1-D Modeling of DMS and SO_2 Chemistry in the Equatorial Pacific

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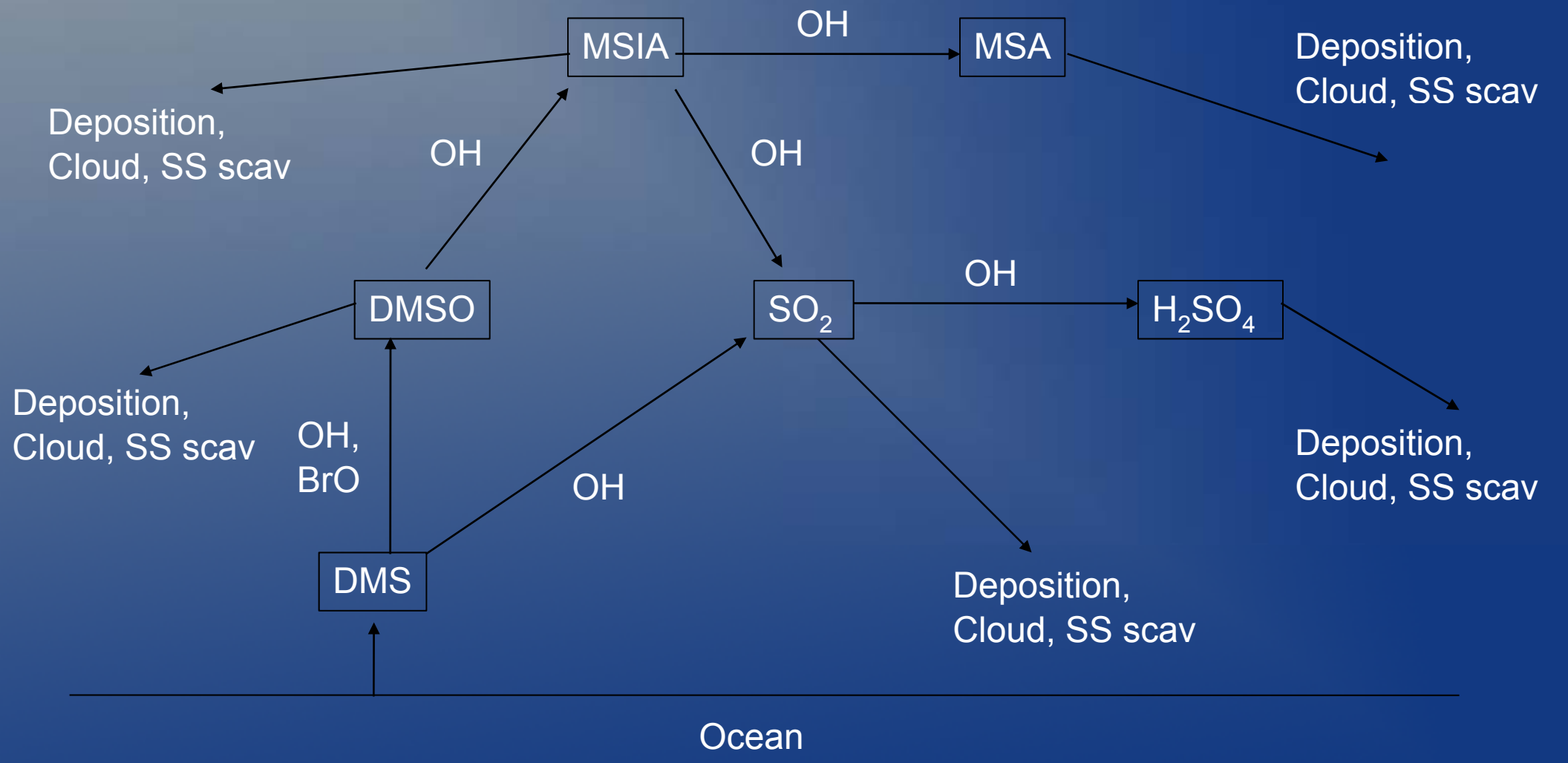
and the PASE Science Team

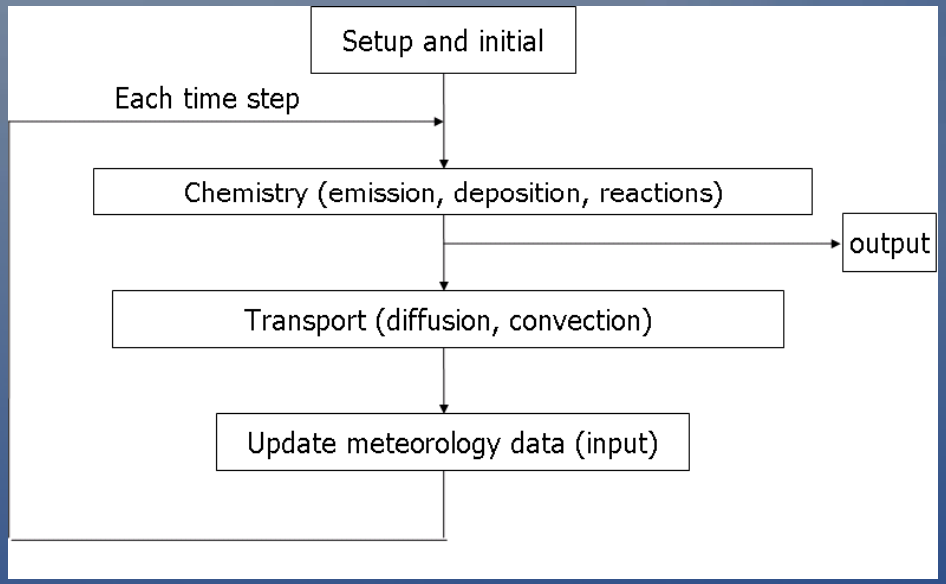
Research Focus

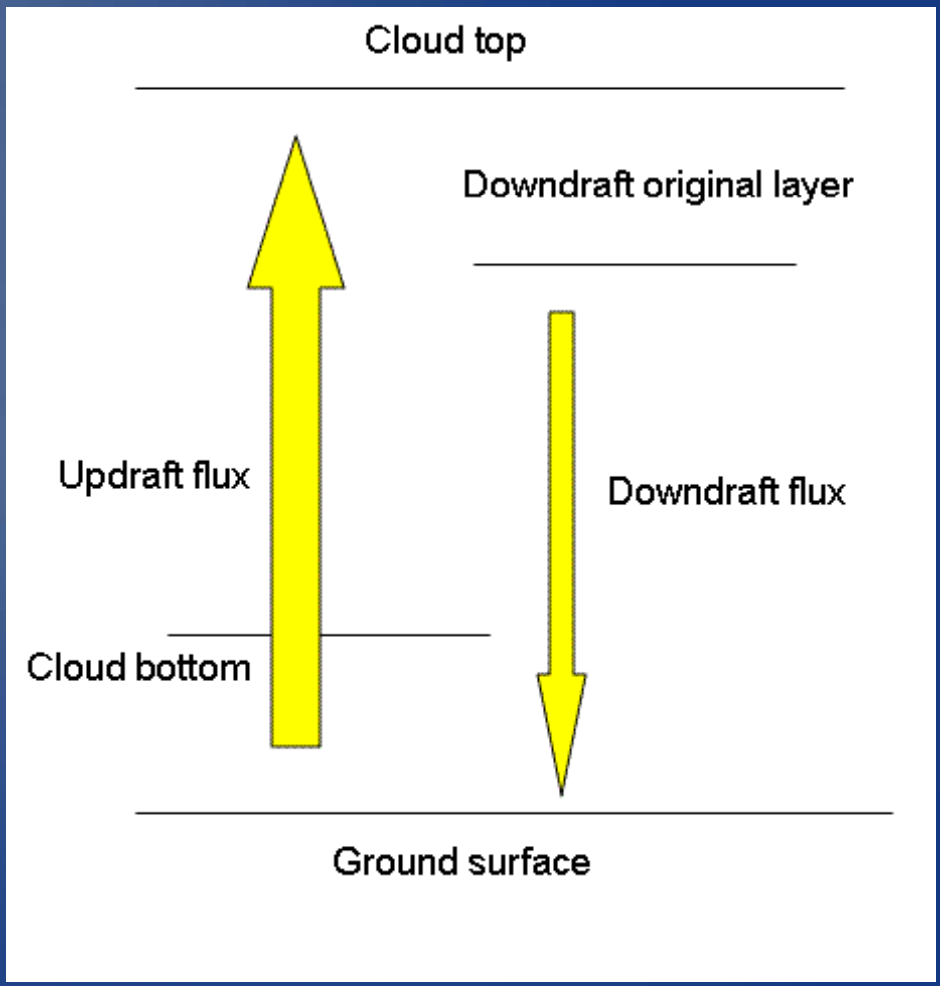
- Prior Studies → Mostly Box Models
  - No convection, diffusion
  - No separation of SO_2 loss to sea-salt scavenging, dry deposition
  - No cloud losses for DMS products
- This Study → 1-D Model
  - Regional chEmical trAnsport Model (REAM) plus WRF meteorological fields
  - PEM Tropics-A and -B data used to constrain diffusion
  - Cloud and sea-salt losses calculated

DMS Chemistry



Model Setup



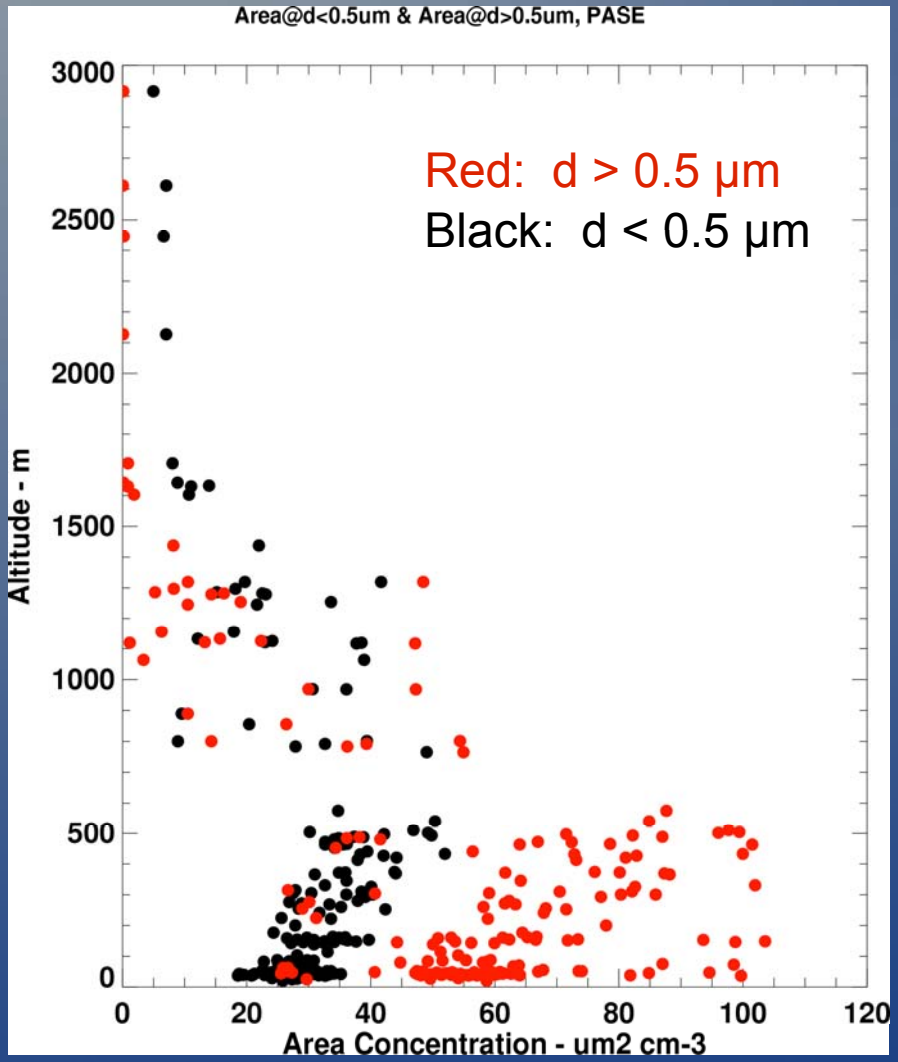


Model constrained with PASE observations of CO and O_3

Modeled Chem and Phys Processes

- Sulfur species: DMS, SO_2, DMSO, MSIA, H_2SO_4, MSA
- DMS concentration set in lowest layer with diurnally varying boundary condition
- DMS loss via OH, BrO
- Chemical prod/loss for other species
- Sinks for soluble species
  - Dry deposition (BL only)
  - Sea-salt scavenging (BL and BuL)
  - Cloud scavenging (BuL only)

Sea-Salt Concentration



- Plot of area concentration for large and small sizes
- Clearly shows three vertical regions
- Size distribution associated with each pair
- Size data used to calculate scav rate

SO_2 Scavenging via Sea Salt

- SO_2 taken up by sea salt, reacts with O_3 in aqueous phase
  - Reaction strongly pH dependent
  - Shuts down at pH ~ 5.5
- Ocean pH buffered by excess alkalinity
  - Sea-salt assumed to have ocean composition
  - pH unaffected by acid addition until excess alkalinity consumed; pH quickly declines after
  - Available alkalinity: 0.07 eq mol per kg
- One mole of SO_2 consumes 2 eq mol alkalinity
- SO_2 loss driven by sea-salt VOLUME flux

