Vertical distribution of HO_x and O_3 in the tropical marine boundary layer during PASE

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1. Introduction

- Hydroxyl (OH) is considered the most important oxidant and the main sink of tropospheric trace gases.
- Hydroperoxy (HO_2) controls the most important pathway for converting NO to NO_2, ultimately leading to O_3 production.
- HO_x ($OH+HO_2$) and O_3 play key roles in tropospheric photochemistry and determine the fate of various trace gases.

1.2 Laboratory kinetics

Initial

$$O_3 + h\nu \rightarrow O_2 + O(^1D)$$

$$O(^1D) + H_2O \rightarrow 2OH$$

Recycling

$$CO/RH + OH \xrightarrow{O_2} CO_2/RO_2 + HO_2$$

$$RO_2 + NO \rightarrow RO + NO_2$$

$$RO + O_2 \rightarrow R'CHO + HO_2$$

$$HO_2 + NO \rightarrow OH + NO_2$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

$$NO_2 + h\nu \xrightarrow{O_2} NO + O$$

Removal

$$OH + HO_2 \rightarrow H_2O + O_2$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$RO_2 + HO_2 \rightarrow ROOH + O_2$$

$$NO_2 + OH + M \rightarrow HNO_3 + M$$

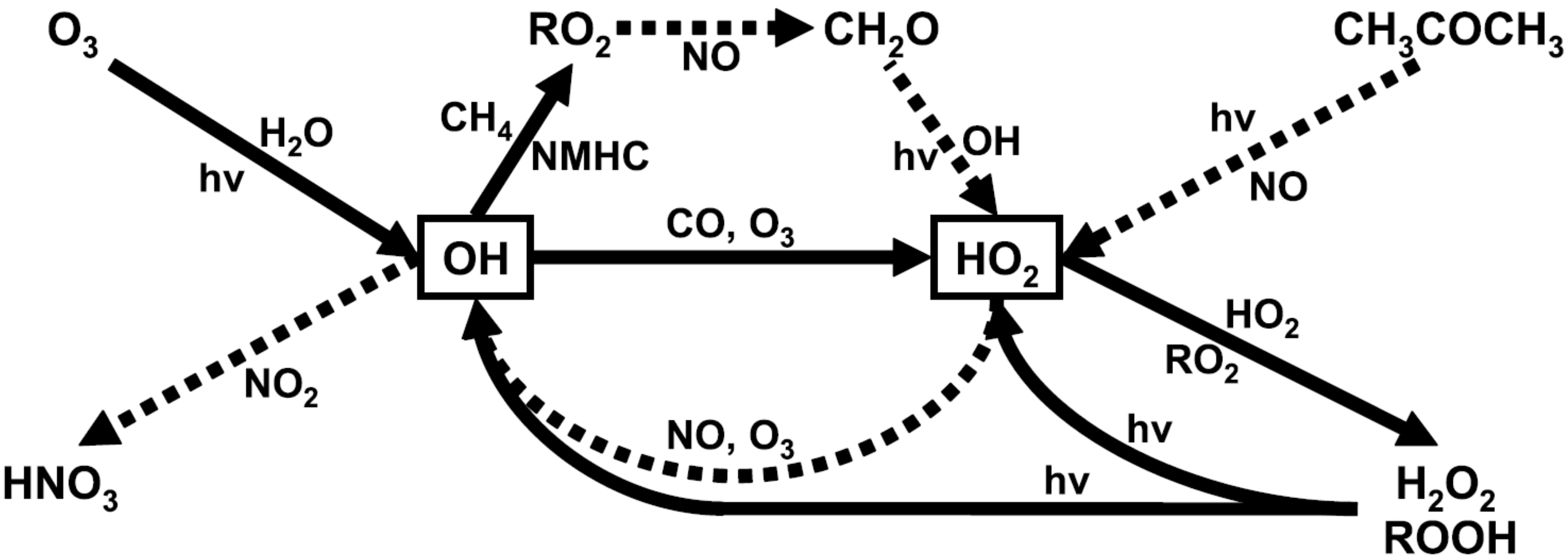
Reservoir

$$H_2O_2 + h\nu \rightarrow 2\,OH$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O$$

