Diagnostic Photochemical Assessment of airborne observations during INTEX-B

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OH Obs/Calc Ratios

ATHOS Instrument/Penn State, Current version of LaRC Model

Altitude (km)	INTEX-B Pacific DC-8	INTEX-A DC-8	TRACE-P DC-8
10-12	0.70	0.62	0.62
8-10	0.69	0.55	0.63
6-8	0.62	0.59	0.64
4-6	0.64	0.60	0.74
2-4	0.55	0.58	0.80
1-2	0.53	0.62	0.80
0-1	0.44	0.73	0.96

OH Obs/Calc Ratios

SICIMS Instrument/NCAR, Current version of LaRC Model

Altitude (km)	INTEX-B Pacific, C-130	TRACE-P P-3B
6-8	0.80	0.73
4-6	0.97	0.91
2-4	1.04	0.90
1-2	1.16	1.10
0-1	1.36	1.48

HO_2 Obs/Calc Ratios

ATHOS Instrument/Penn State, Current version of LaRC Model

Altitude	INTEX-B Pacific, DC-8	INTEX-A DC-8	TRACE-P DC-8
10-12	0.63 (0.63)**	1.73 (0.89)**	0.89 (0.88)**
8-10	0.63 (0.63)**	0.95 (0.73)**	0.84 (0.84)**
6-8	0.64	0.68	0.85
4-6	0.69	0.66	0.81
2-4	0.70	0.66	0.80
1-2	0.71	0.79	0.79
0-1	0.58	0.88	0.79

** Numbers in parenthesis limited to NO_x < 250 ppt above 8 km
(100% of INTEX-B data, 29% INTEX-A data, 95% TRACE-P data)

HO_2 Obs/Calc Ratios

SICIMS Instrument/NCAR, Current version of LaRC Model

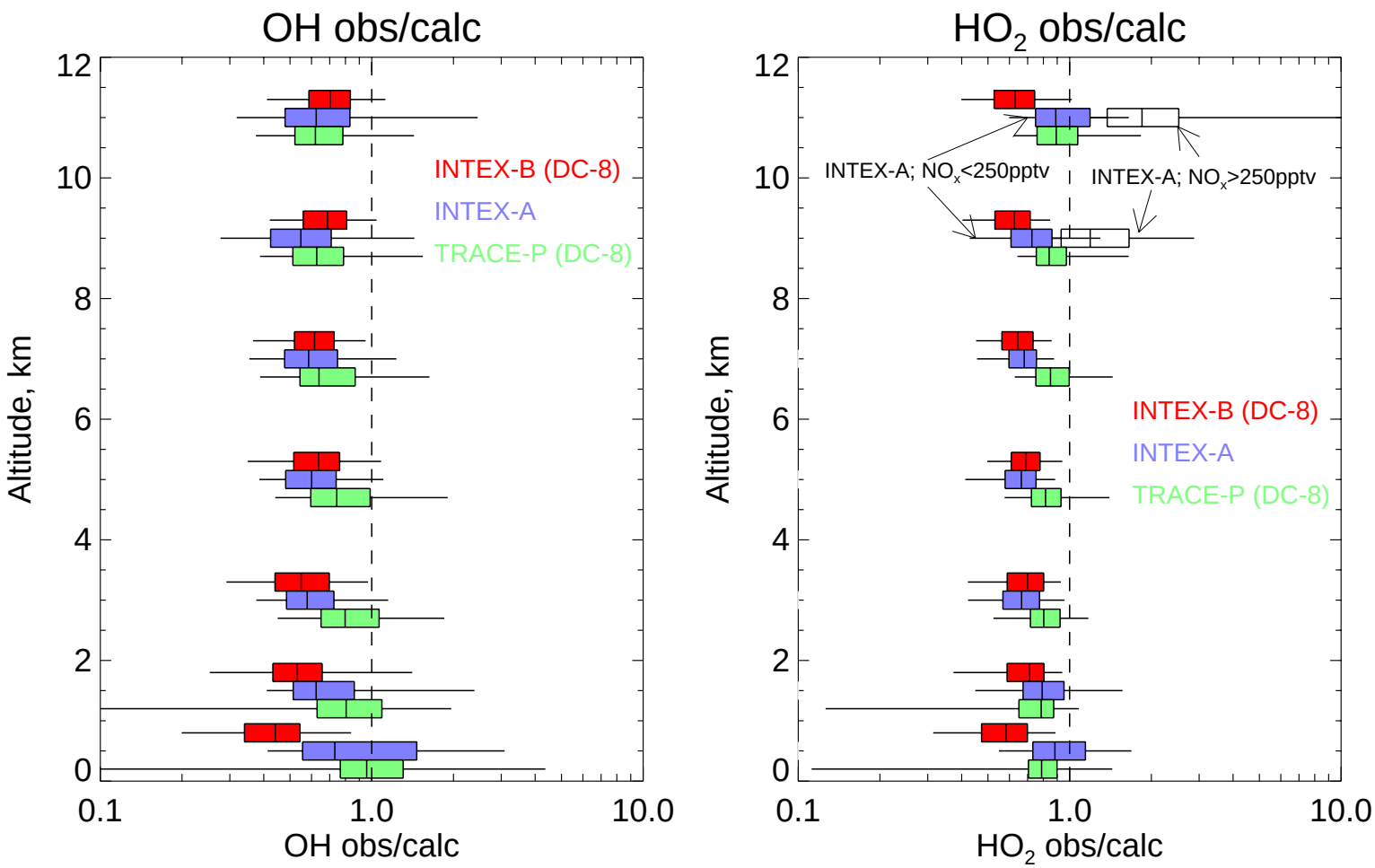
Altitude (km)	INTEX-B Pacific, C-130
6-8	0.66
4-6	1.02
2-4	1.00
1-2	1.13
0-1	1.24