SO_2 Scavenging via Sea Salt

$$\frac{dF}{dR} = V_D \square \frac{dN}{dR}$$

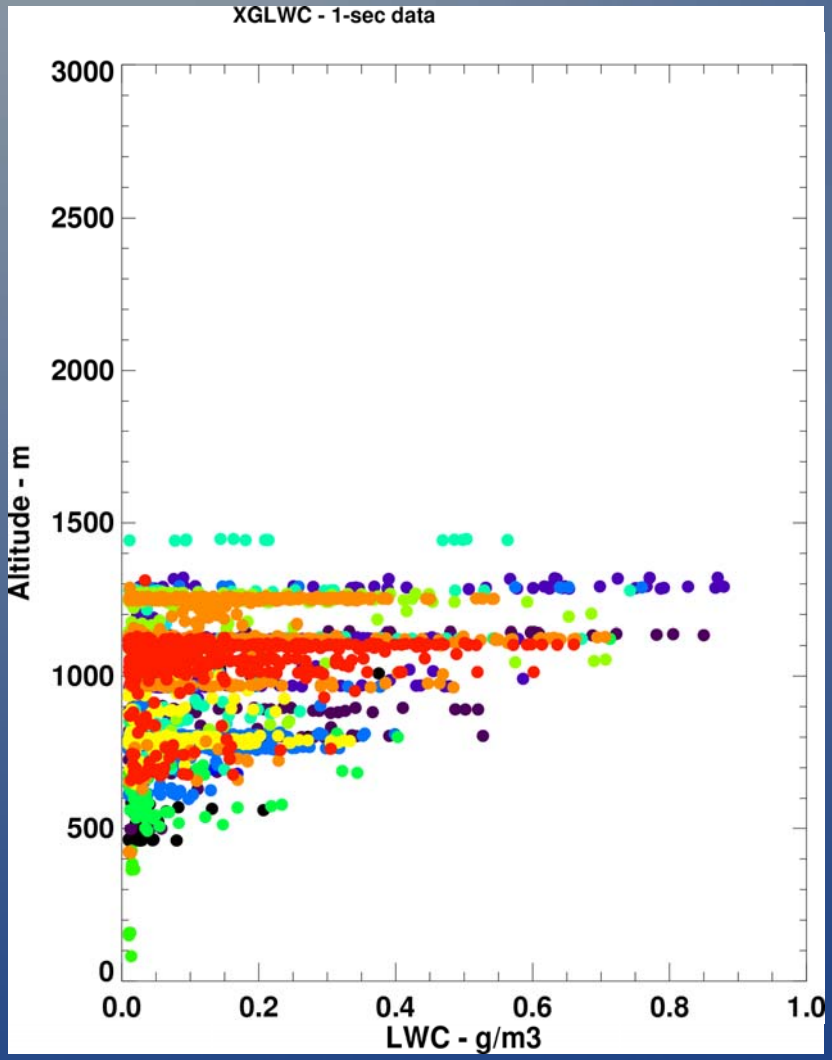
$$\frac{dF_V}{dlogD} = V \square V_D \square \frac{dN}{dlogD}$$

- Convert particle flux eqn to volume flux eqn
- Multiply volume flux by alkalinity concentration
- SO_2 scav rate is half of alkalinity flux
- BL: 10×10^{12} molec cm^{-2} day^{-1}
  - Global avg: 50 – 200×10^{12}

SS Scav for Other Solubles

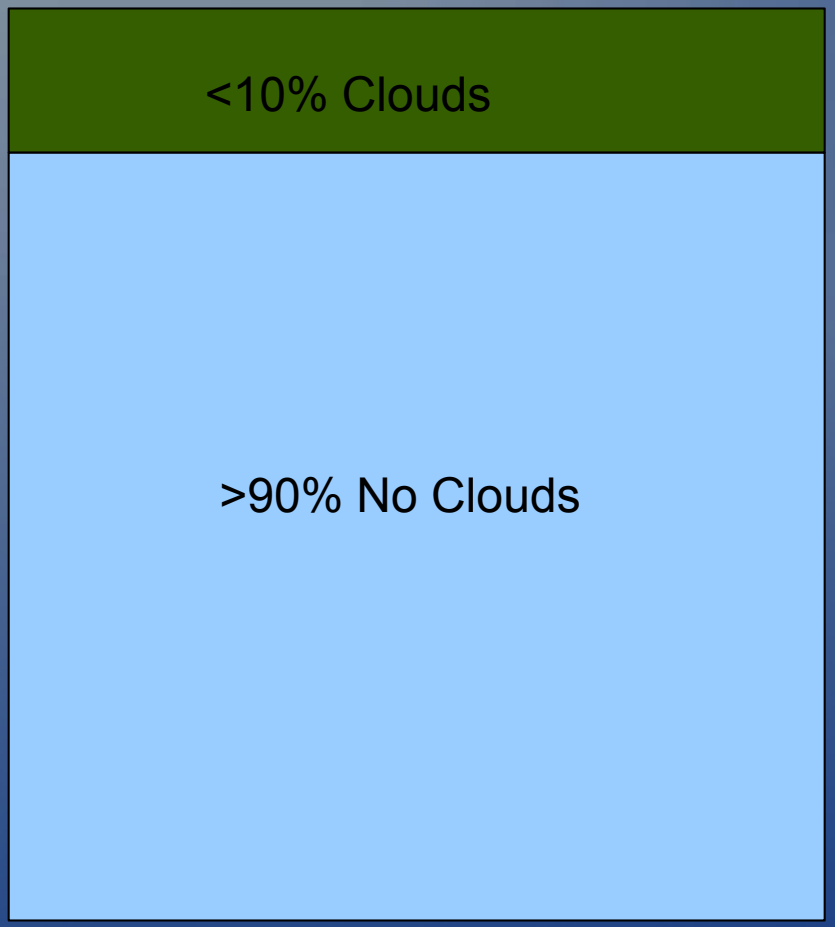
- Other solubles: DMSO, MSIA, H_2SO_4, MSA
- Assumption: Saturation not reached
- These limited by kinetics, not available alkalinity
  - Use Dahneke formulation for flux rate to sea-salt surface
  - Loss rate depends on surface area concentration
- BL rates (s^{-1}): $H_2SO_4 = 1.4x10^{-3}$, MSA = $3.8x10^{-4}$

Cloud Scavenging



- Assumption: Soluble species scavenged instantly upon contact with cloud
- From XGLWC sensor, LWC > 0.01 g/m3 for < 10% of BuL
- Cloud scav driven by BuL mixing time

Cloud Scavenging

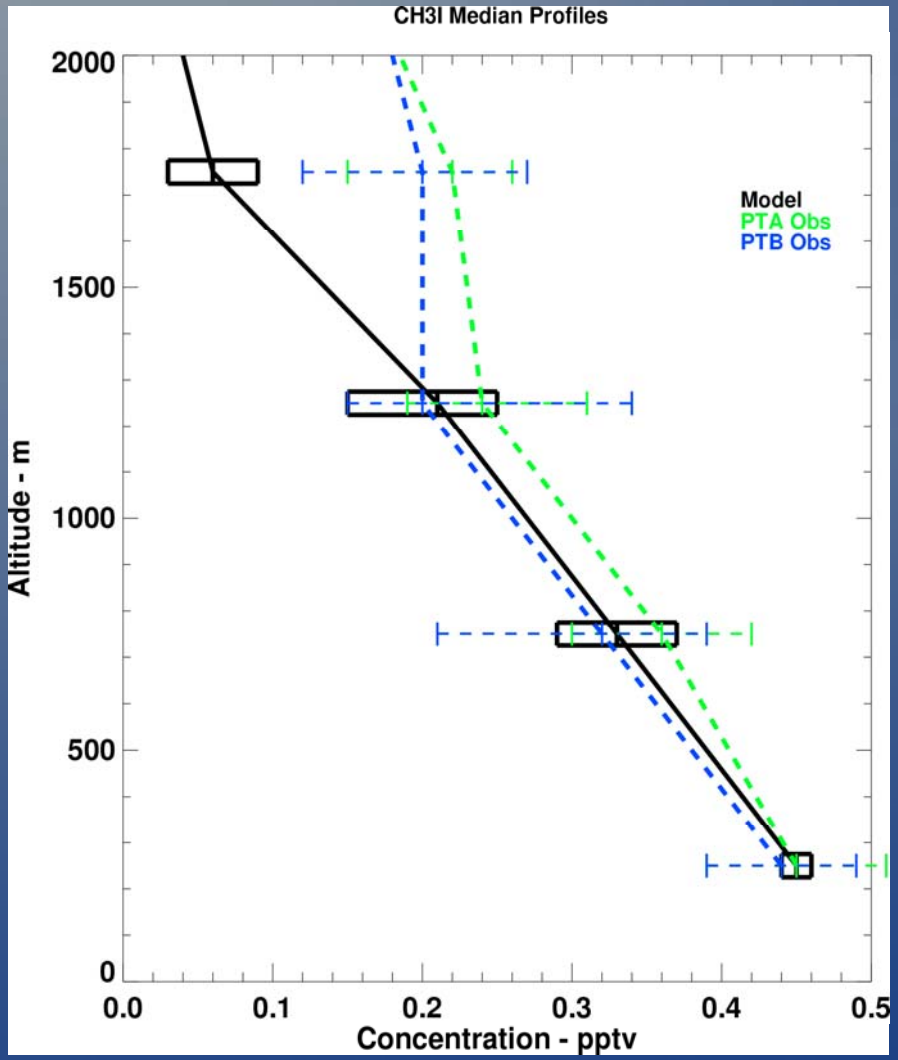


- Mixing timescale within a layer: $\tau = h^2/2K_z$
- If <10% clouds, h will not vary much, so scav rate ~constant
- τ ~ 1.5 days in BuL

PASE Data

- PASE data used for daytime comparison to model
- One model per each PASE flight used
  - Models constrained with PASE CO, O_3
  - BuL mixing constrained with PEM-TA, TB CH_3I
- Flights included: 2, 3, 5, 8, 9, 12
  - RF01 → No DMS
  - RF04 → Different region
  - RF06, RF13 → Night flights
  - RF07 → Too short

