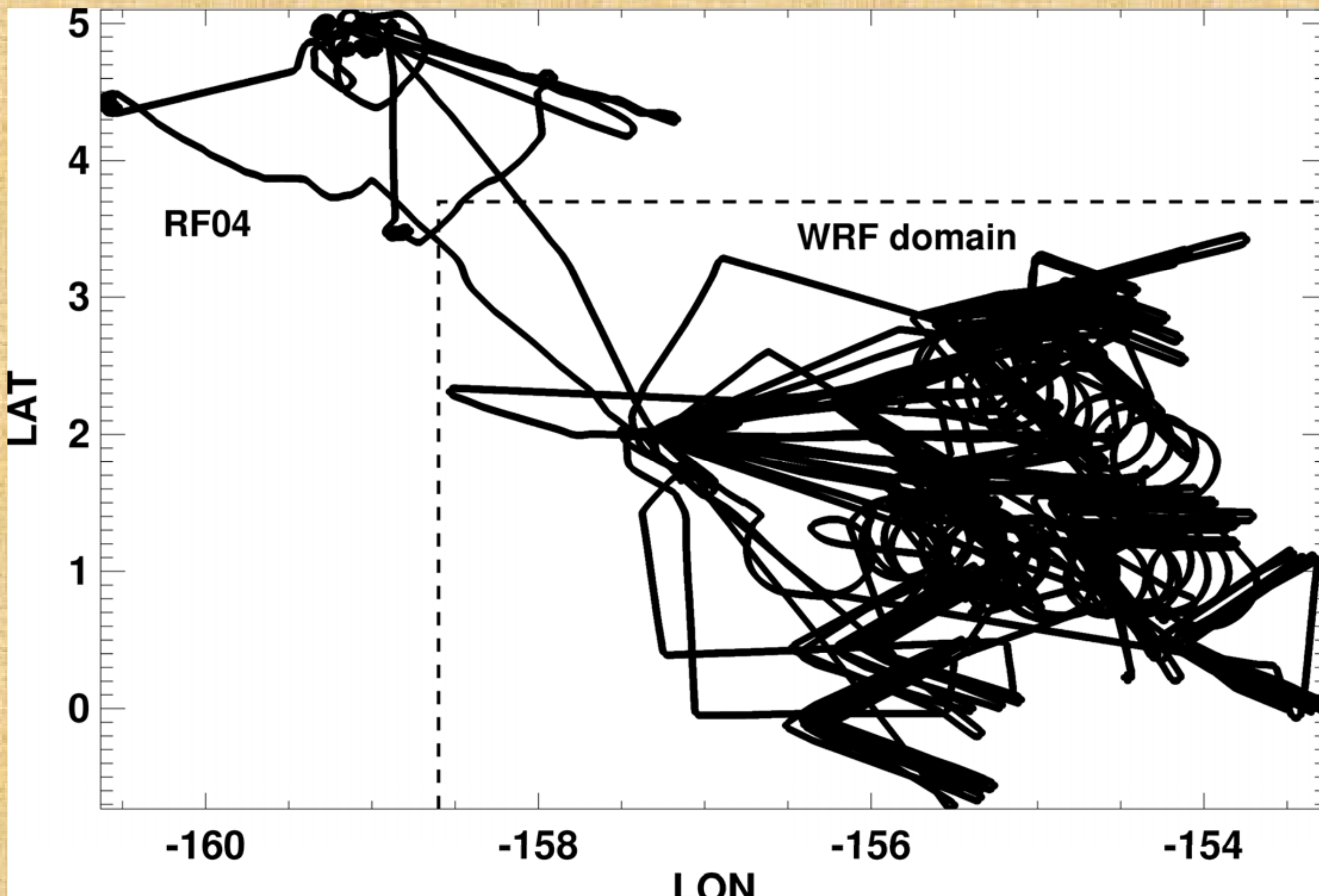
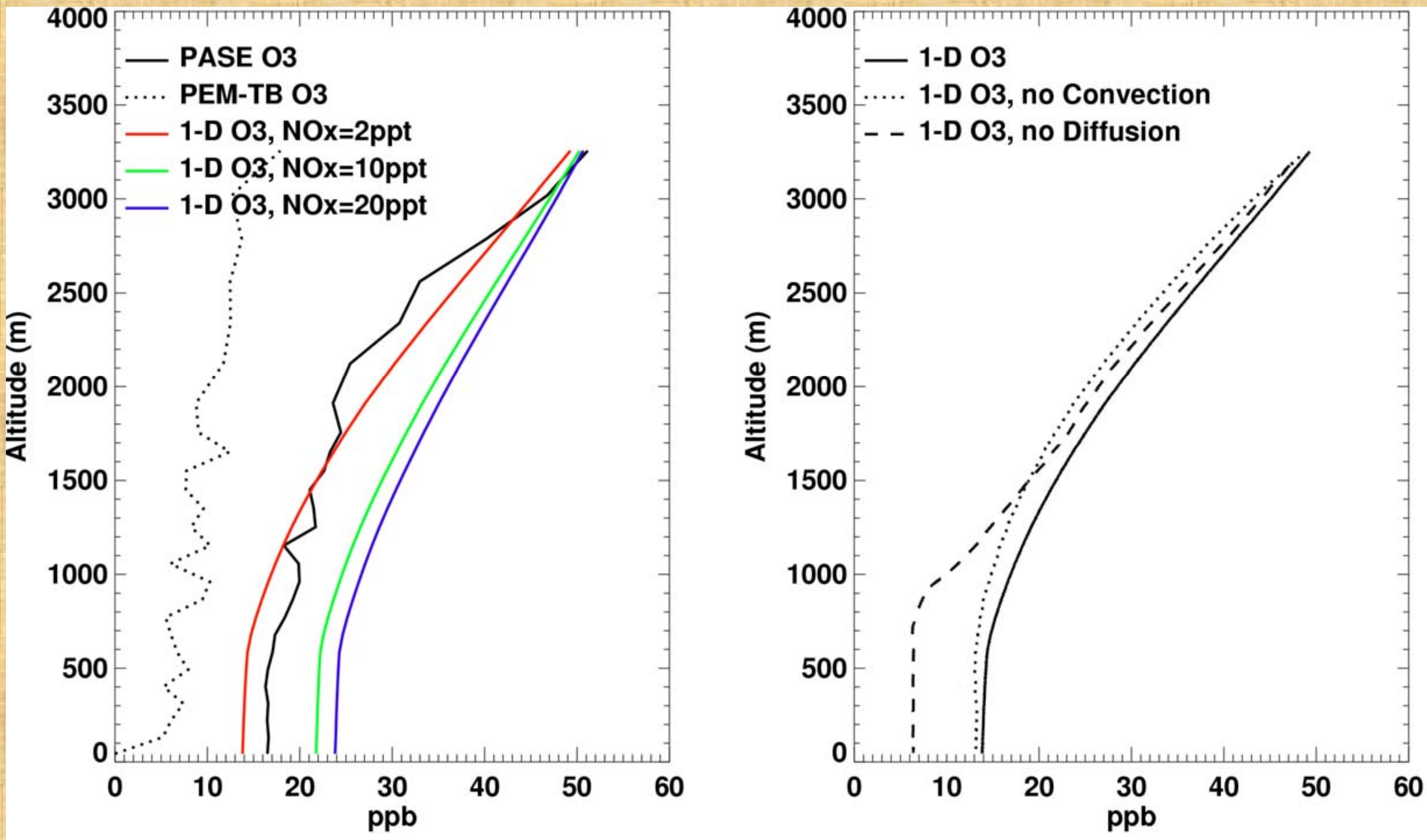
WRF (10-km resolution) modeling domain