CH_2O Obs and (Obs/Calc Ratios)

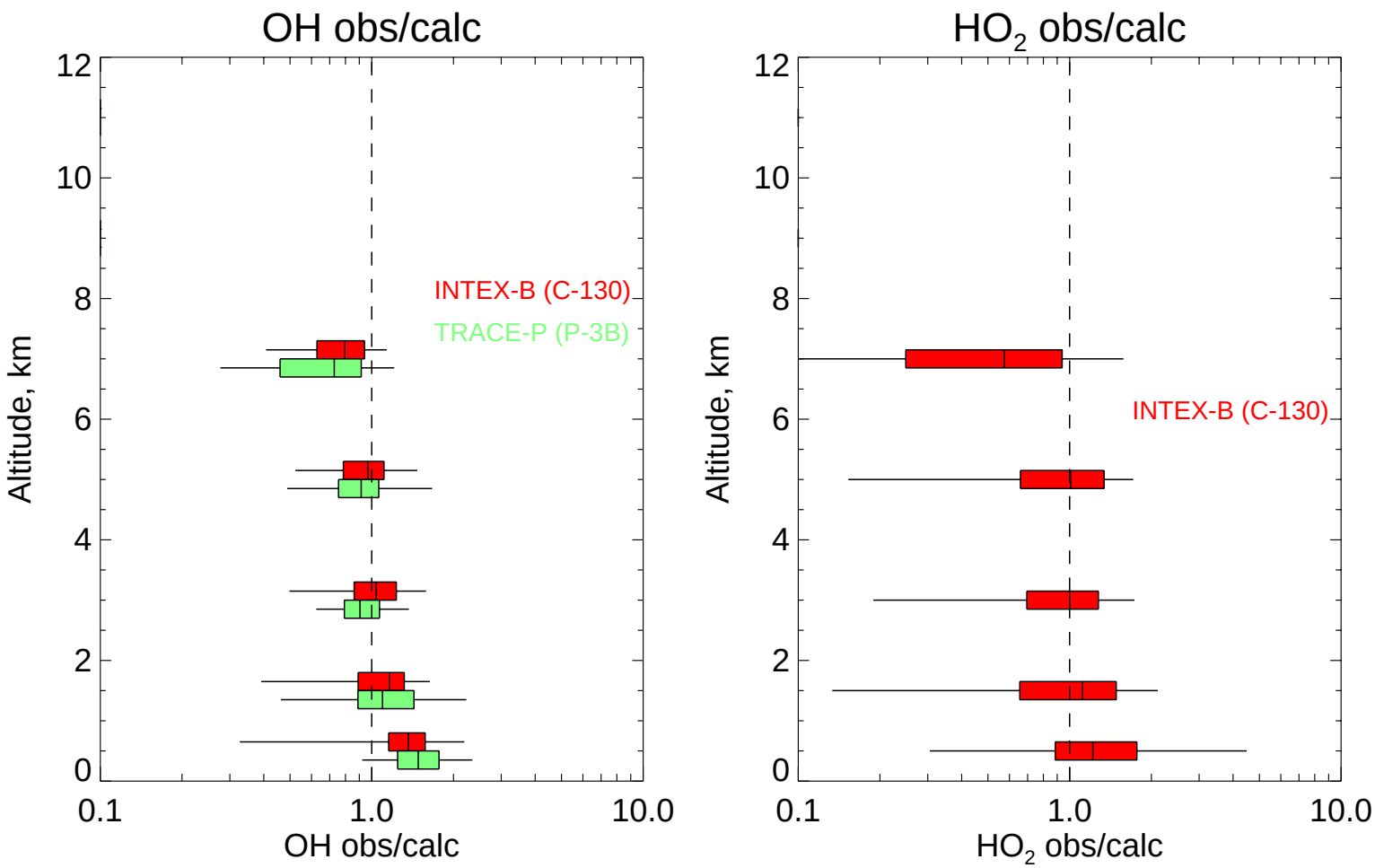
TDLAS Instrument/NCAR, Current version of LaRC Model