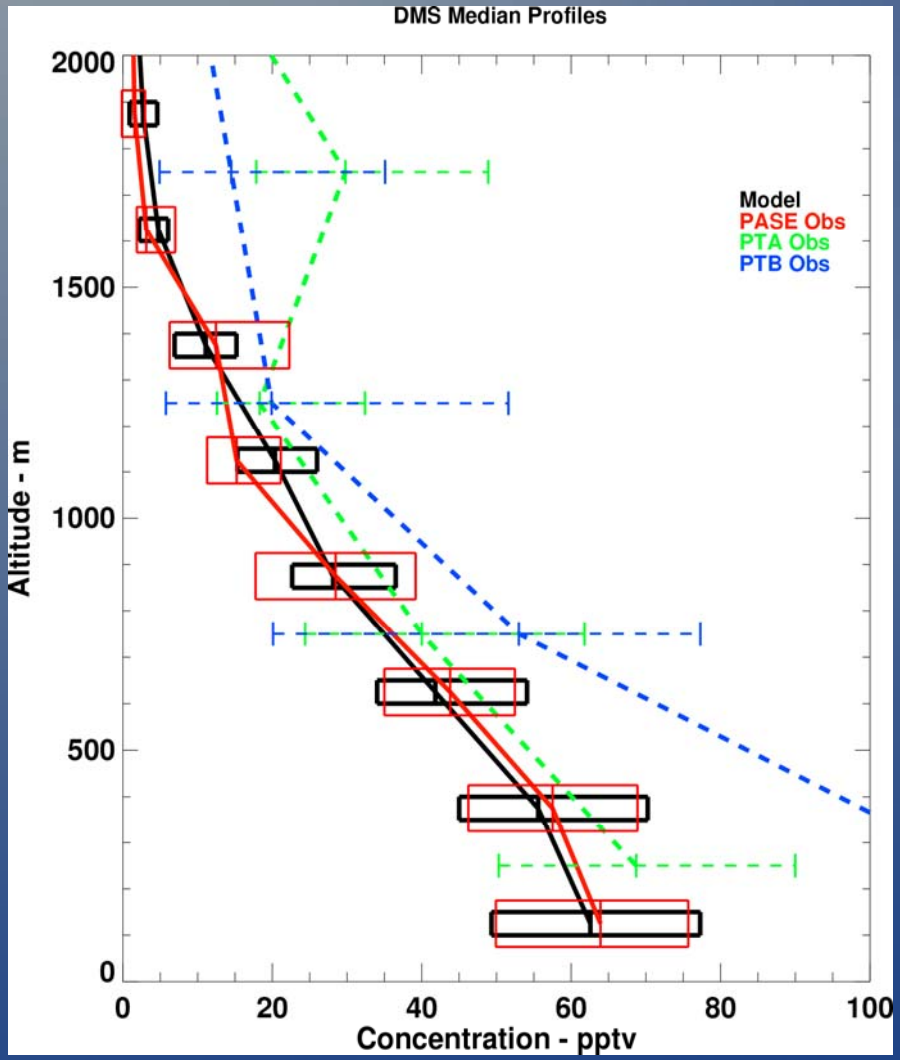
Diffusion, Convection

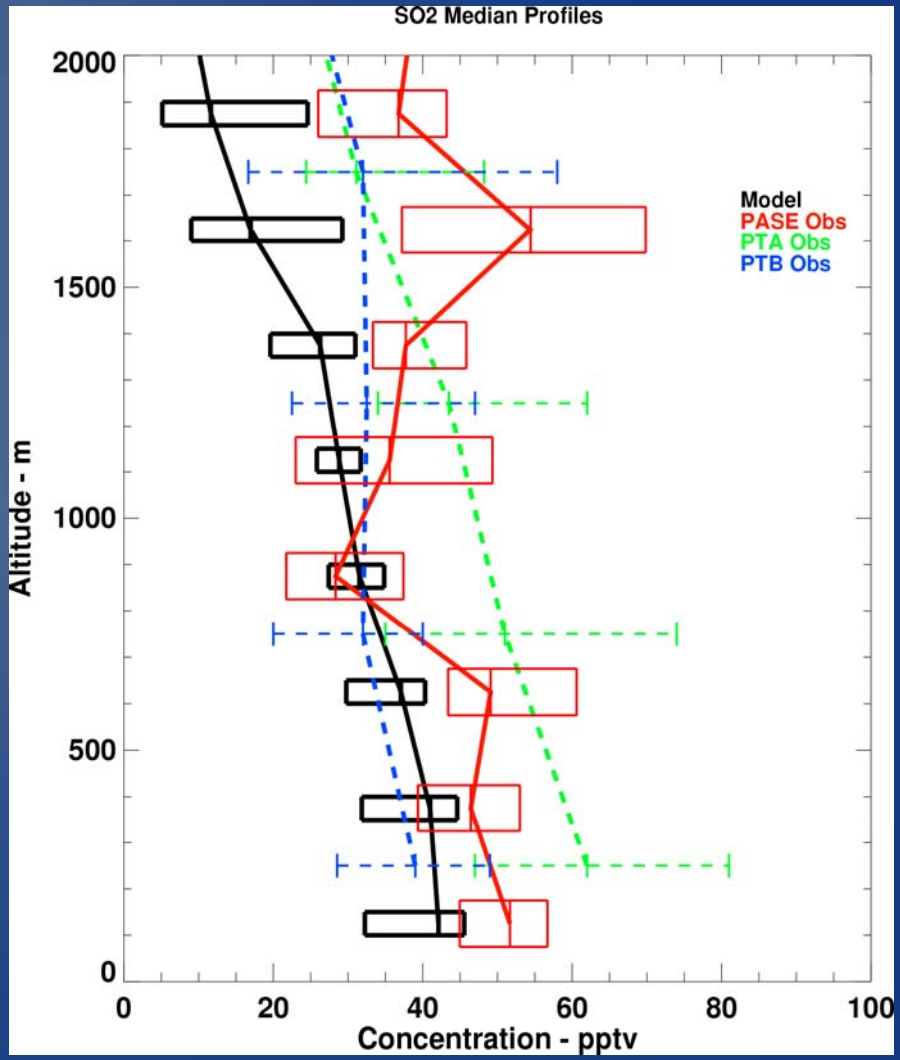


- BuL diffusion determined via CH_3I comparison to PEM Tropics-A, -B
  - BL diffusion determined by WRF
  - BuL K_z = 3 m^2/sec
- Shallow convection calculated by WRF
  - Model appears to be low compared with

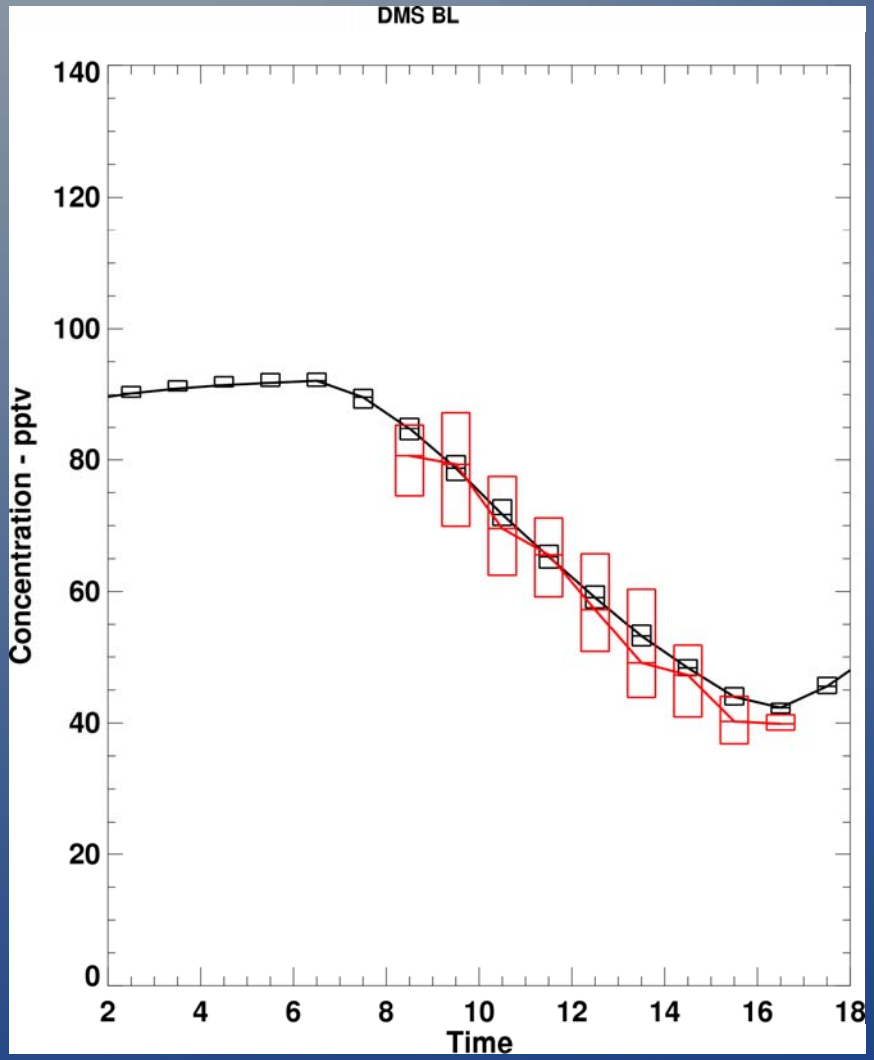
Results for DMS, SO_2

(using WRF-calculated Shallow Convection)



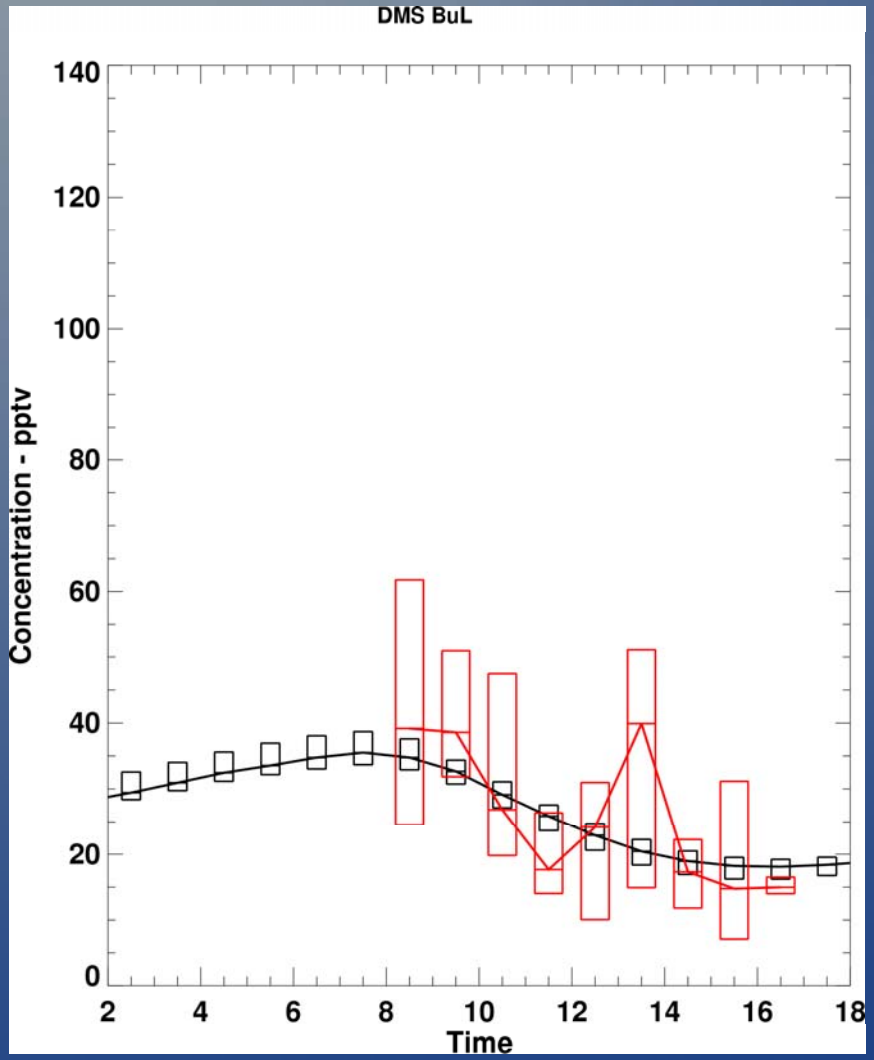


BL DMS



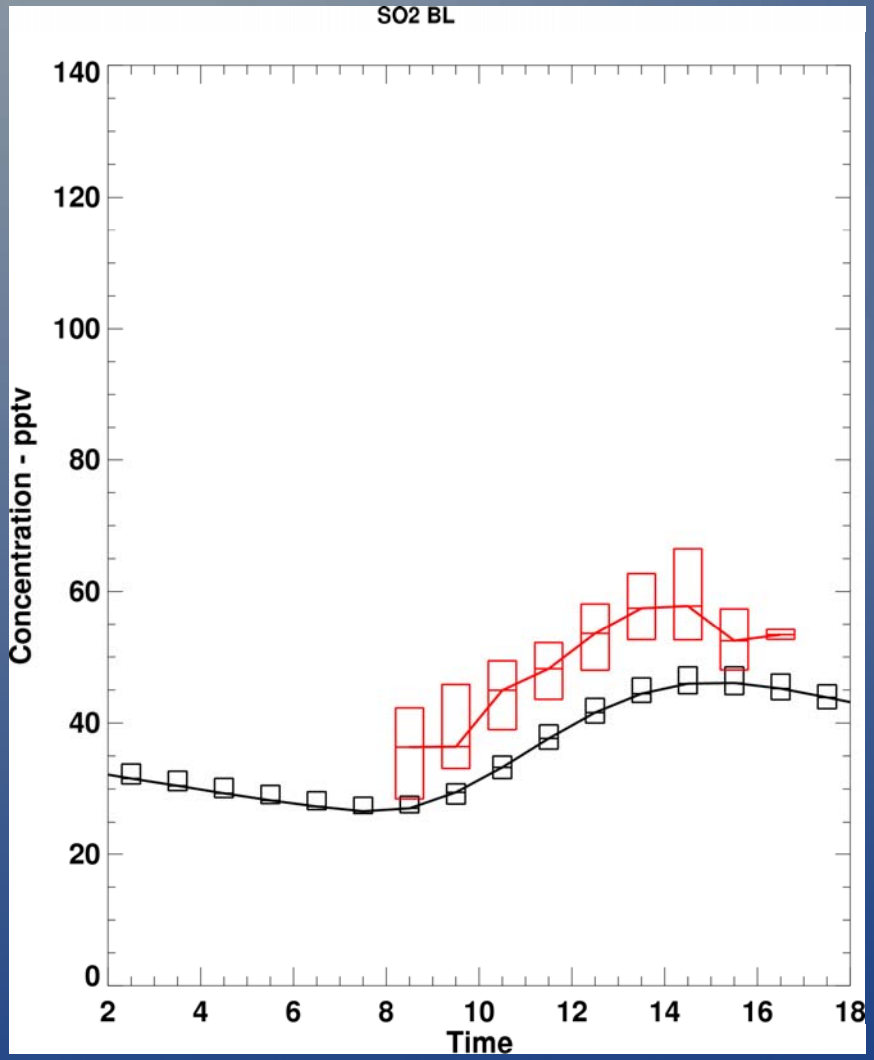
- Six model layers comprise BL
- Value in lowest layer via diurnally varying boundary condition