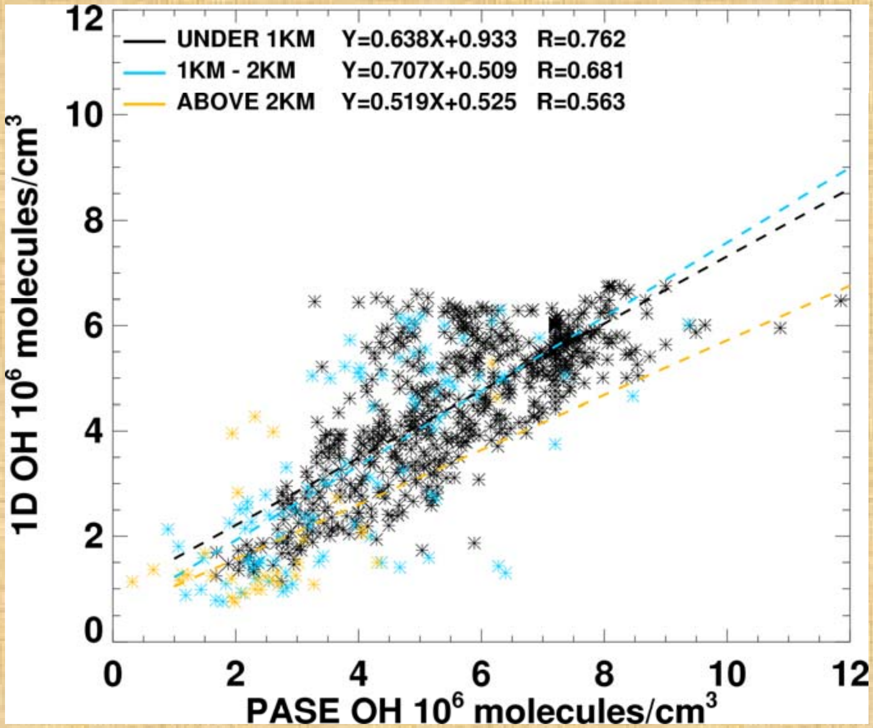
Model Setup

- 1-D chemical transport model (REAM)
- Assimilated meteorological fields using WRF
- O_3, CO, and water vapor concentrations are specified as observed (limited to the first 8 flights). Total ozone column from OMI.
- Diurnal steady-state OH, HO_2, H_2O_2, and CH_3OOH.