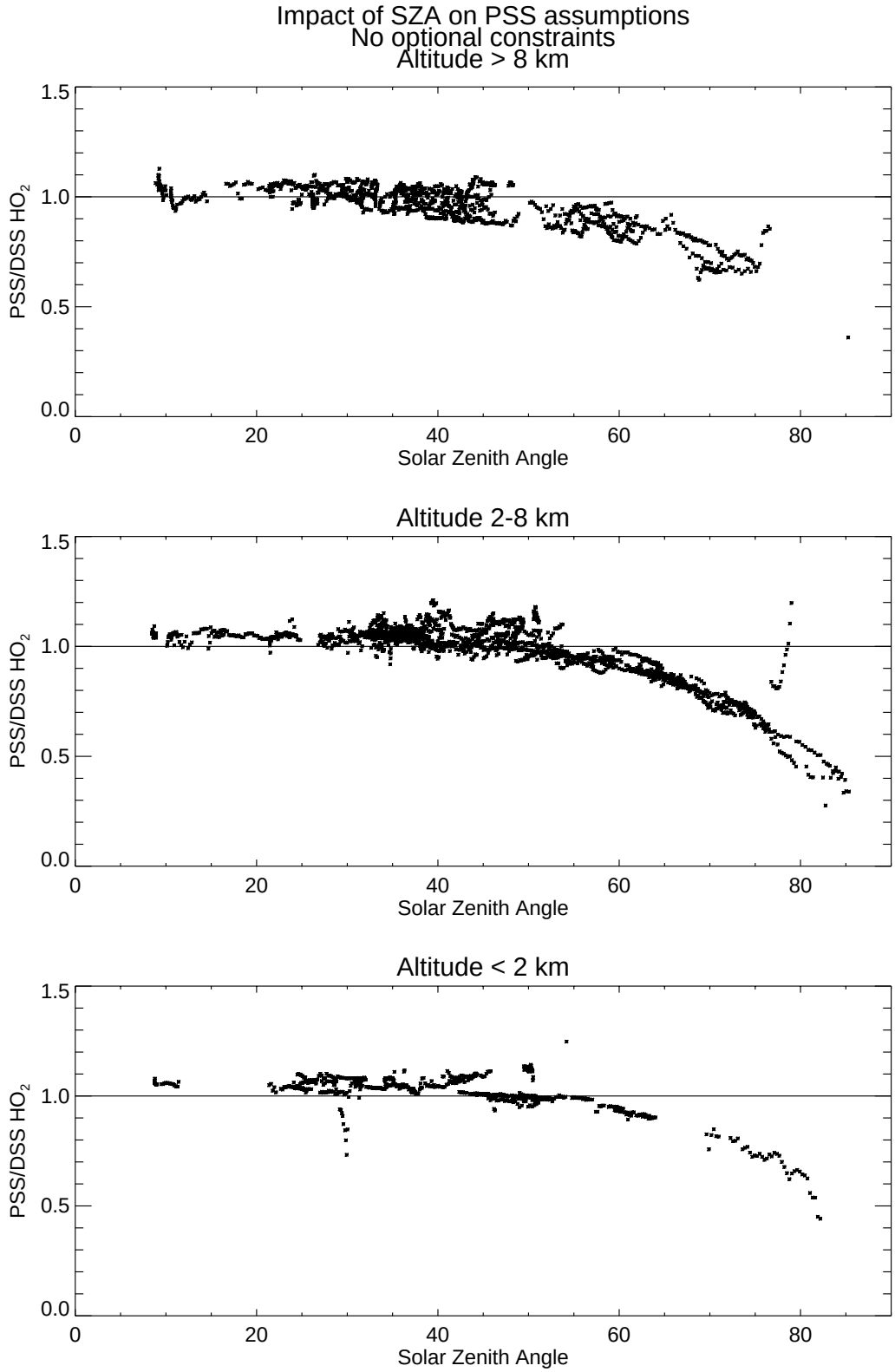
Altitude (km)	INTEX-B Pacific, C-130	INTEX-B Pacific DC-8	INTEX-A DC-8	TRACE-P DC-8
10-12	----	33 pptv (0.65)	***115 pptv (1.06)***	37 pptv (0.78)
8-10	----	26 pptv (0.51)	155 pptv (0.91)	51 pptv (0.72)
6-8	32 pptv (0.32)	52 pptv (0.63)	158 pptv (0.89)	68 pptv (0.82)
4-6	62 pptv (0.51)	57 pptv (0.61)	***286 pptv (1.23)***	85 pptv (0.71)
2-4	112 pptv (0.65)	153 pptv (0.85)	***483 pptv (1.28)***	165 pptv (0.85)
1-2	225 pptv (0.90)	***196 pptv (1.07)***	***1194 pptv (1.71)***	***246 pptv (1.21)***
0-1	748 pptv (0.89)	***242 pptv (1.02)***	***1761 pptv (1.62)***	***350 pptv (1.25)***