BuL DMS



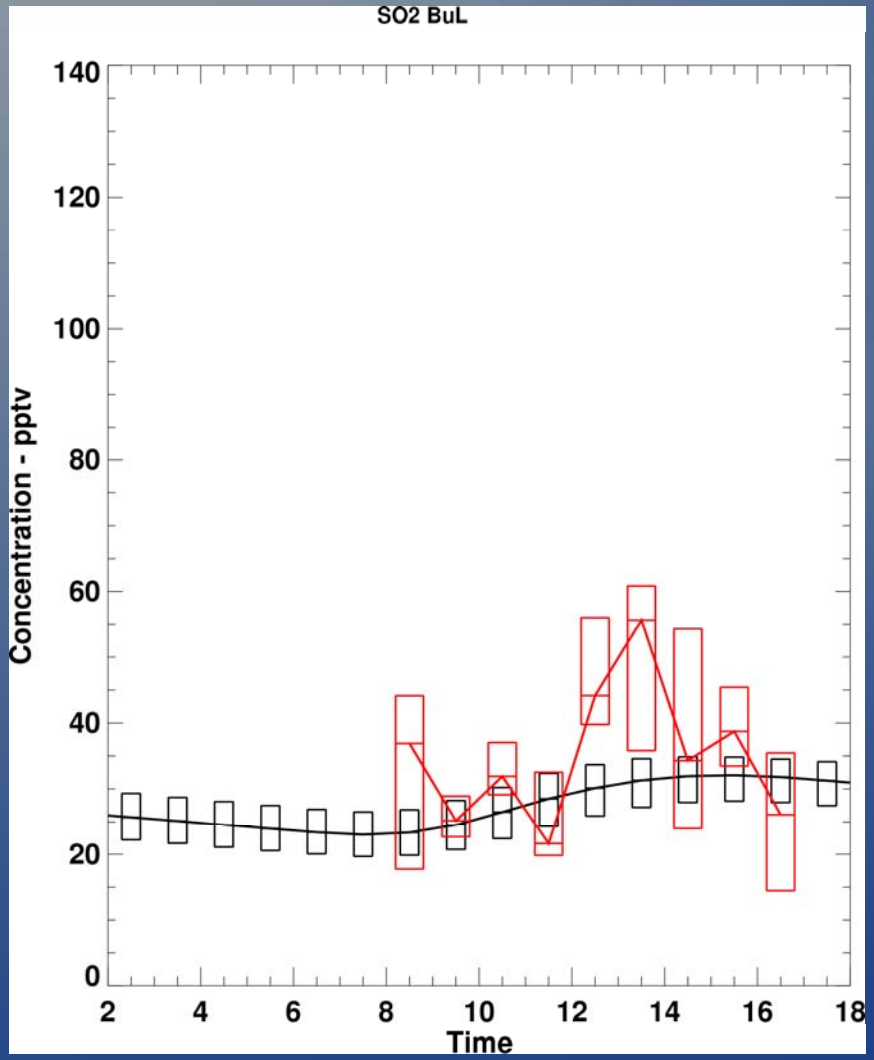
- Model simulates PASE BuL obs reasonably well
- Significant variability in BuL observations

BL SO_2



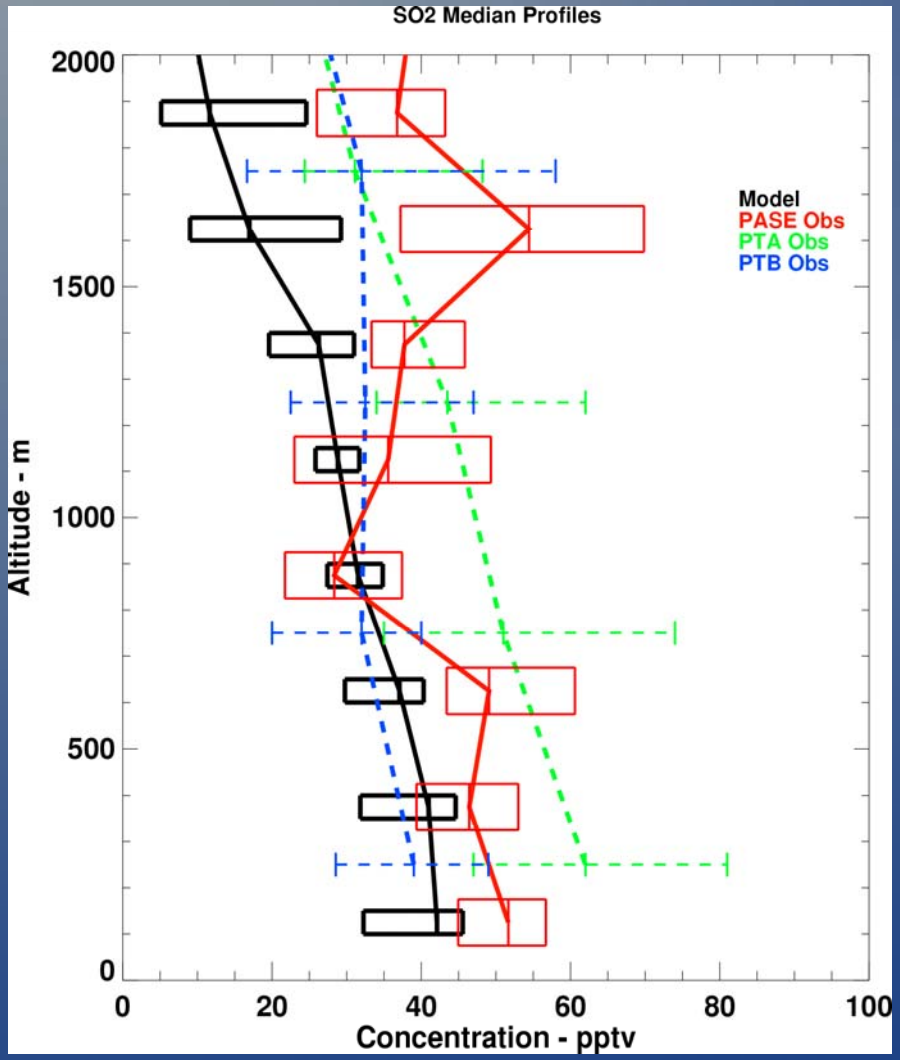
- Model underestimates SO_2 concentration
- Lifetimes:
  - SS Scav: 5 days
  - Chem: 7 days
  - Deposition if V_D is 0.1 cm/s: 6 days

BuL SO_2



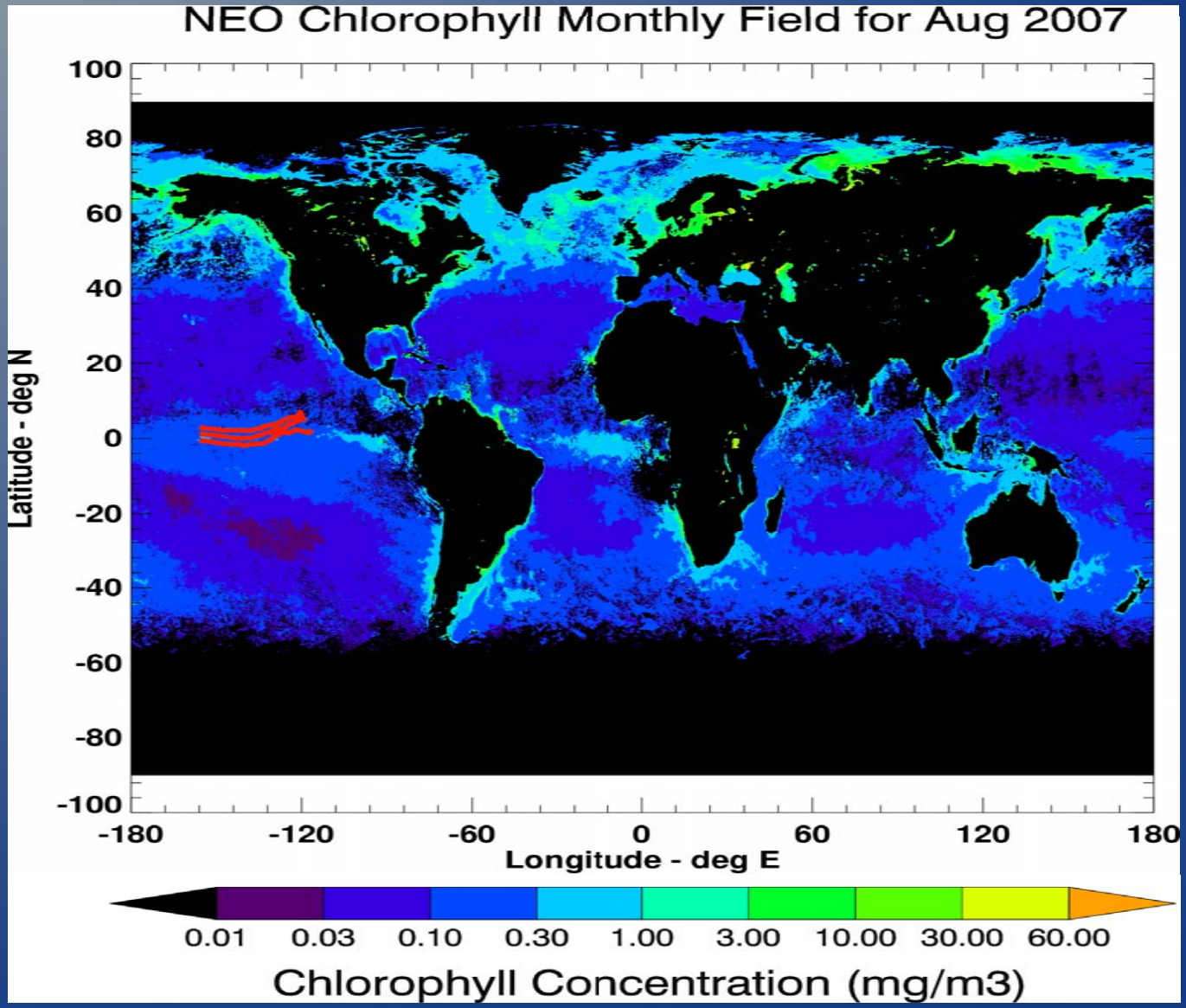
- Model slightly low vs observation
- Lifetimes:
  - SS Scav: 30 days
  - Chem: 7 days
  - Clouds: **1.5 days**

Hypotheses for SO_2 in Lower FT

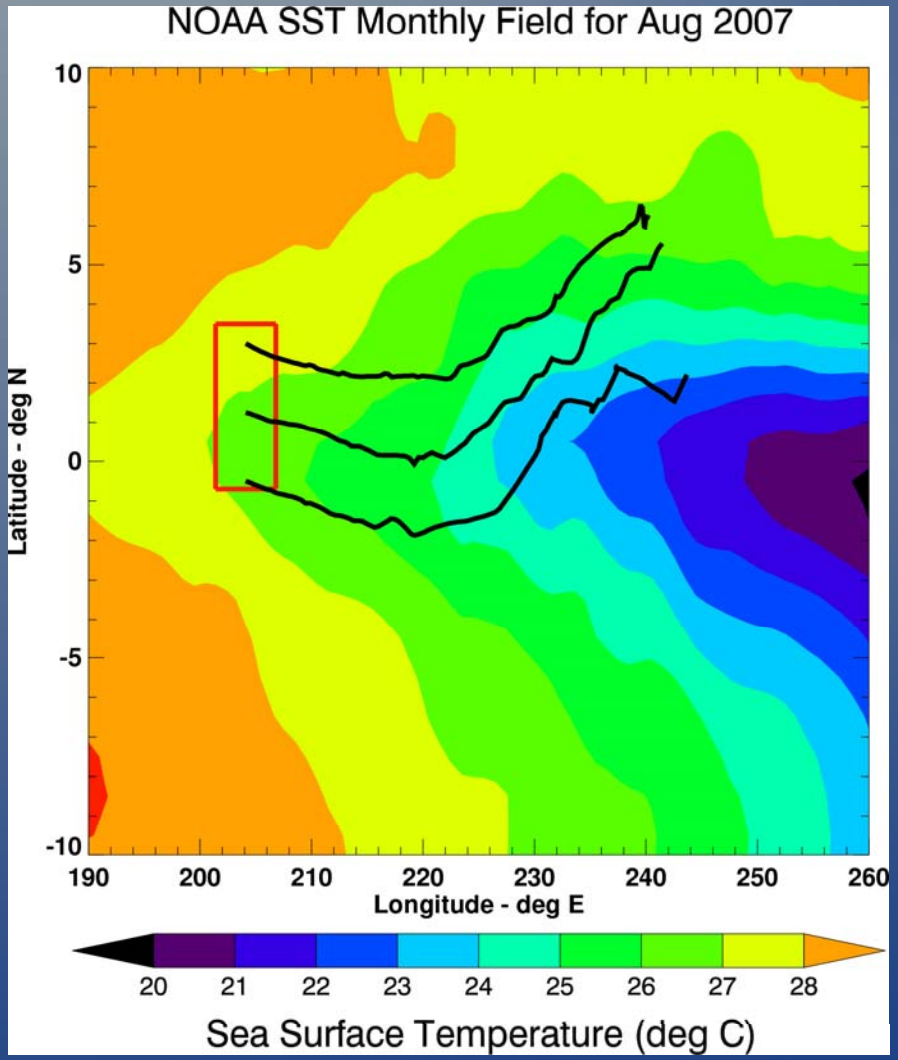


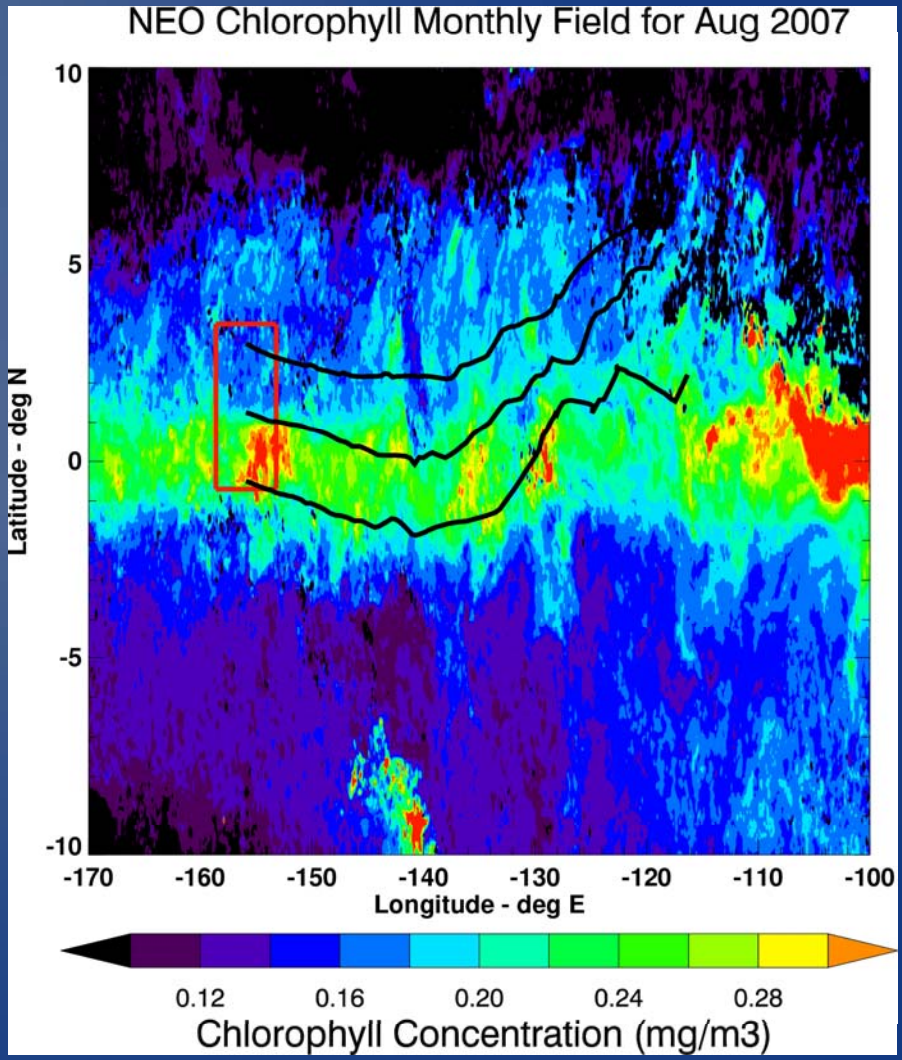
- Advection from an area with a higher DMS flux
- Convection much higher than predicted by WRF