• Low NOx (2 ppt) is most consistent with the obs
• Diffusion transport is more important than convective transport for O_3



- Reasonably good comparison with the obs
- The range of simulated HO_2 is higher than measured



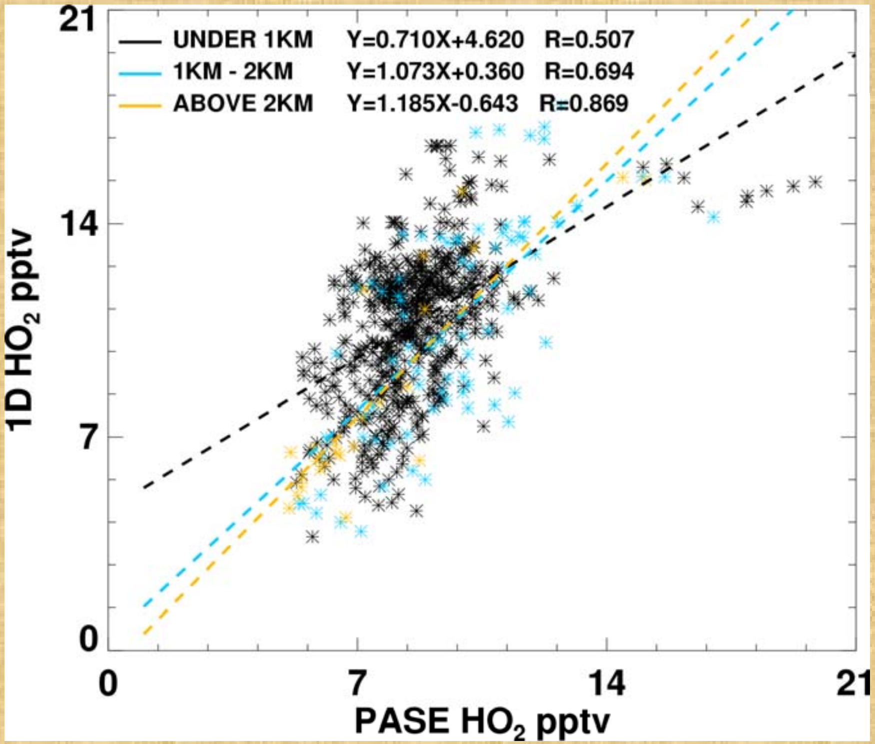


Table 1. Observation-to-Model ratio of OH and HO_2 in previous studies

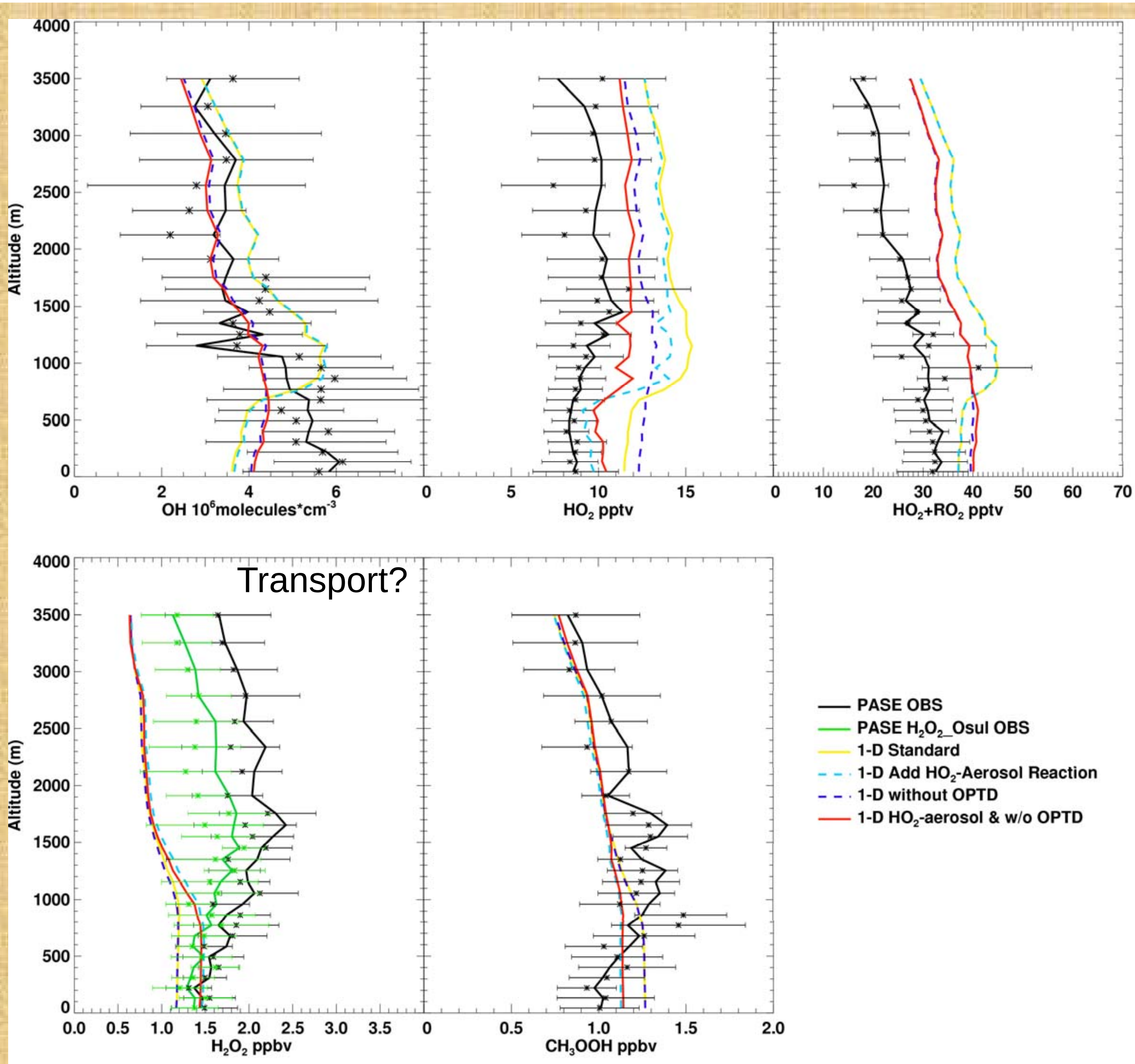
OH OBS/Mod	HO_2 OBS/Mod	Campaign (Location)	Reference
1.28	1.43	SUCCESS	[*Jaegle et al.*, 2001]
0.83	0.83	SONEX	[*Jaegle et al.*, 2001]
1.10	0.97	PEM-TB	[*Olson et al.*, 2001]
0.71~0.93	0.81	TRACE-P	[*Olson et al.*, 2004]
0.53	0.74~1.04		[*Kanaya et al.*, 2007]
0.95	1.28	INTEX-A	[*Ren et al.*, 2008]
1.27	0.81	PASE	this work