$$CH_3OOH + h\nu \rightarrow CH_3O + OH$$

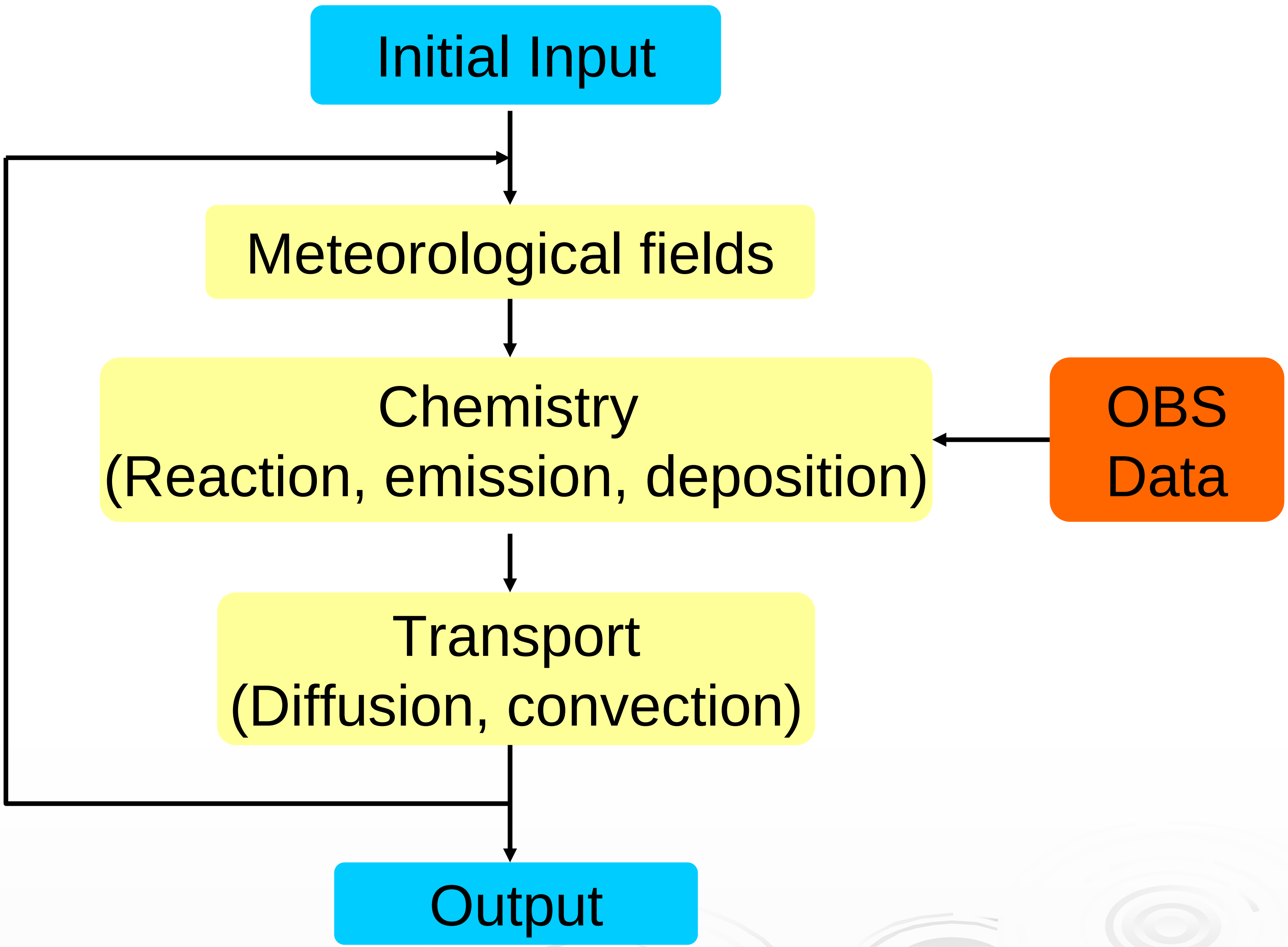
$$CH_3OOH + OH \rightarrow HCHO + OH + H_2O$$