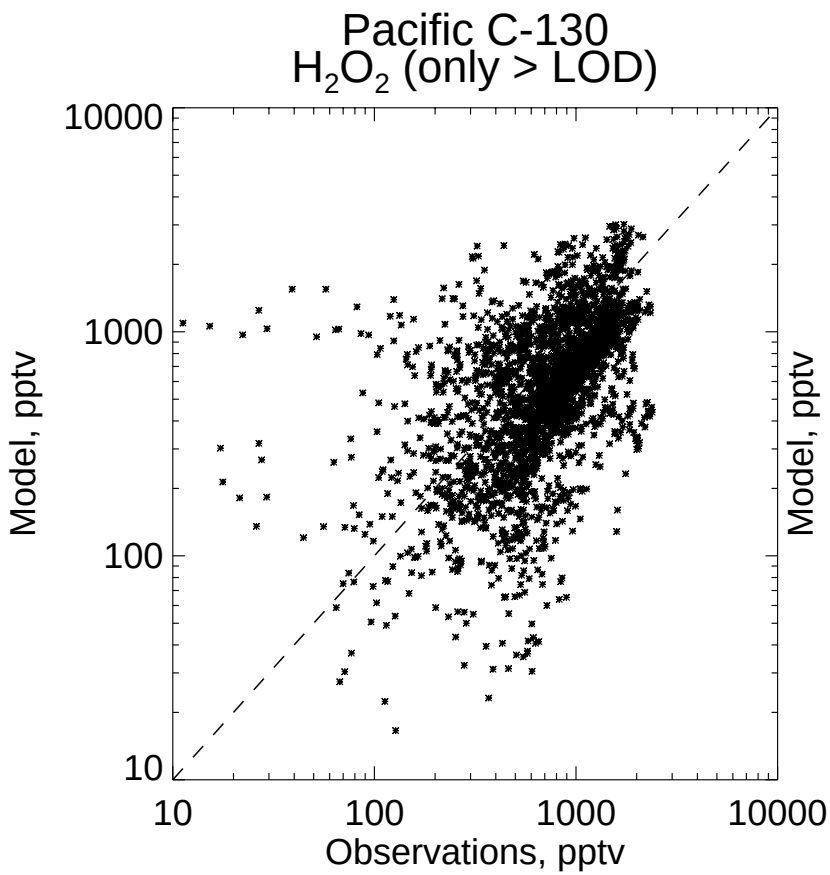
ATHOS HO_x vs. LaRC boxmodel



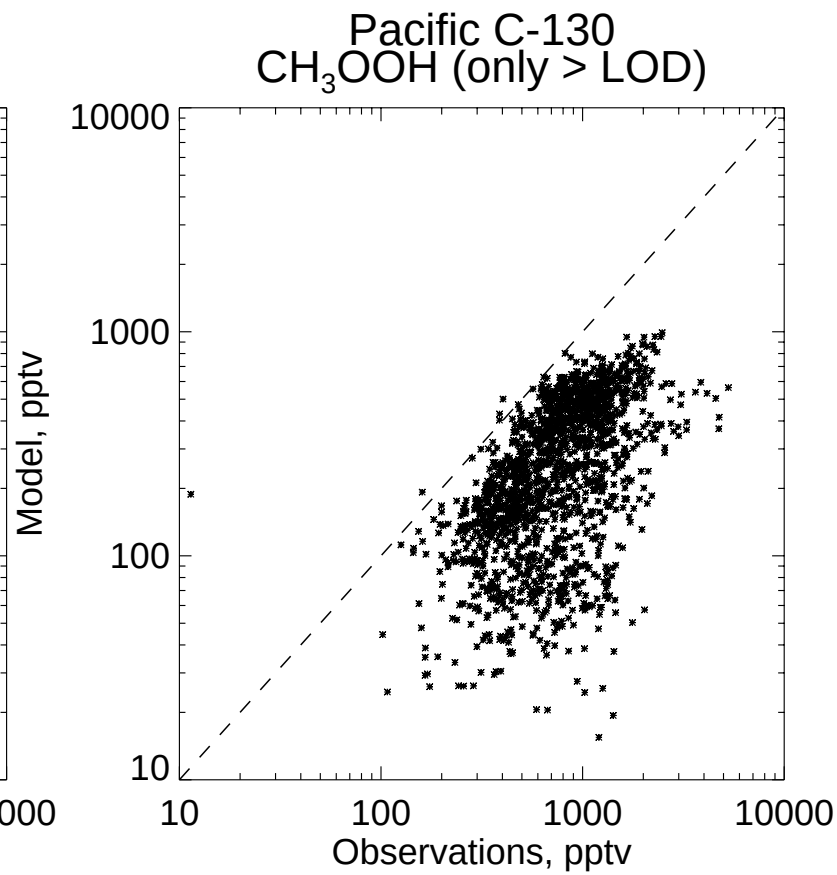
SICIMS HO_x vs. LaRC boxmodel



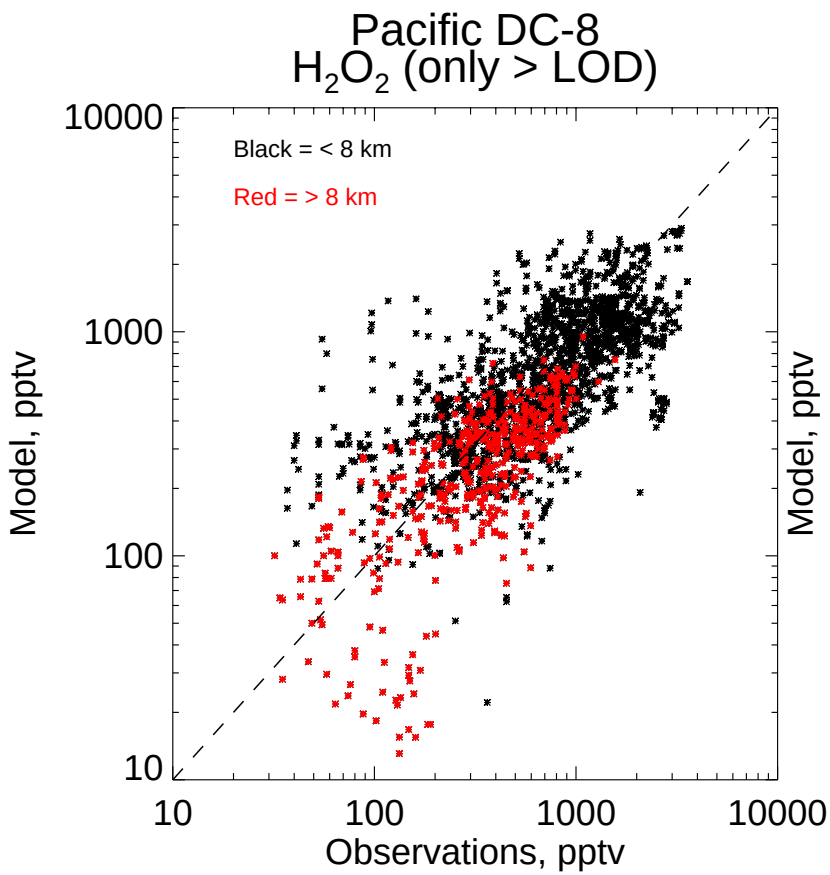

Impact of SZA on PSS assumptions
No optional constraints
Altitude > 8 km
PSS/DSS HO_2
Solar Zenith Angle
Altitude 2-8 km
PSS/DSS HO_2
Solar Zenith Angle
Altitude < 2 km
PSS/DSS HO_2
Solar Zenith Angle
0.0
0.5
1.0
1.5
0
20
40
60
80