Heterogeneous loss of HO_2

$$\frac{d[HO_2]}{dt} = -\left(\frac{r_p}{D_{HO_2}} + \frac{4}{\gamma\omega}\right)^{-1} A[HO_2]$$

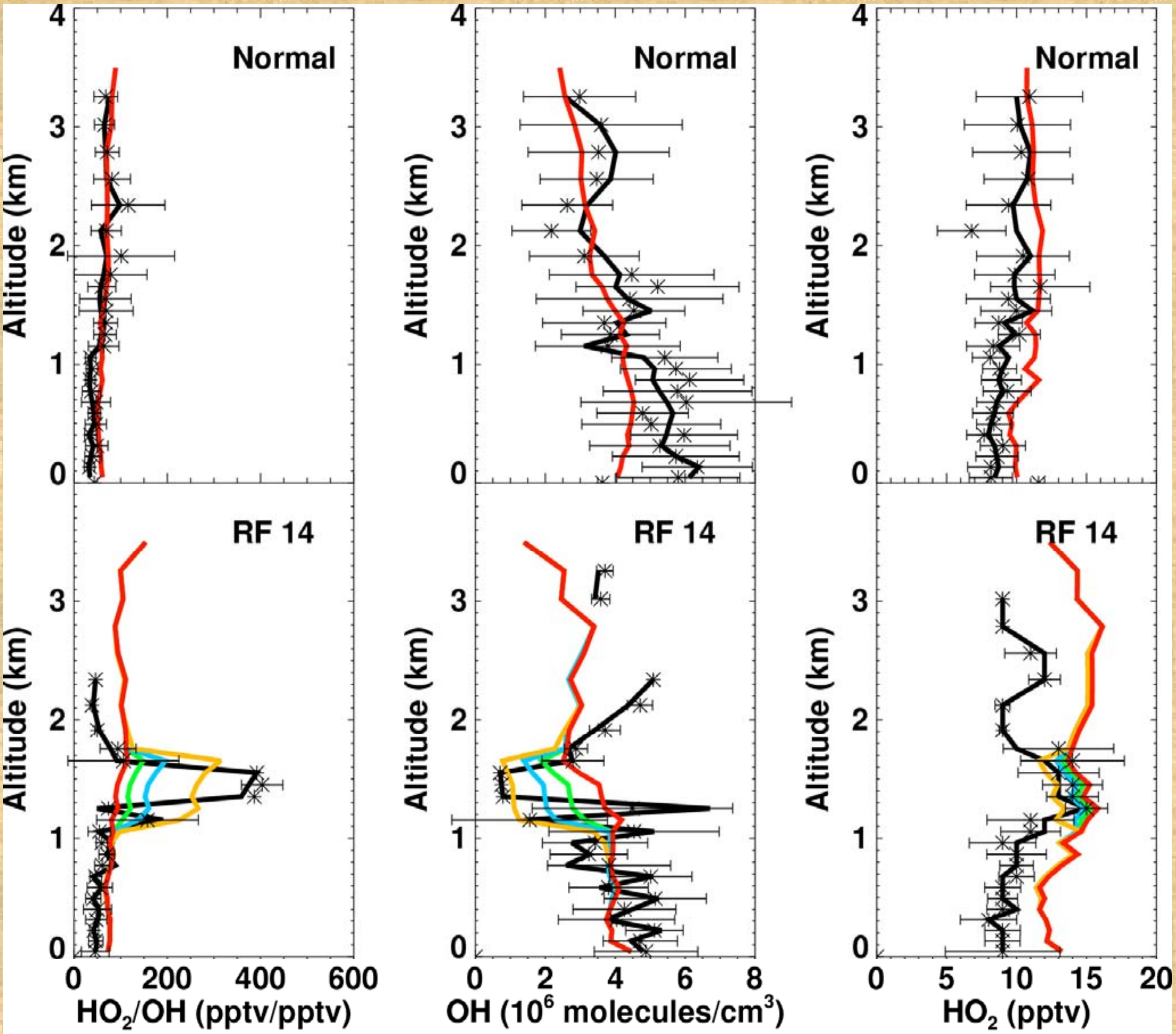
Table 2. Heterogeneous reaction probabilities of HO_2 in previous studies