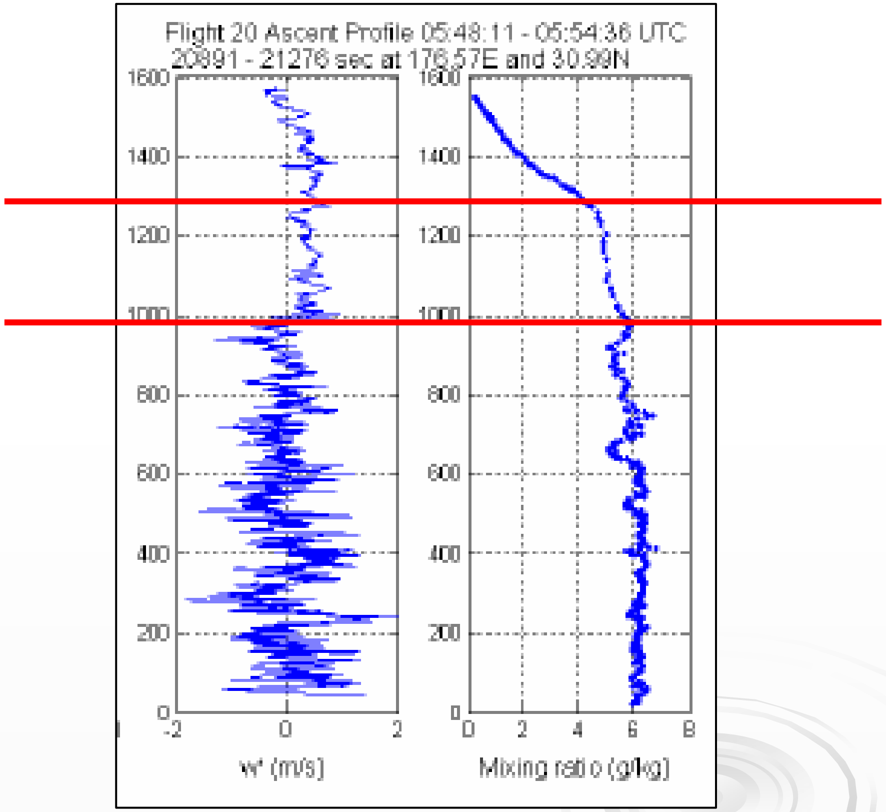
[*Olson et al.*, 2006]