Chlorophyll Map with 5-day HYSPLIT Backtrajectories



SST and Chlorophyll MAPS

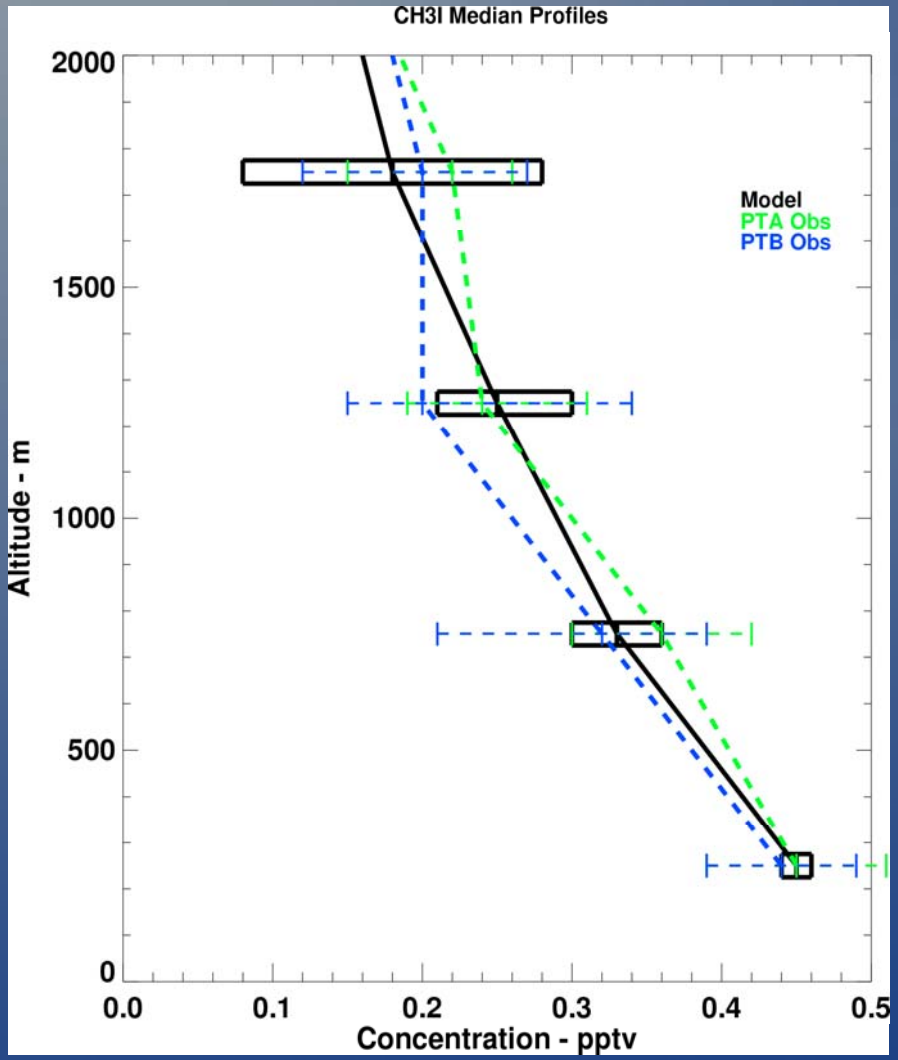


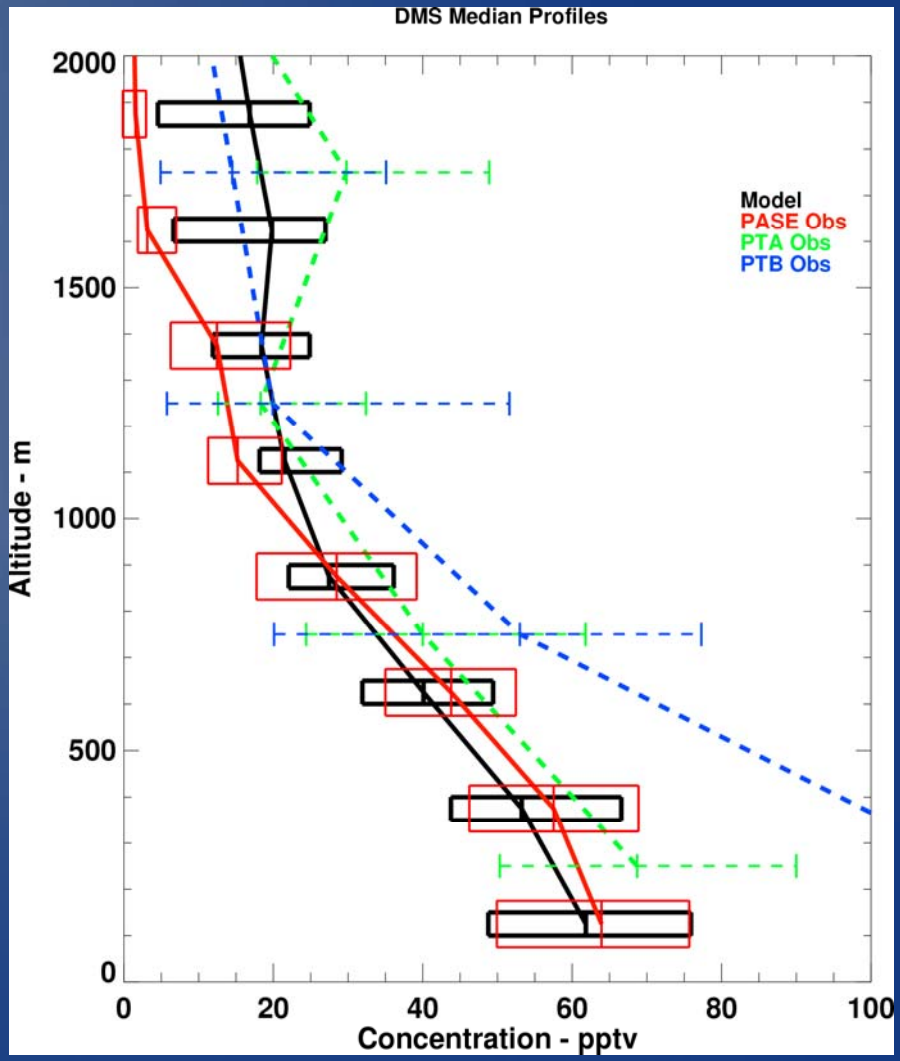


Summary Regarding Advection

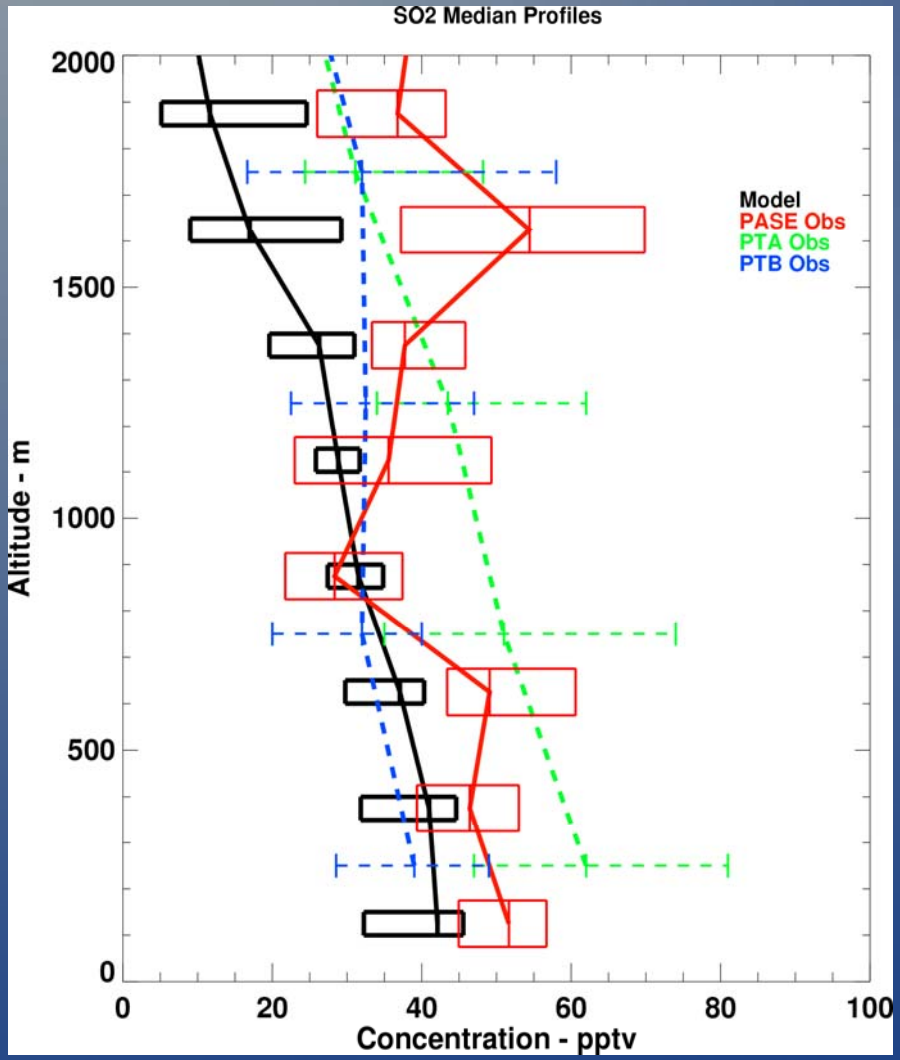
- HYSPLIT indicates advection from cooler waters, which could indicate greater upwelling
- However, this area does not have higher chlorophyll concentration, so it *may* not have higher DMS productivity
- Conley et al. (2009): Advection vector for PASE generally perpendicular to DMS gradient
  - On average, advection not large DMS source during PASE