Aerosol Type					γ	*Reference*
Sulfate	Black Carbon	Organic Carbon	Sea Salt	Dust		
				X	0.1	[*Dentener et al.*, 1996]
X	X				0.2~0.5	[*Tie et al.*, 2001]
X	X	X		X	0.2	[*Liao et al.*, 2003]
X	X	X	X	X	0.2	[*Martin et al.*, 2003]
X					0.01~0.8	[*Thornton and Abbatt*, 2005]
X	X	X	X	X	0.1~0.3	[*Thornton et al.*, 2008]



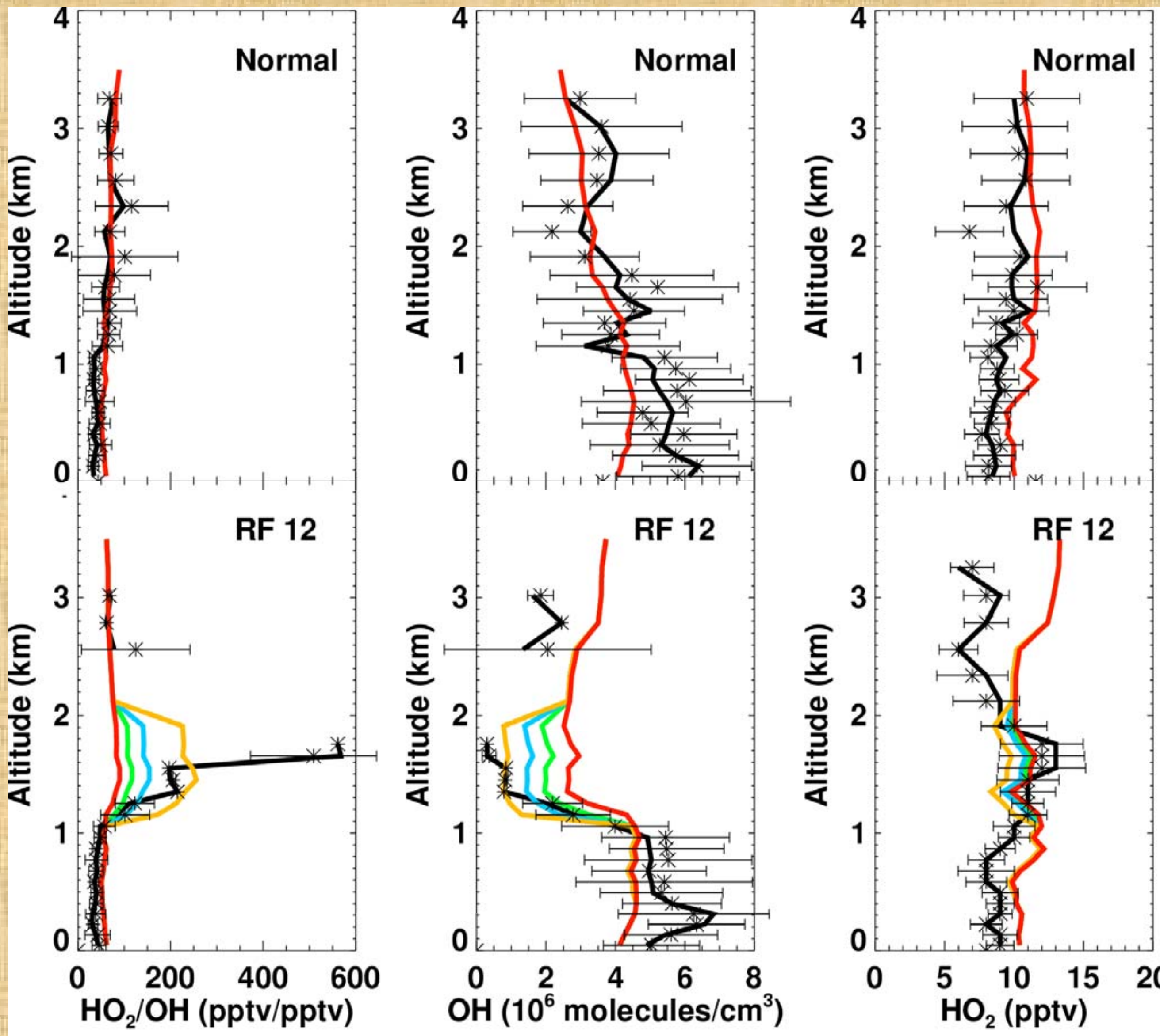
Transport?
Altitude (m)
OH 10^6 molecules*cm^-3
HO2 pptv
HO2+RO2 pptv
H2O2 ppbv
CH3OOH ppbv
PASE OBS
PASE H2O2_Osul OBS
1-D Standard
1-D Add HO2-Aerosol Reaction
1-D without OPTD
1-D HO2-aerosol & w/o OPTD