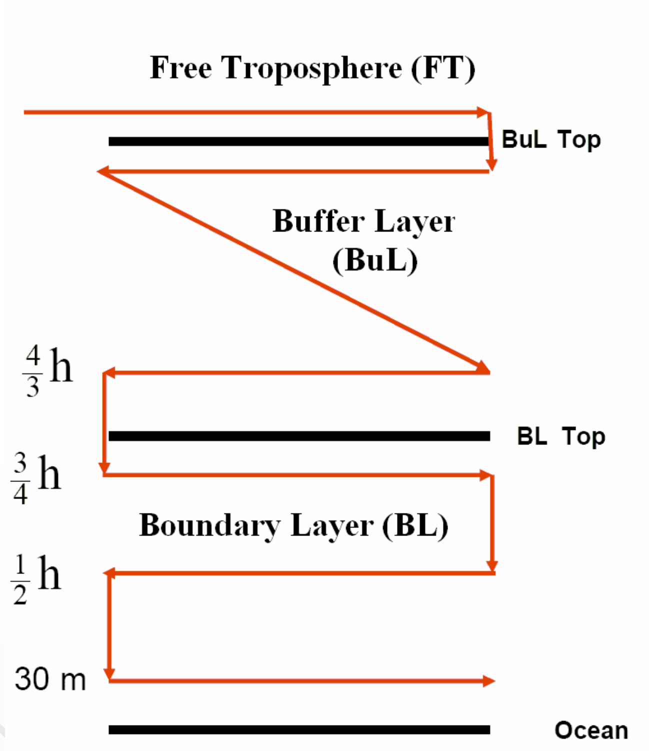
3. Model & Data

- 1-D model
  - Constructed from the 3-D Regional chEmical trAnsport Model (REAM)
  - Dry/wet deposition, photochemistry modules are from Harvard GEOS-Chem model
  - Meteorological fields are assimilated from Weather Research and Forecasting model (WRF)
  - Horizontal resolution of 10 x 10 km^2, 45 vertical layers below 10 mb.

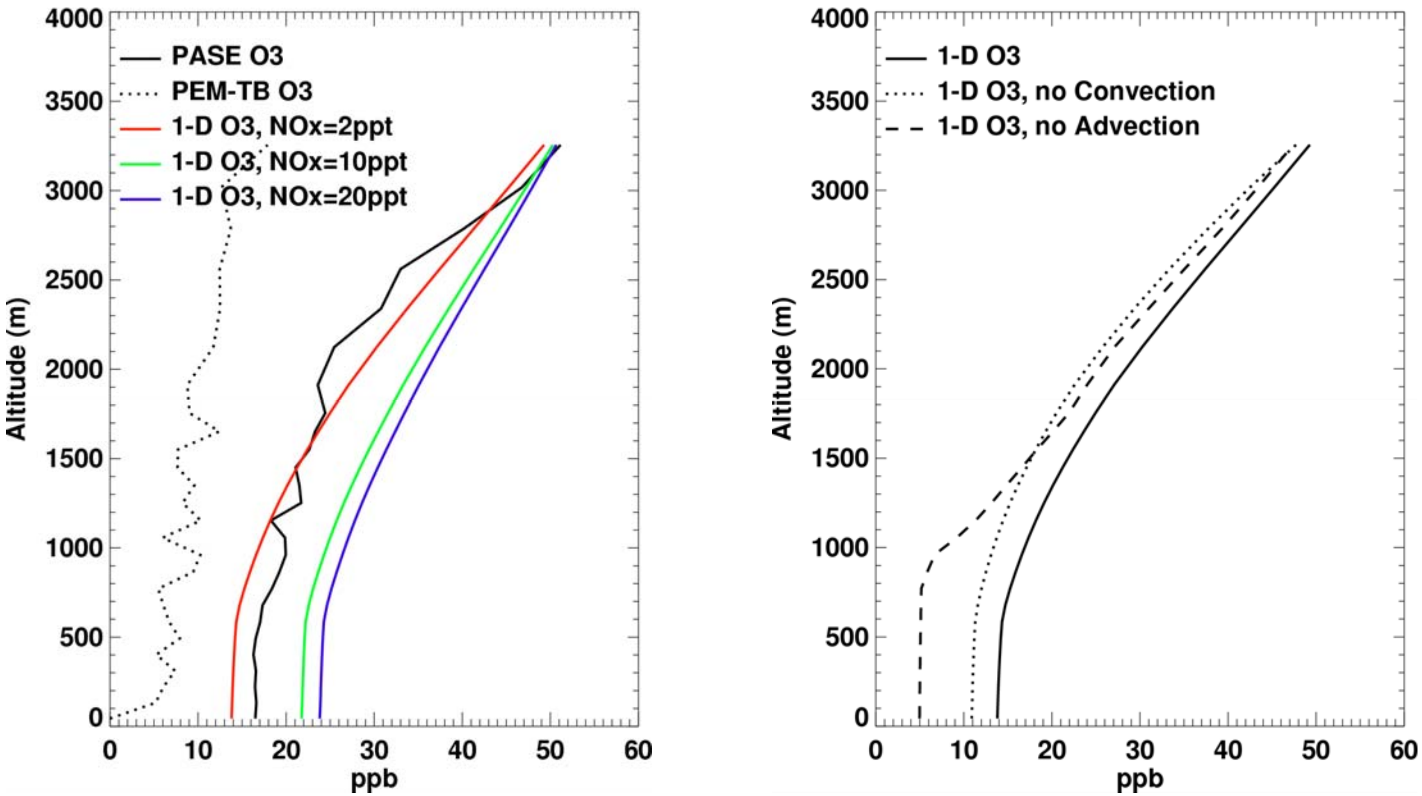

Initial Input
Meteorological fields
Chemistry
(Reaction, emission, deposition)
OBS
Data
Transport
(Diffusion, convection)
Output