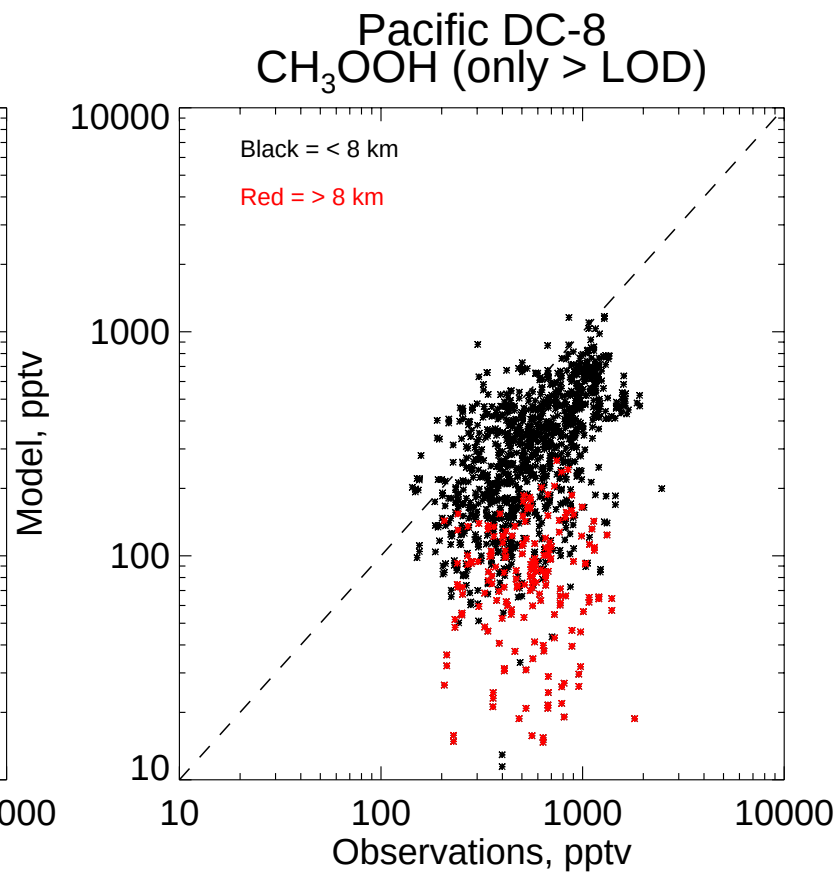
Median obs/calc = 1.36784



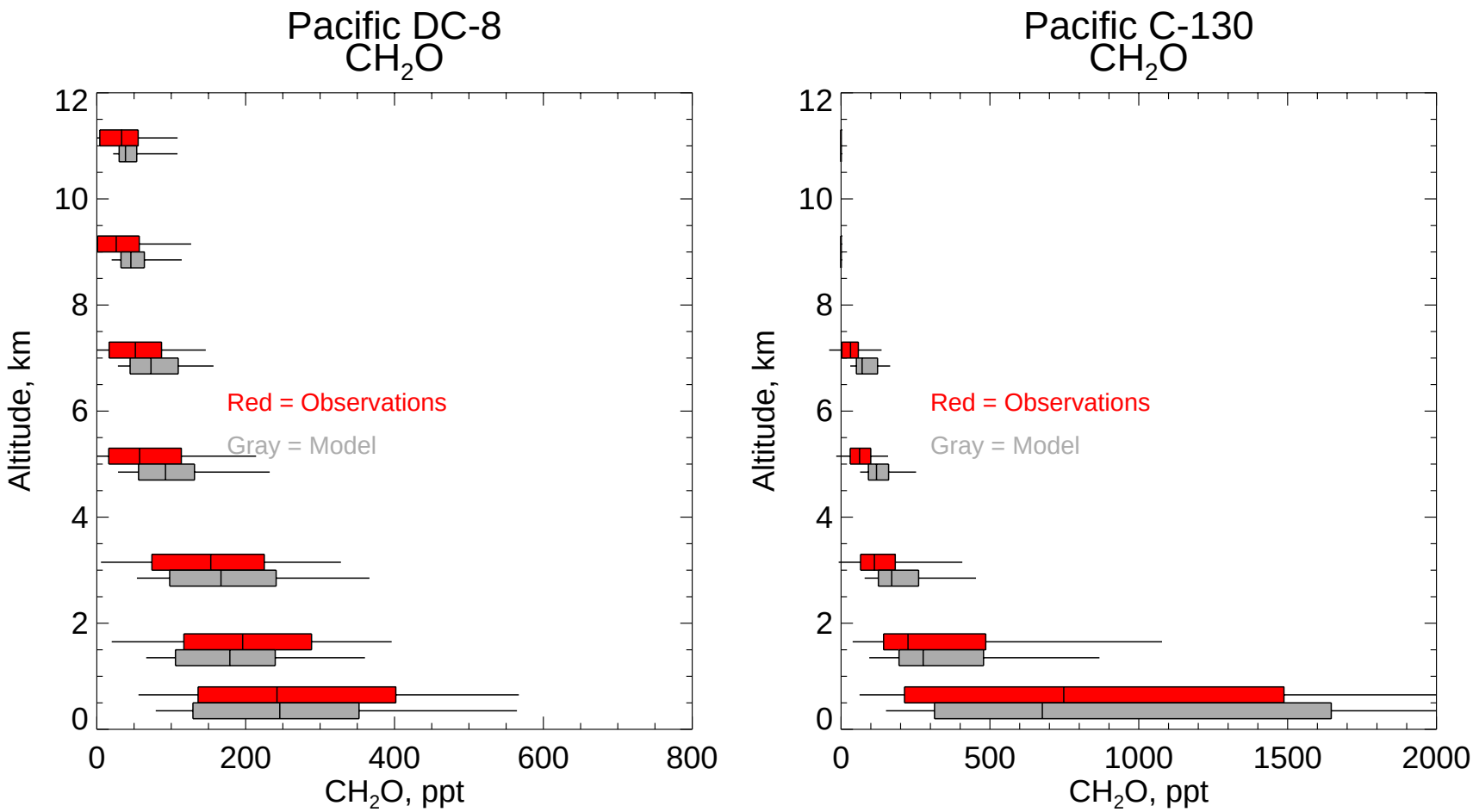
Median obs/calc = 2.69898

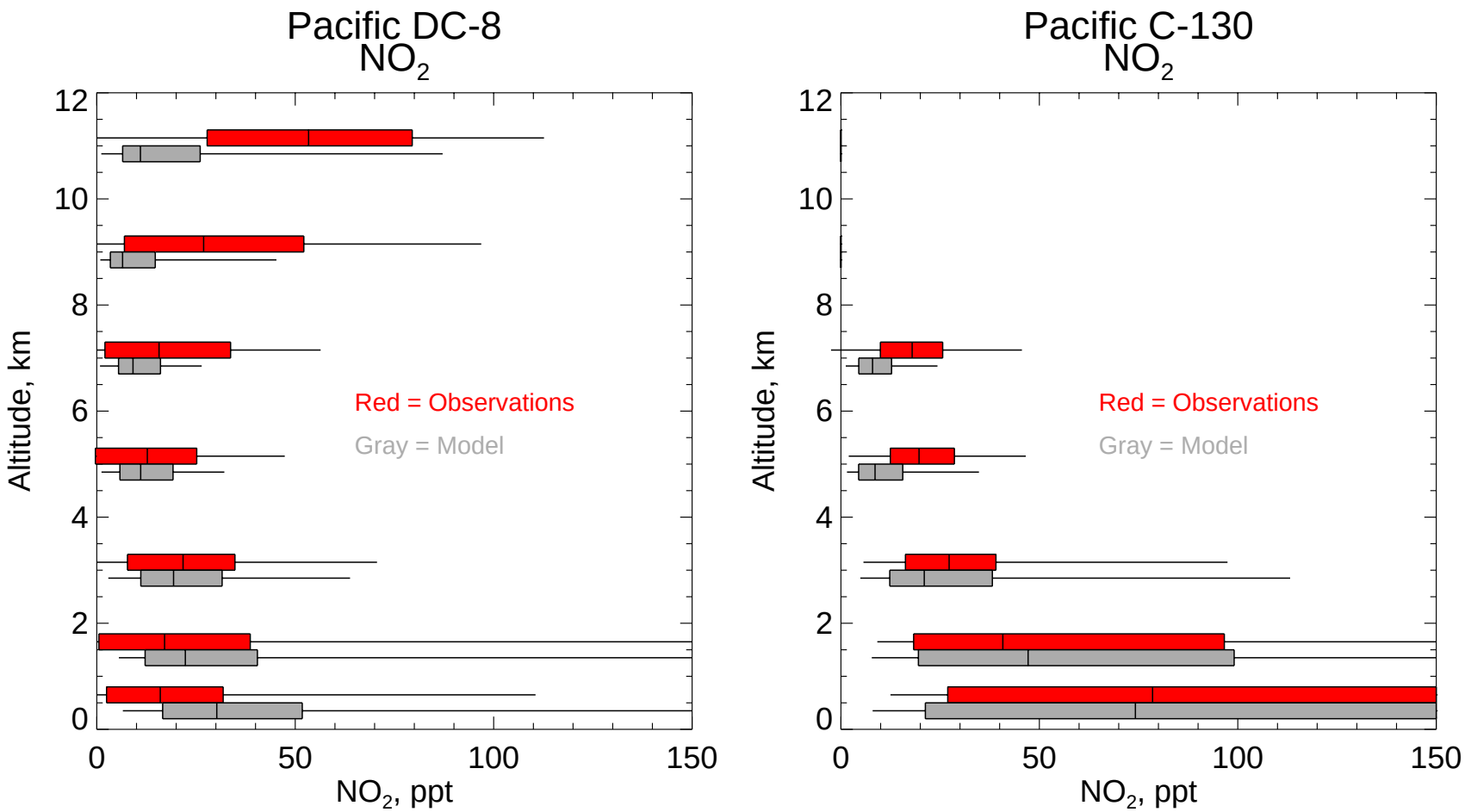


Median obs/calc below 8 km = 1.11313



Median obs/calc below 8 km = 1.85266


Pacific DC-8
CH2O
Altitude, km
CH2O, ppt
Red = Observations
Gray = Model
0
2
4
6
8
10
12
0
200
400
600
800
Pacific C-130
CH2O
Altitude, km
CH2O, ppt
Red = Observations
Gray = Model
0
500
1000
1500
2000


Pacific DC-8
NO2
Pacific C-130
NO2
Altitude, km
NO2, ppt
Red = Observations