Abnormal OH during RF 12 and 14



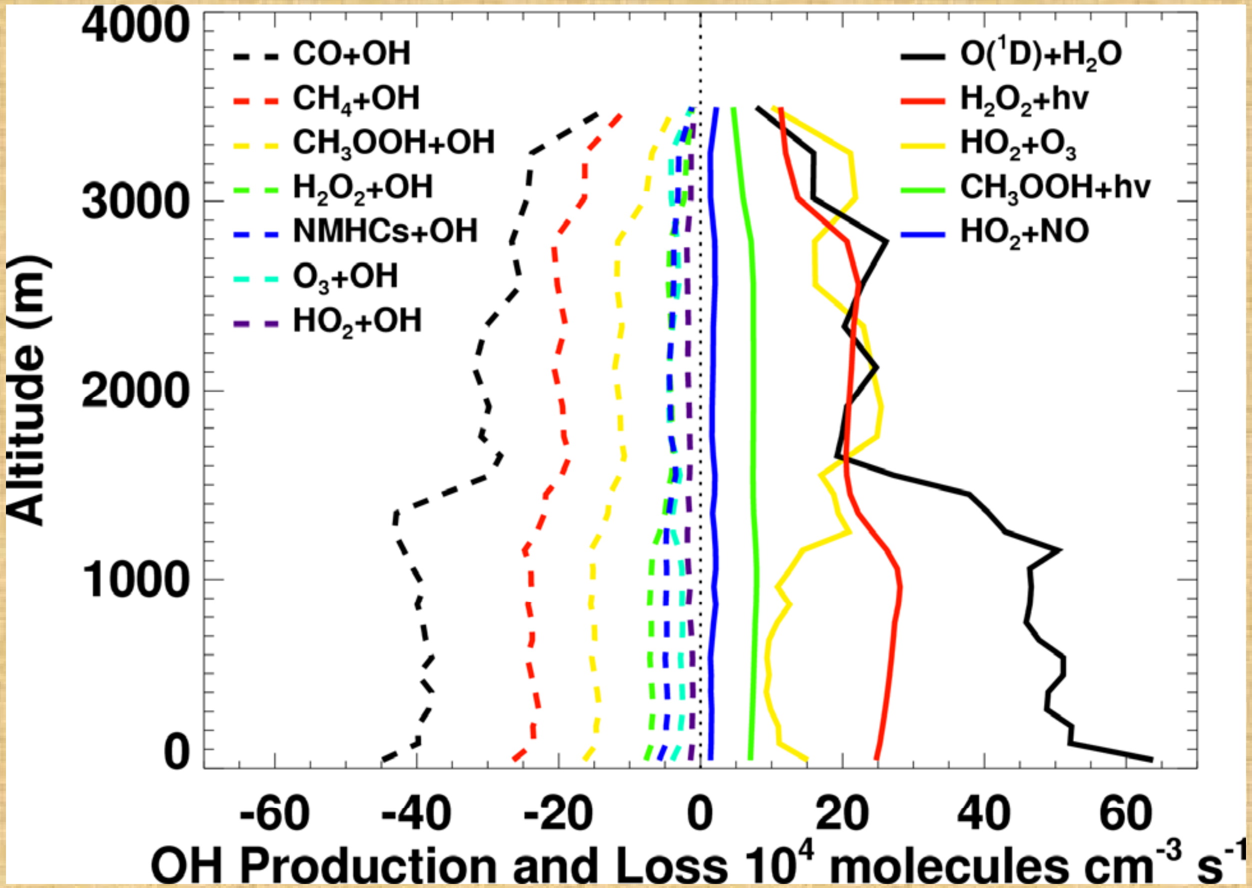
HO_2/OH OH HO_2

Abnormal OH during RF 12 and 14



HO_2/OH OH HO_2

OH Production and Loss and HO_2/OH ratio



$$\frac{[HO_2]}{[OH]} = \frac{k_{OH+CO}[CO] + k_{OH+CH_4}[CH_4] + k_{OH+O_3}[O_3] + k_{OH+NMHCs}[NMHCs]}{k_{HO_2+NO}[NO] + k_{HO_2+O_3}[O_3] + k_{HO_2+BrO}\underline{[BrO]} + P(OH)_{primary}/[HO_2]}$$

Evidence for oceanic VOCs?