- Pacific Atmospheric Sulfur Experiment (PASE)
  - Christmas Island (2 N, 157 W), Aug – Sep, 2007
  - Fourteen C-130H flights, including 2 nighttime.
  - Measurements: OH, HO_2, H_2O, O_3, CO, H_2O_2, DMS, SO_2, DMSO, MSA, H_2SO_4,, CH_3OOH, aerosol conc and sizes.



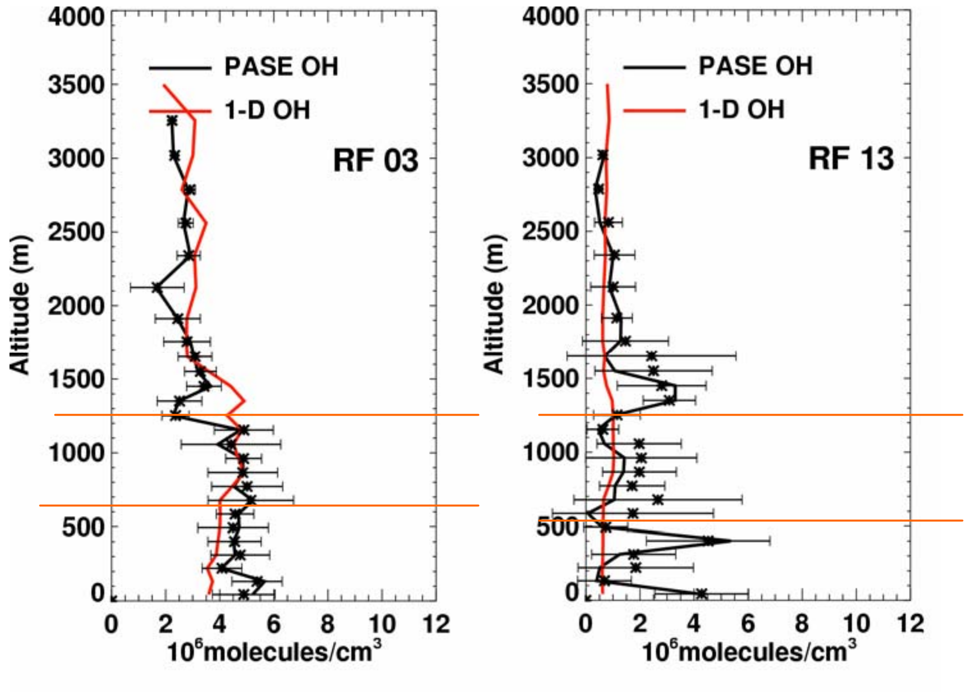


4.1 O_3 vertical distribution



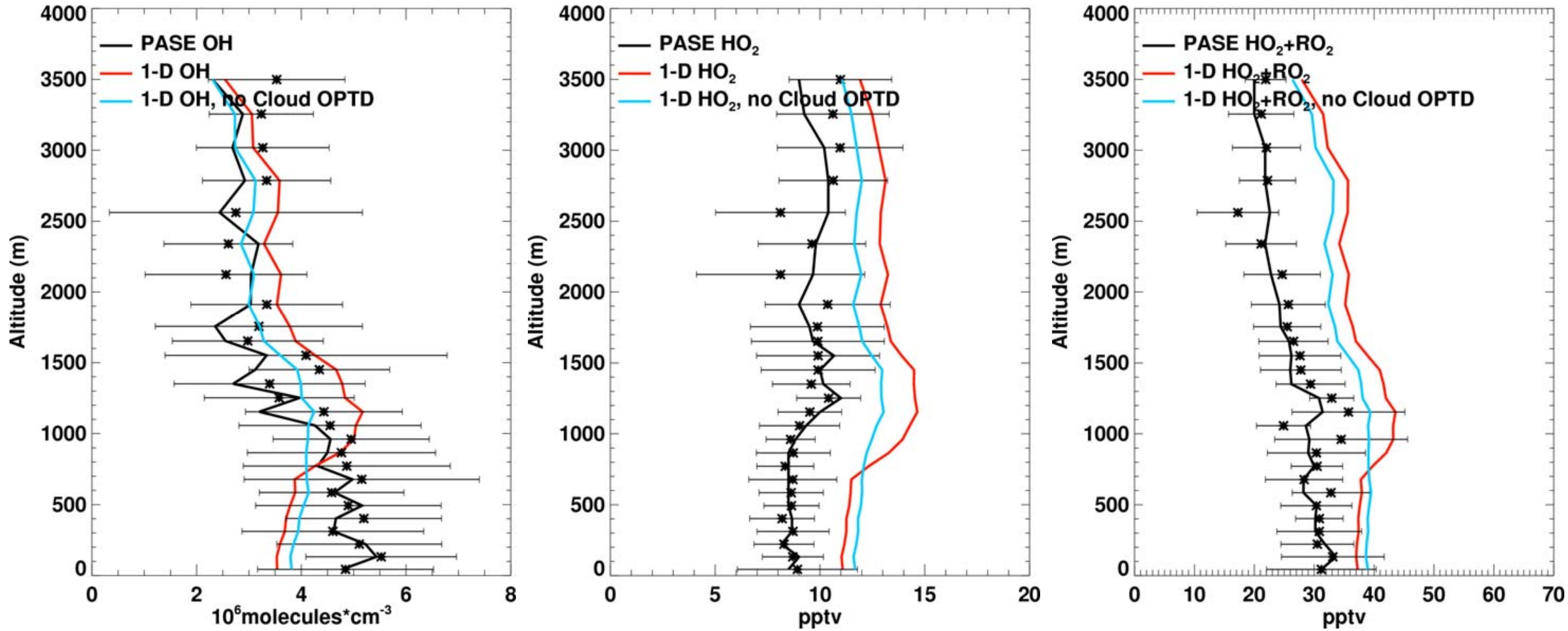
- Boundary layer O_3 mixing ratio increased as NO_x increased. It shows good sensitivity of O_3 on NO_x.
- Compared with PEM-TB (Spring), PASE (Summer) O_3 mixing ratio significantly increased, showing stronger photochemistry in summer.
- Vertical advection (large-scale subsidence) and cloud convection made significant contributions for boundary layer O_3.

4.2 OH vertical distribution



- RF03 represents the typical daytime vertical profiles. High OH value in BL showing strong HO_x source of O(1D) + H_2O during daytime.
- RF13 is represents the typical nighttime vertical profiles. OH and HO_2 in night is significant lower than daytime.
- BL height do not change much from day to night, due to the heat capacity of ocean.
- There were intermittent turbulence at BuL. And strong temperature inversion above BuL produced significant gradient between free troposphere and BuL.

4.3 Cloud effect



- Cloud optical density has a significant impact on solar radiation energy in troposphere, and then impact the O(1D)+H_2O reaction.
- The mixing ratios in low altitudes increased when set cloud OPTD to zero, because the enhancement of radiation under clouds.
- The mixing ratios in high altitudes decreased when set cloud OPTD to zero, because the deduction of actinic flux in clouds.

5. Summary

- O_3 vertical distribution fits OBS with 2 pptv NOx, while vertical transports contribute most BL O_3.
- Daytime and nighttime vertical distributions of OH suggested the structure of tropical marine BL and BuL is significantly impacted by ocean surface heat flux.
- Actinic flux is significantly impact by cloud coverage.

Thank you!