Gray = Model
0
2
4
6
8
10
12
0
50
100
150

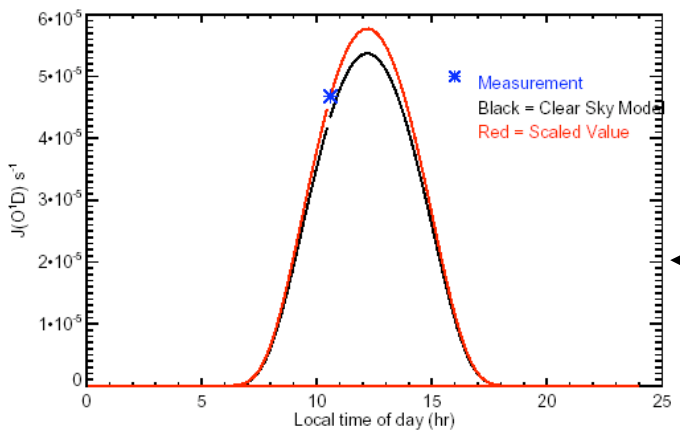
LaRC Model Description

Mechanism and rates:

Gas phase chemistry based primarily on *Lurmann et al., 1986* with rates updated to *JPL 2006 and IUPAC 2004.*
Near-IR photolysis of HNO_4 is included (*Roehl et al., 2002*)

Surface deposition for selected species assumed for lowest 2 km
Rainout of peroxides, aldehydes, nitric acid as in *Logan et al., 1981*

Photolysis rate coefficients from DISORT four-stream implementation of TUV (*Madronich and Flocke, 1998*).