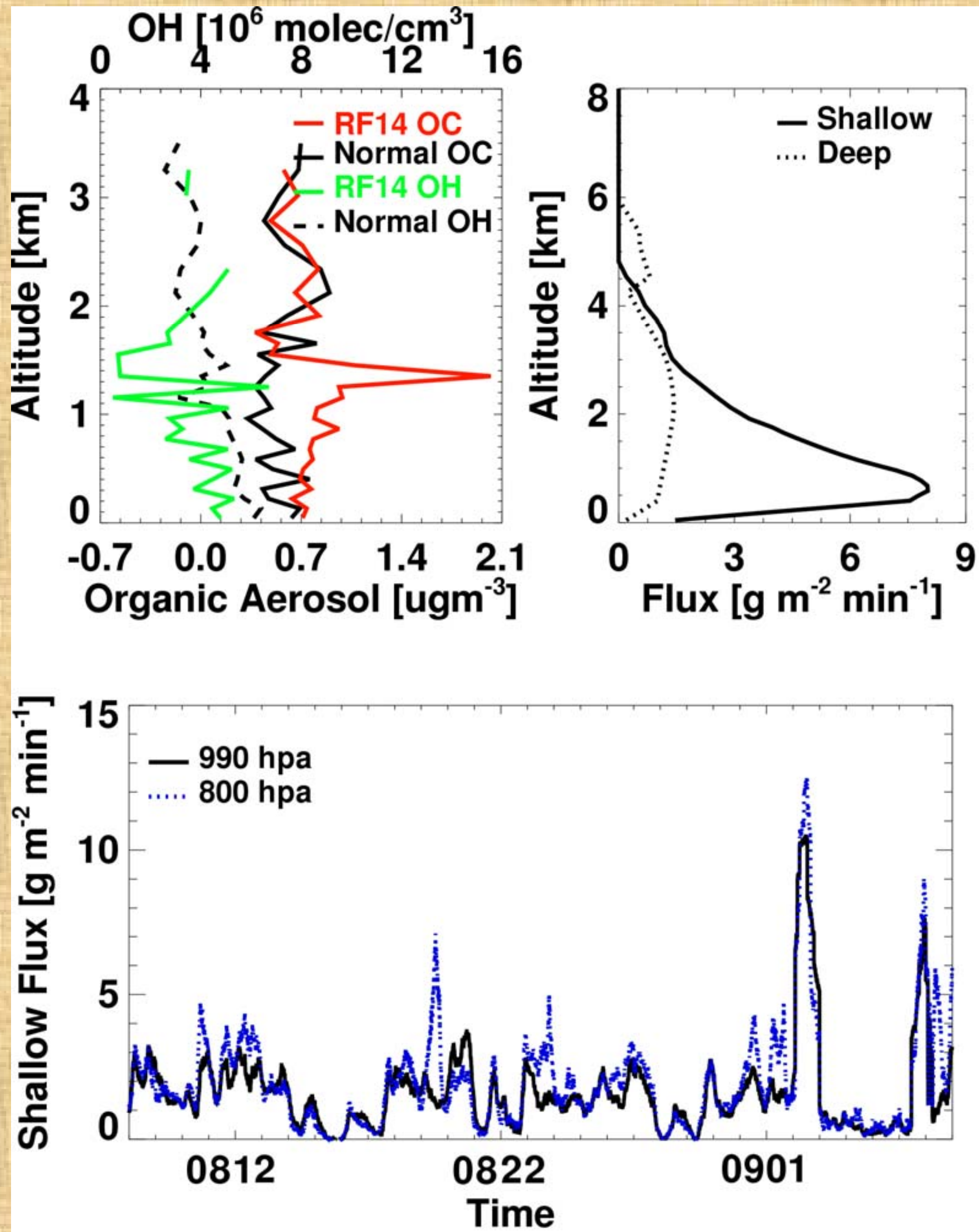
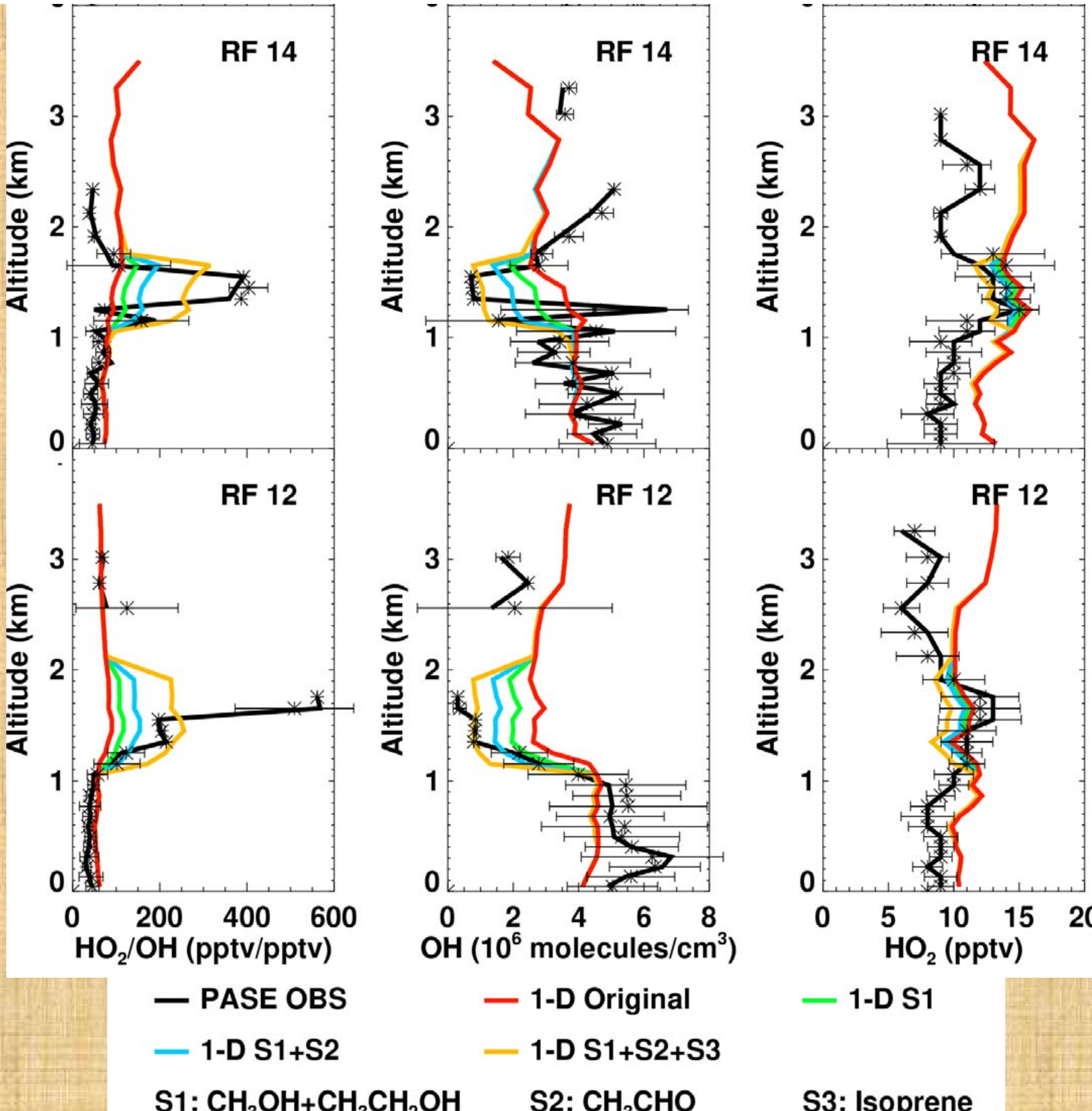