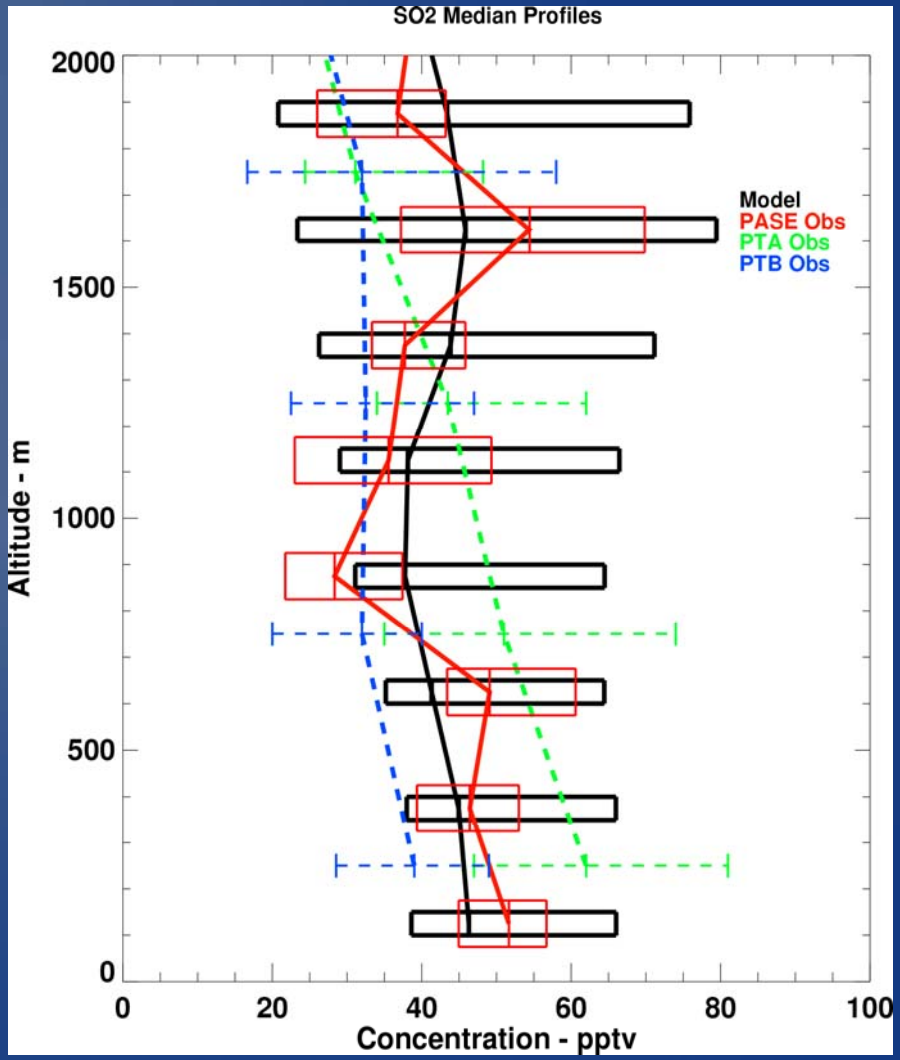
10X WRF Convection



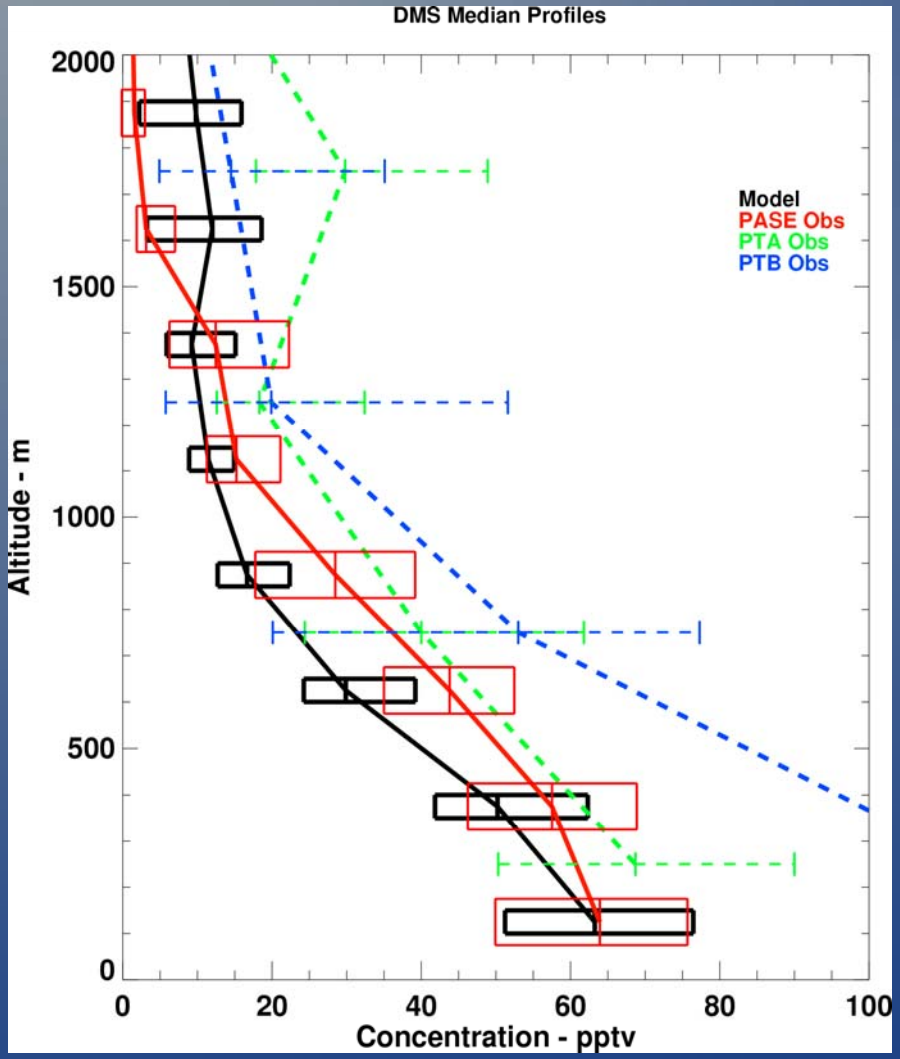


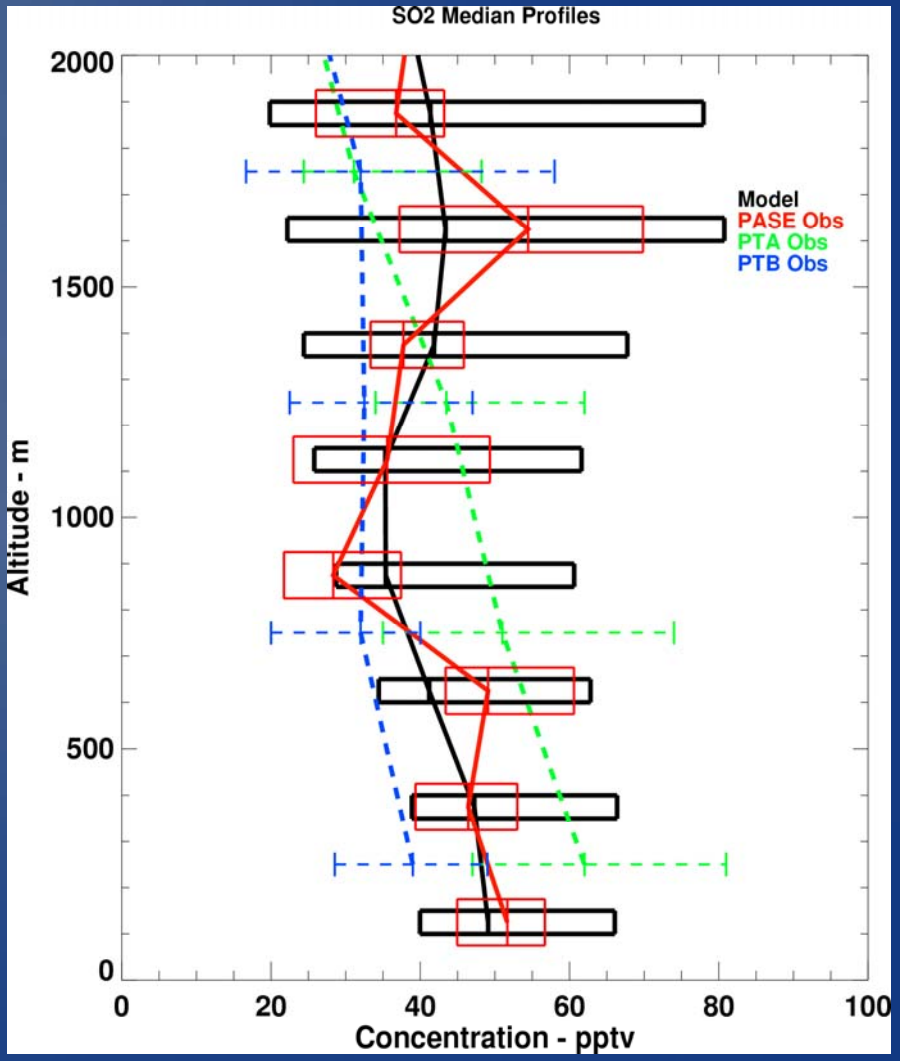
SO_2: 1X vs 10X Conv





DMS, SO_2 10X Conv and 2pptv BrO



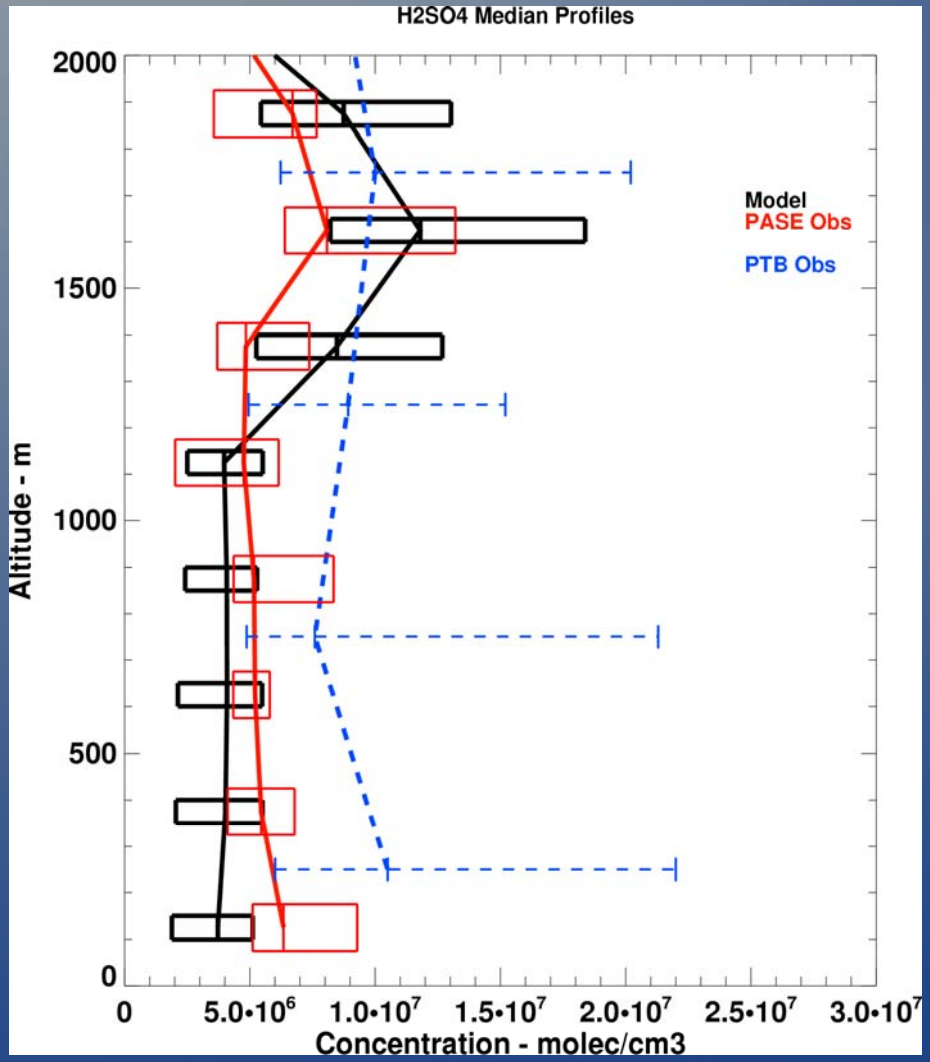


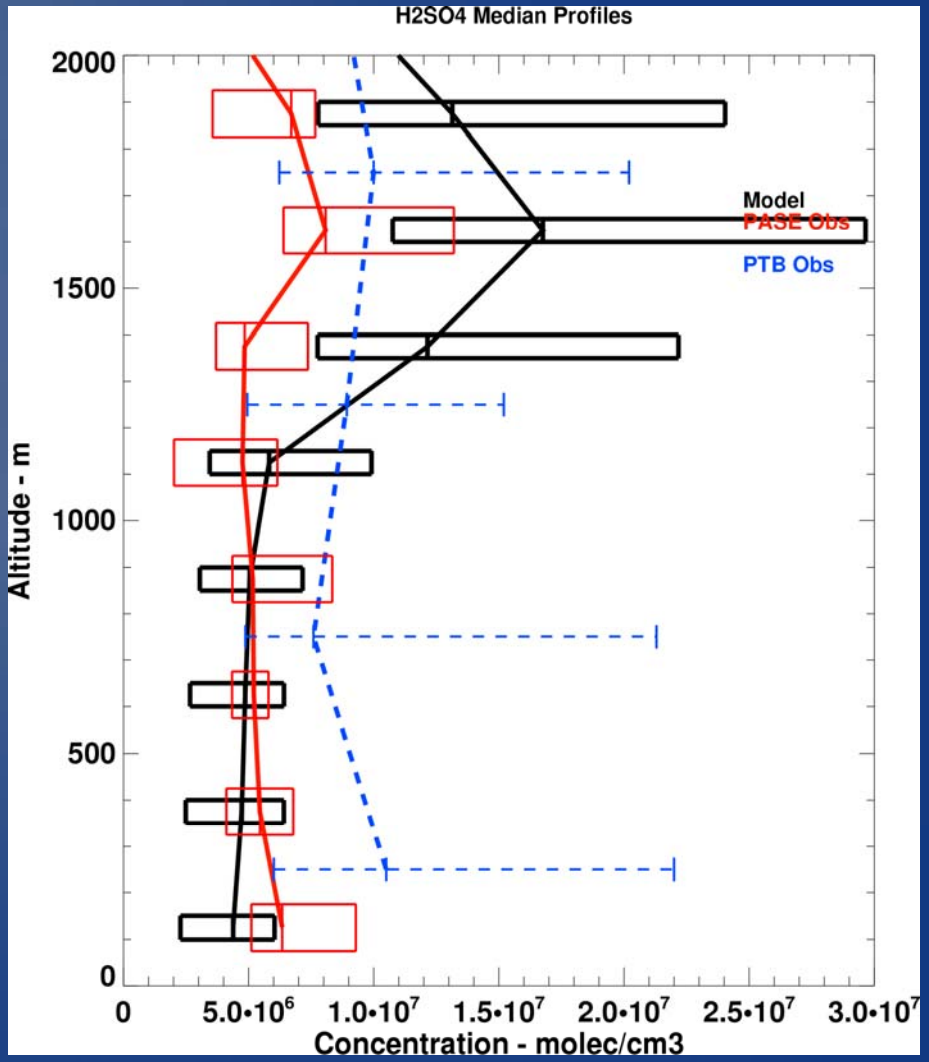
Summary

- Primary SO_2 loss mechanism in the CBL is cloud scavenging
  - tau_chemistry = 7 days
  - tau_deposition = 6 days (Vd = 0.1 cm/sec)
  - tau_ss in BL = 5 days, tau_ss in BuL = 30 days
  - tau_cloud = 1.5 days
- High SO_2 concentration in lower FT strongly suggests high shallow convection or advection from stronger DMS production region
  - High DMS in shallow conv offset by BrO?