Clear-sky calculations are normalized throughout the day to match in-situ spectroradiometer photolysis measurements at time of measurement

Modeling approach

Diurnal steady state (i.e., repeatable diurnal cycles of all calculated species.)

Model always requires observations (constraint) of O_3, CO, NO (or NO_2), temperature, pressure, dew/frost point, latitude, longitude, altitude, overhead O_3 column

The following are always constrained when available, and are interpolated or filled through data gaps: NMHCs, acetone, MEK, methanol and ethanol

Optional constraints (constrained when observations are available, otherwise calculated by model): H_2O_2, CH_3OOH, HNO_3, PAN

Why diurnal steady state rather than instantaneous steady state?

For cases when optional constraints are not available, PSS gives increasingly erroneous values with increasing solar zenith angle.

Boundary layer conditions for ATHOS flights

Median values for BL (<2 km)

	INTEXB (DC-8)	INTEXA	TRACEP (DC-8)
OH obs/calc	0.48	0.68	0.92
$[OH]_{obs}$	0.05 ppt	0.15 ppt	0.10 ppt
OH obs-model	-0.05 ppt	-0.06 ppt	-0.008
O_3	49 ppb	49 ppb	52 ppb
NO_x	42 ppt	137 ppt	40 ppt
H_2O	1.86×10^{17} molec/cm^3	3.58×10^{17} molec/cm^3	2.86×10^{17} molec/cm^3
CO	149 ppb	128 ppb	176.0 ppb
$J(O^1d)$	1.73×10^{-5} s^{-1}	2.59×10^{-5} s^{-1}	1.80×10^{-5} s^{-1}
Primary source [OH]	1.78×10^{6} molec/cm^3 s	4.50×10^{6} molec/cm^3 s	1.98×10^{6} molec/cm^3 s
HO_2+NO source	0.65×10^{6} molec/cm^3 s	2.34×10^{6} molec/cm^3 s	0.66×10^{6} molec/cm^3 s
$CH_2O_{(obs)}/CH_2O_{(calc)}$	231/209	1596/865	322/273

Boundary layer conditions for SICIMS flights

Median values for BL (<2 km)

	INTEXB (C130)	TRACE-P (P3-B)
OH obs/calc	1.27	1.39
$[OH]_{obs}$	0.17 ppt	0.20 ppt
OH obs-model	+0.03 ppt	+0.04 ppt
O_3	59 ppb	56 ppb
NO_x	73 ppt	135 ppt
H_2O	1.28×10^{17} molec/cm^3	2.63×10^{17} molec/cm^3
CO	144 ppb	199 ppb
$J(O^1d)$	2.4×10^{-5} s^{-1}	1.87×10^{-5} s^{-1}
Primary source [OH]	1.74×10^{6} molec/cm^3 s	2.54×10^{6} molec/cm^3 s
HO_2+NO source	1.24×10^{6} molec/cm^3 s	1.67×10^{6} molec/cm^3 s
$CH_2O_{(obs)}/CH_2O_{(calc)}$	291/347	---/310

Upper troposphere conditions for ATHOS flights

Median values for altitudes > 8 km

	INTEXB (DC-8)	INTEXA	TRACEP (DC-8)
OH obs/calc	0.69	0.57	0.62
$[OH]_{obs}$	0.12 ppt	0.36 ppt	0.13 ppt
OH obs-model	-0.05 ppt	-0.28 ppt	-0.07
O_3	74 ppb	82 ppb	62 ppb
NO_x	44 ppt	374 ppt	74 ppt
H_2O	0.16×10^{15} molec/cm^3	1.64×10^{15} molec/cm^3	1.01×10^{15} molec/cm^3
CO	118 ppb	97 ppb	100 ppb
$J(O^1d)$	3.8×10^{-5} s^{-1}	4.8×10^{-5} s^{-1}	4.8×10^{-5} s^{-1}
Primary source [OH]	0.25×10^5 molec/cm^3 s	0.68×10^5 molec/cm^3 s	0.21×10^5 molec/cm^3 s
HO_2+NO source	2.38×10^5 molec/cm^3 s	12.0×10^5 molec/cm^3 s	3.0×10^5 molec/cm^3 s
$CH_2O_{(obs)}/CH_2O_{(calc)}$	30/42	143/138	47/59