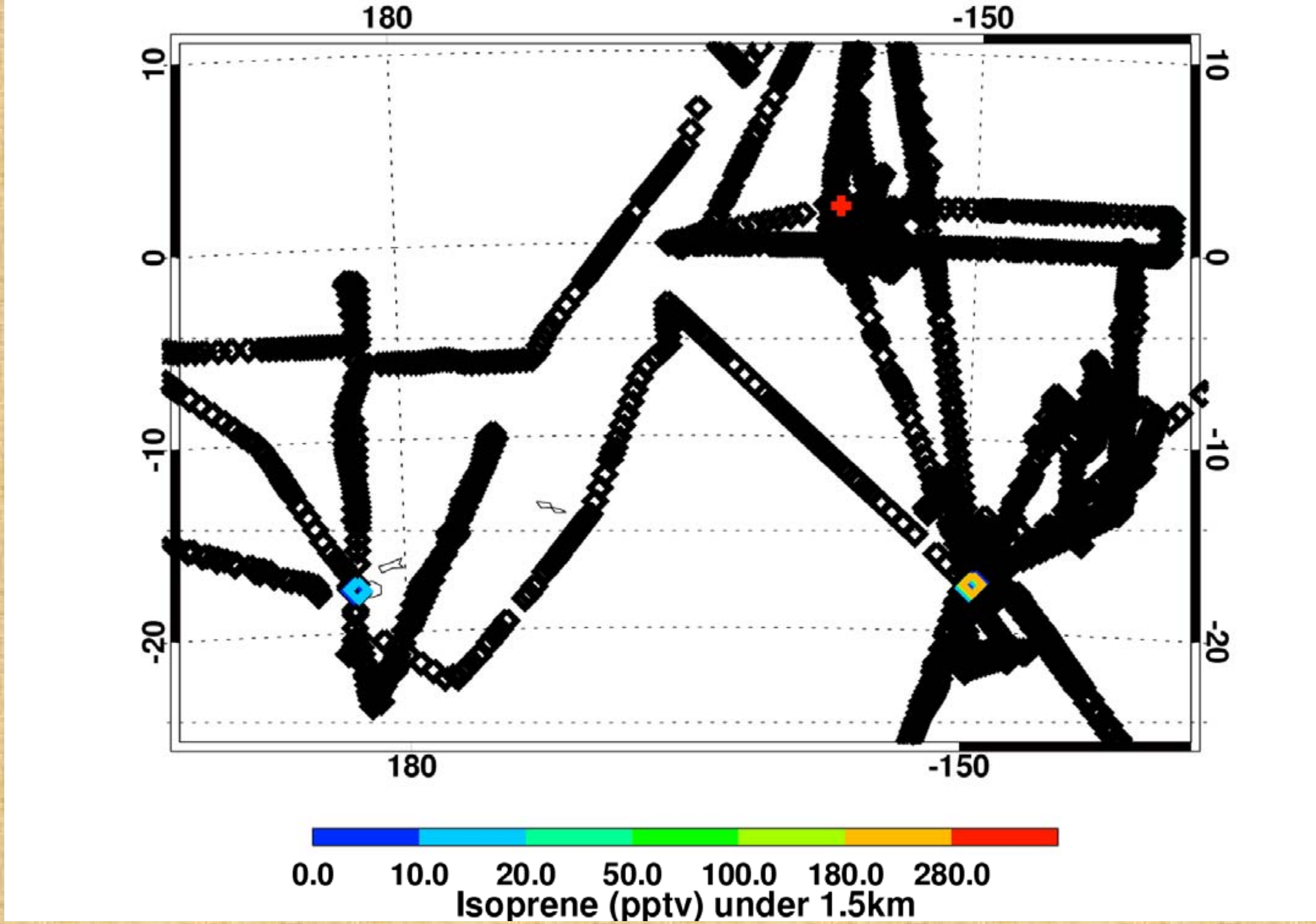
Table 3. Background and episode levels of NMHCs used in simulations

	Background (pptv)	Episode (pptv)
Isoprene	0	100
CH_3CHO	30	200
CH_3OH	400	1300
CH_3CH_2OH	20	110
Acetone	200	800



RF 14
RF 12
Altitude (km)
HO2/OH (pptv/pptv)
OH (10^6 molecules/cm^3)
HO2 (pptv)
PASE OBS
1-D Original
1-D S1
1-D S1+S2
1-D S1+S2+S3
S1: CH3OH+CH3CH2OH
S2: CH3CHO
S3: Isoprene

But there is no evidence for oceanic isoprene



PEM-TB isoprene by D. Blake

Conclusions

- OH and HO_2 are reasonably reproduced in general.
- Simulated CH_3OOH is good but simulated H_2O_2 is too low.
- There is indirect evidence of fast-reacting oceanic VOCs during RF 12 and 14, which greatly reduces OH levels. These VOCs are enhanced by convection.