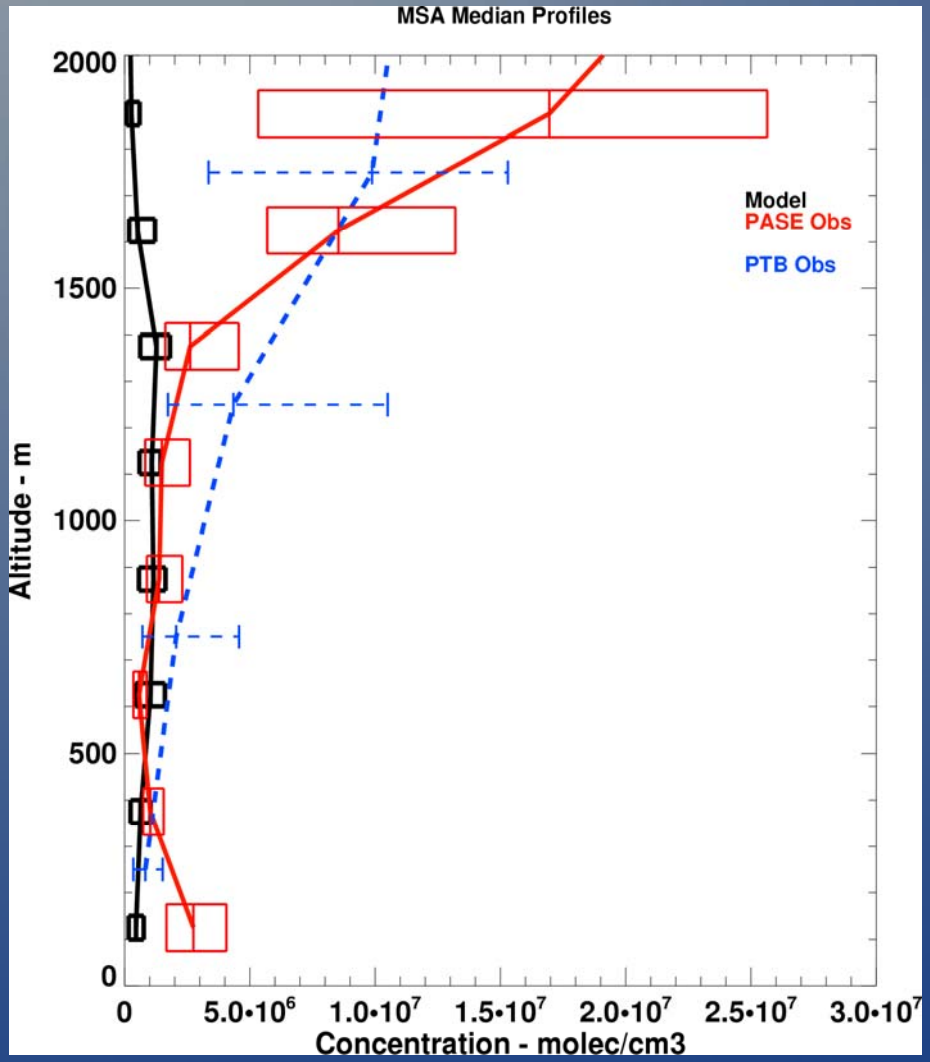
Future Work

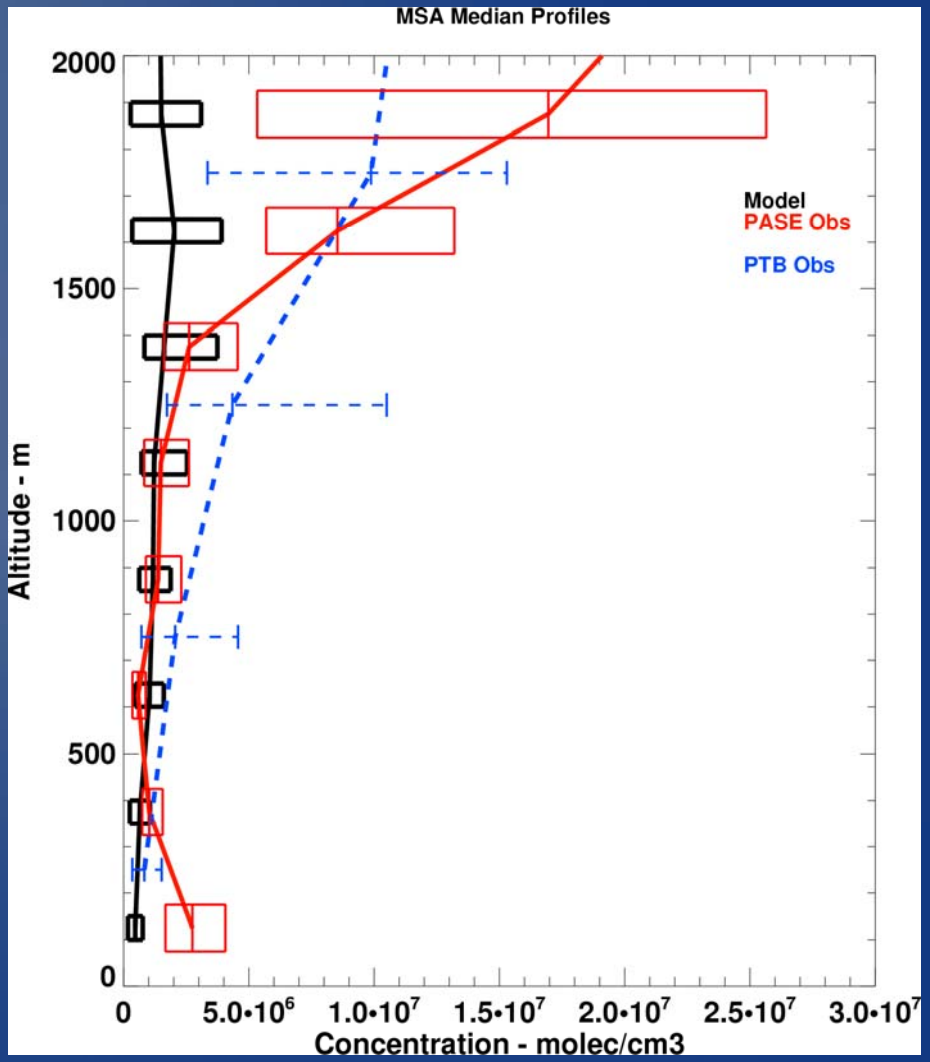
H_2SO_4: 1X vs 10X Conv



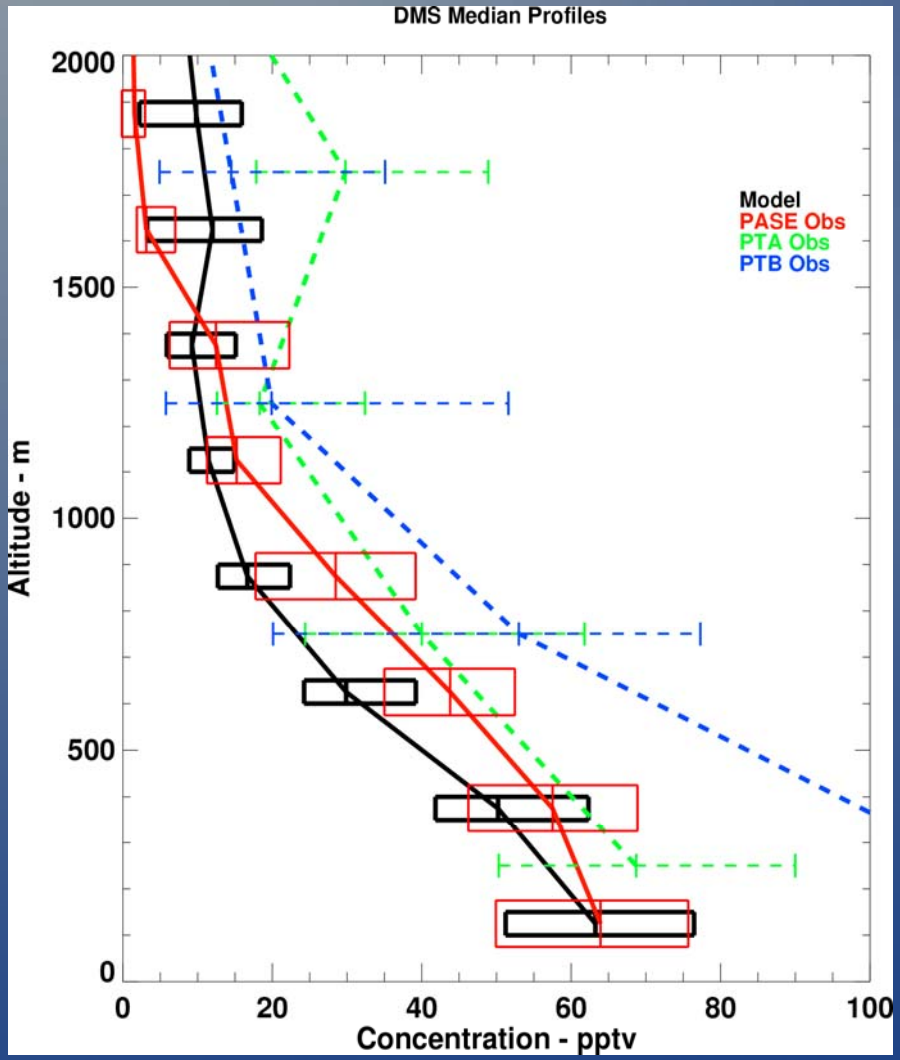


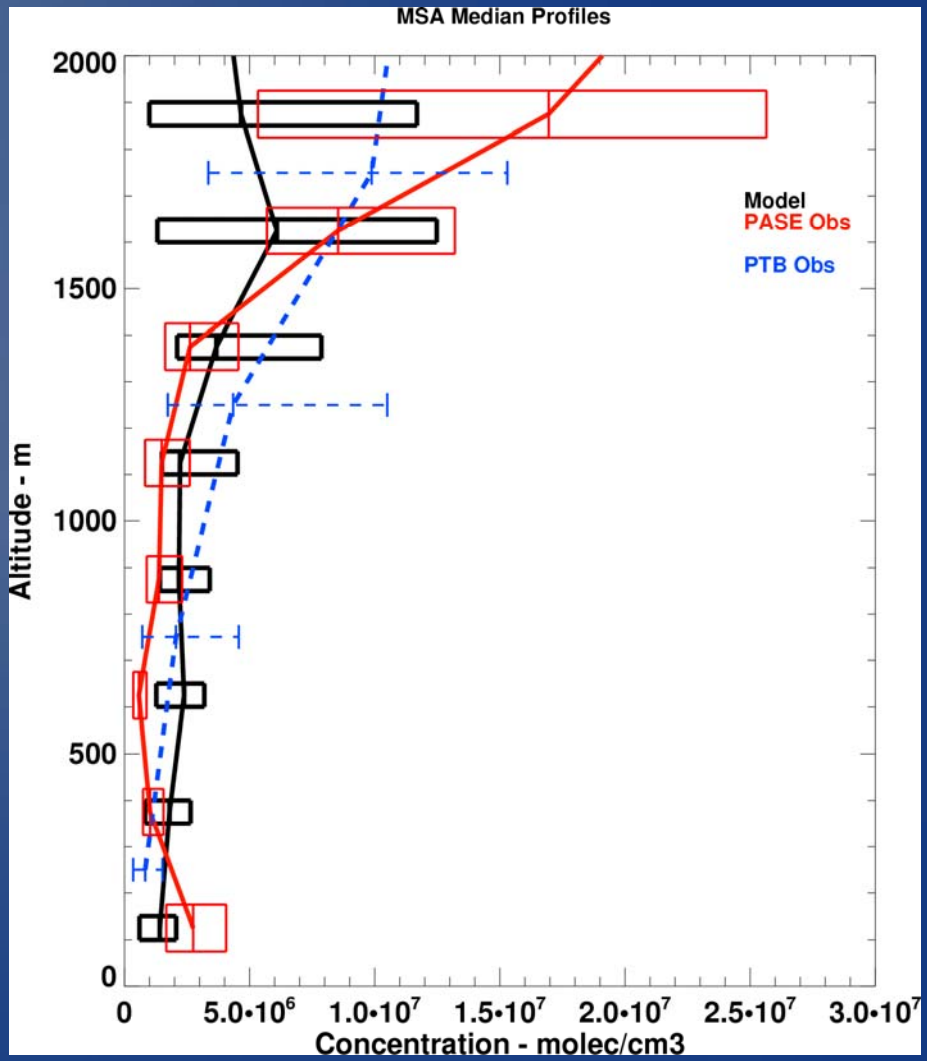
MSA: 1X vs 10X Conv





10X Conv with 2pptv BrO





Summary

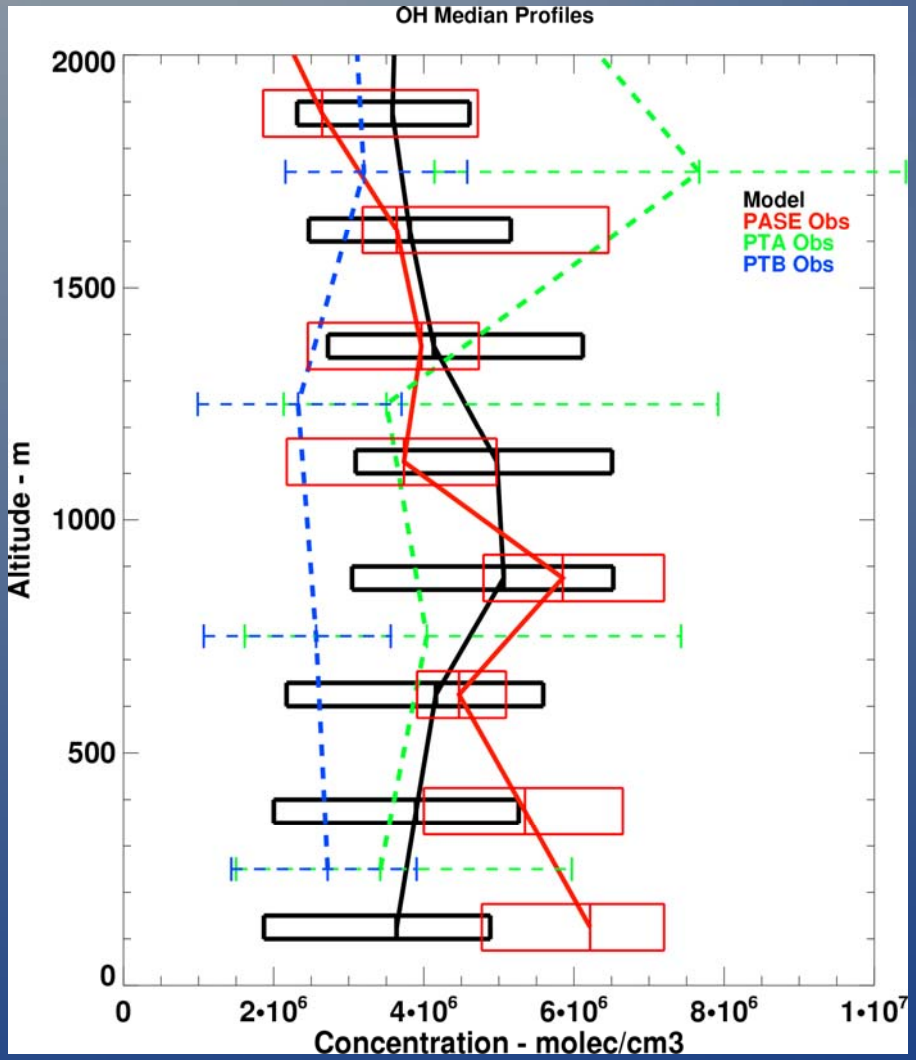
- Possible source for MSA near ocean surface
  - BrO
- Hypotheses for enhanced MSA in lower FT
  - Halogen chemistry
  - Transport from high-DMS region
  - pH dependence in aerosol sink
    - Sharp pH decrease with increasing altitude?
    - Need to model NH_3 and H_2SO_4 uptake

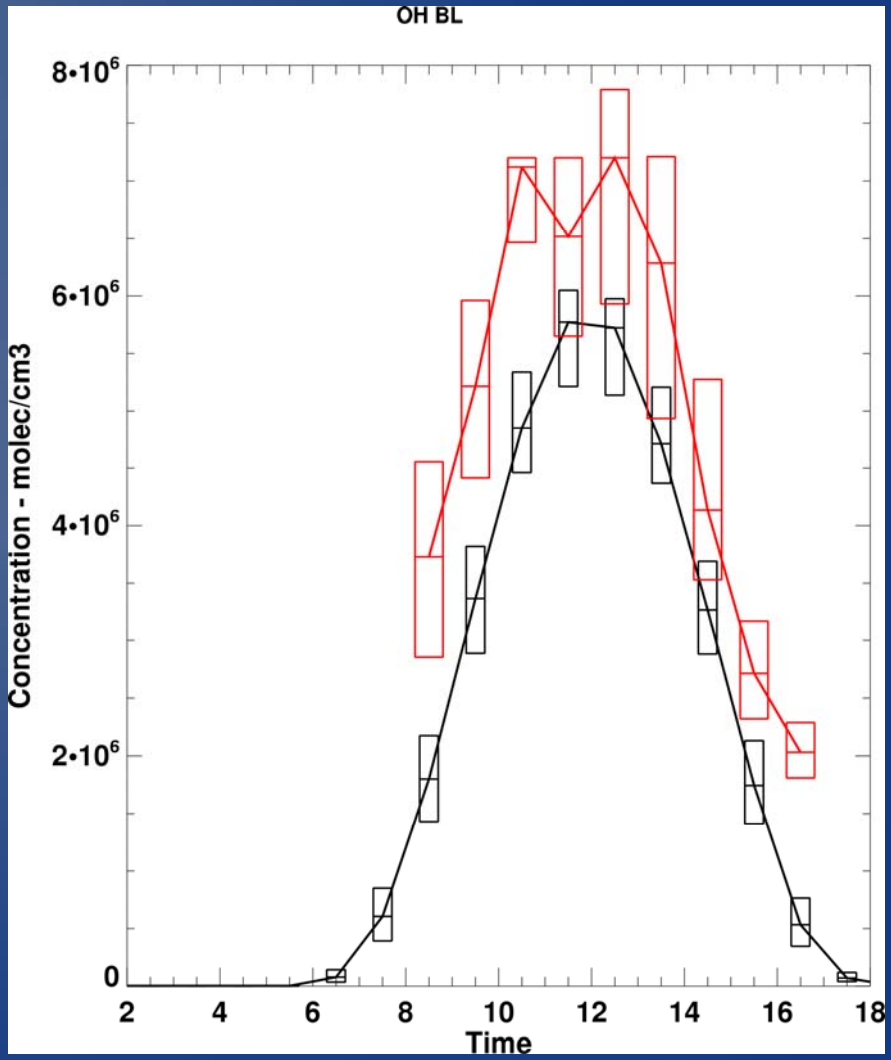
Supplementals

Summary (continued)

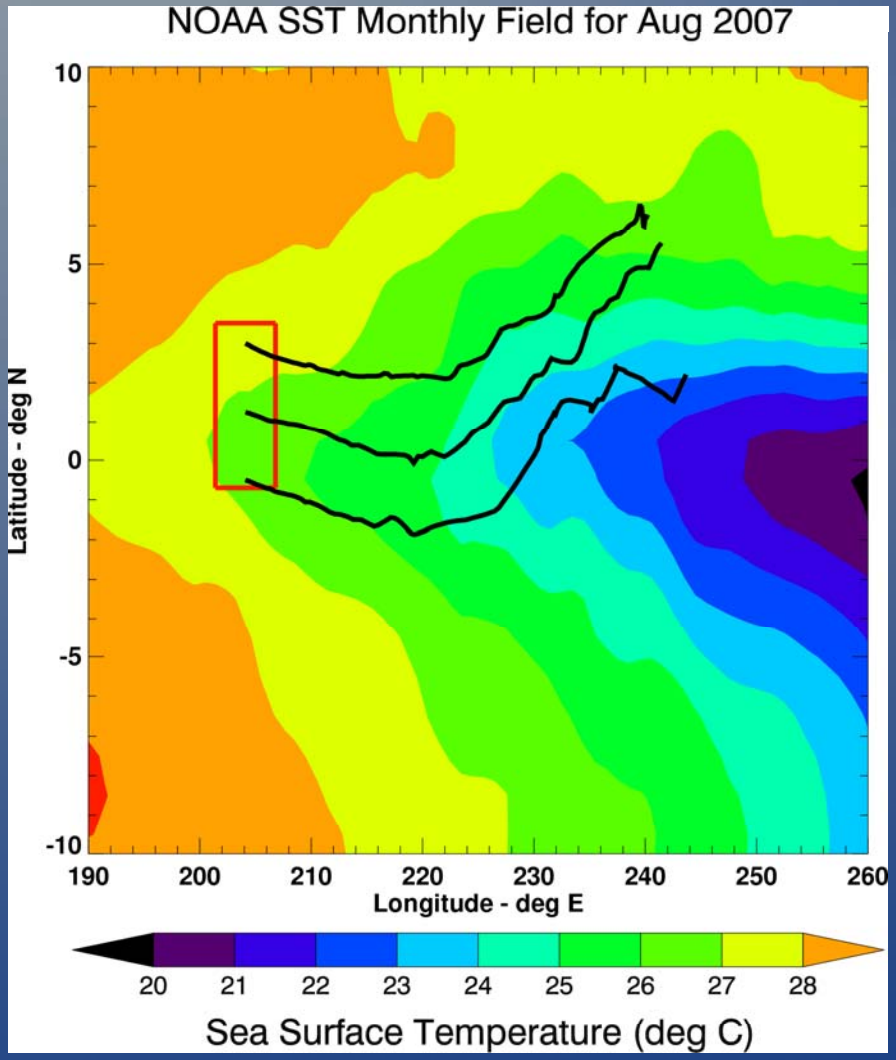
- Even with 10X convection, model MSA in lower FT much too small
- However, addition of 2 pptv BrO to all layers greatly improves DMS and MSA comparison with 10X convection; H_2SO_4 worse
- MSA concentration still too small with 10x conv and 2 pptv BrO
  - More halogen chemistry in lower FT?
  - Cloud source for MSA from upper BuL?

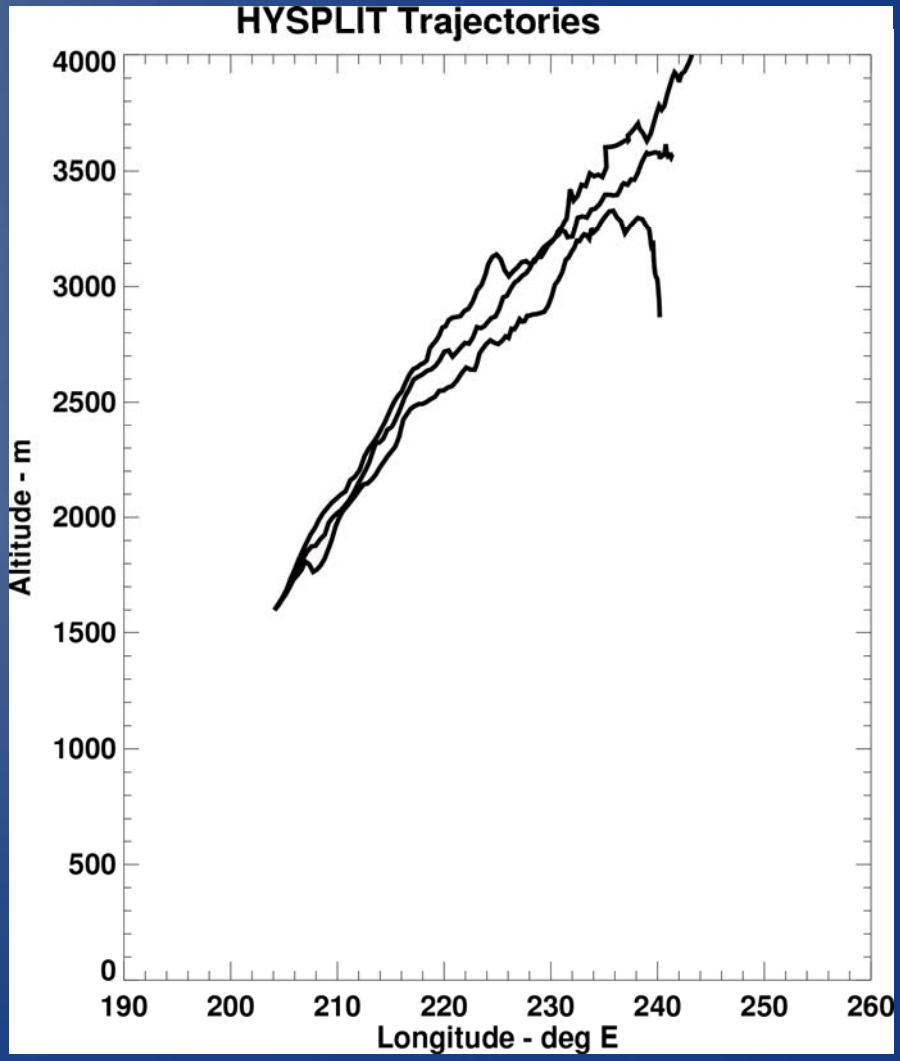
OH


OH Median Profiles
Model
PASE Obs
PTA Obs
PTB Obs
Altitude - m
Concentration - molec/cm3
0
500
1000
1500
2000
2•10^6
4•10^6
6•10^6
8•10^6
1•10^7


OH BL
Concentration - molec/cm3
Time
0
2•10^6
4•10^6
6•10^6
8•10^6
2
4
6
8
10
12
14
16
18

SST


NOAA SST Monthly Field for Aug 2007
Latitude - deg N
10
5
0
-5
-10
190
200
210
220
230
240
250
260
Longitude - deg E
20
21
22
23
24
25
26
27
28
Sea Surface Temperature (deg C)


HYSPLIT Trajectories
Altitude - m
4000
3500
3000
2500
2000
1500
1000
500
0
190
200
210
220
230
240
250
260
Longitude - deg E