Bromine oxide in the tropical free troposphere: Sources, relevance, research aircraft and mountaintops

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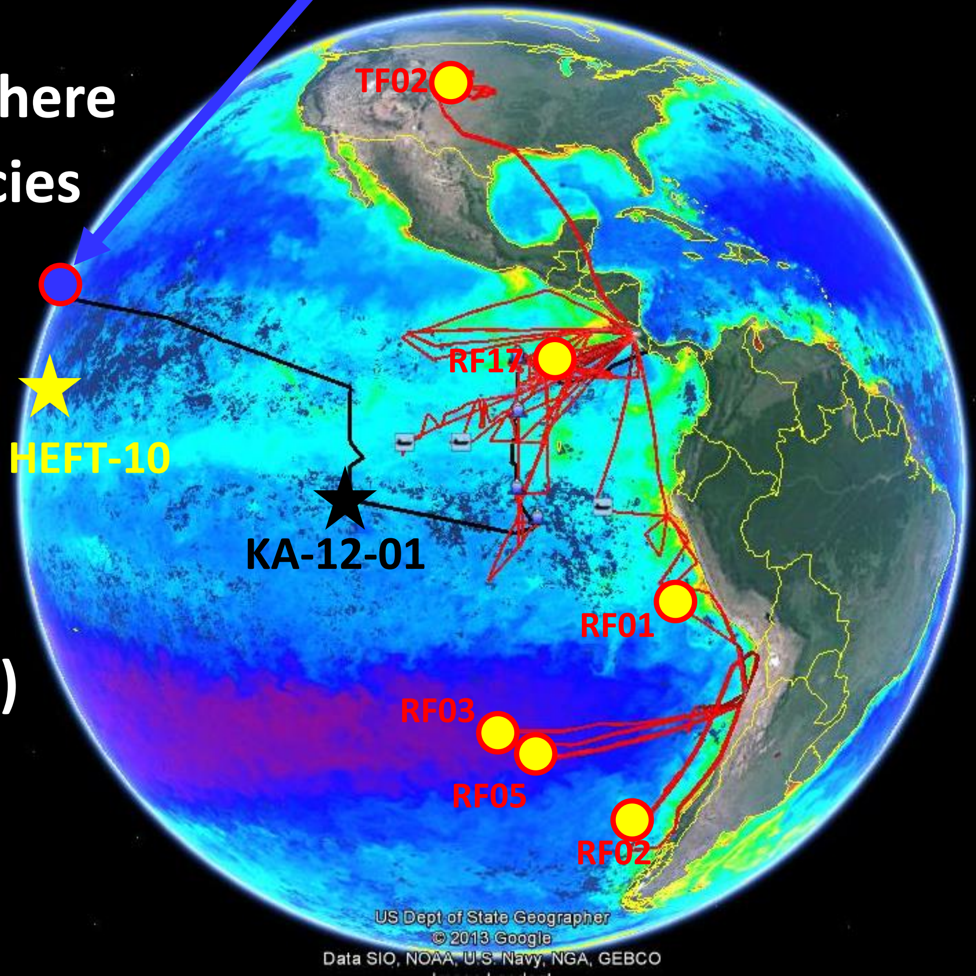
MLO (since Jan 2014)

TORERO – Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated voc

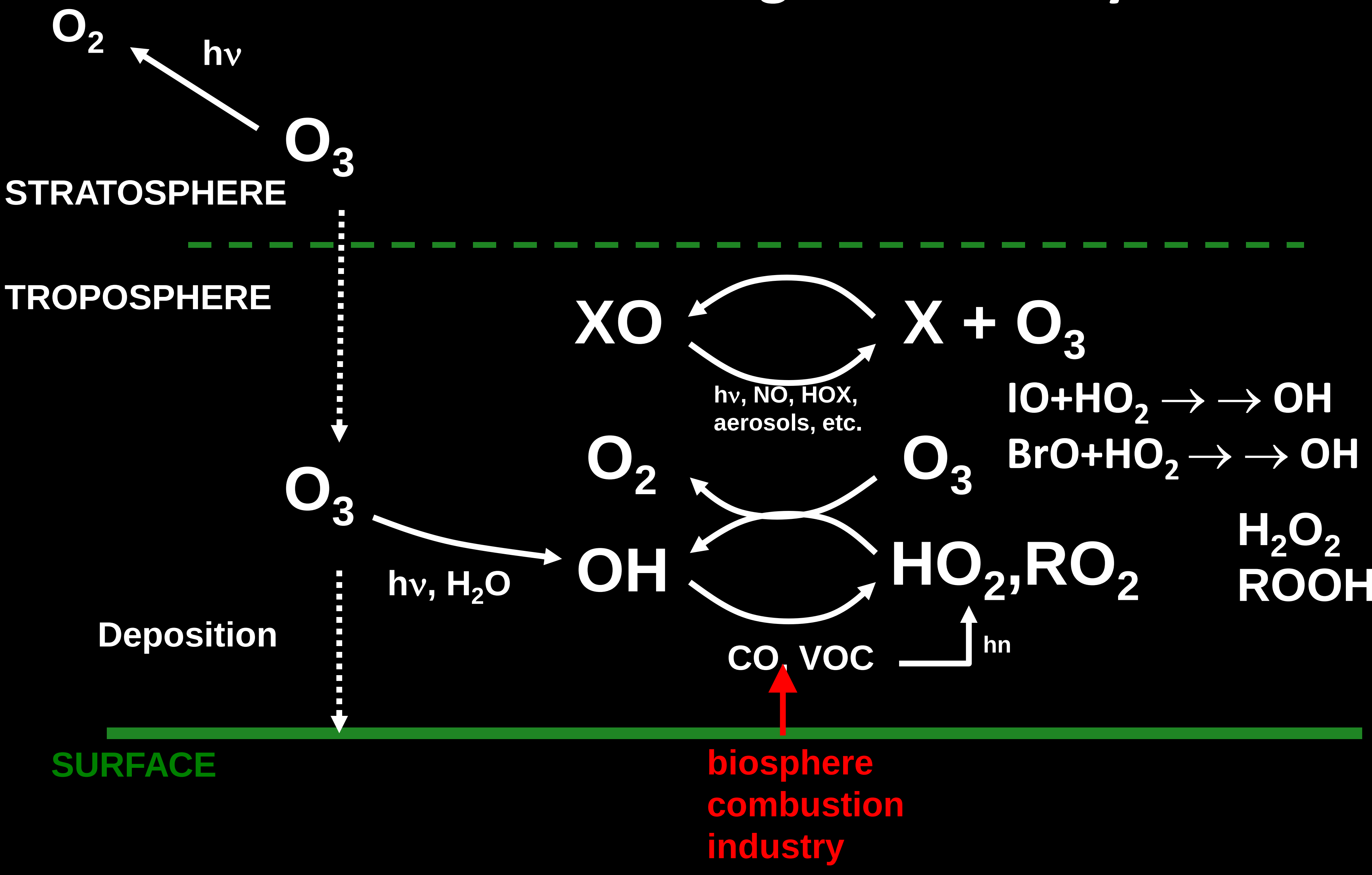
- BrO and IO vertical profiles
- Missing sources
- O_3 loss rates
- Mercury oxidation rates

- Mauna Loa Observatory (3.4km)

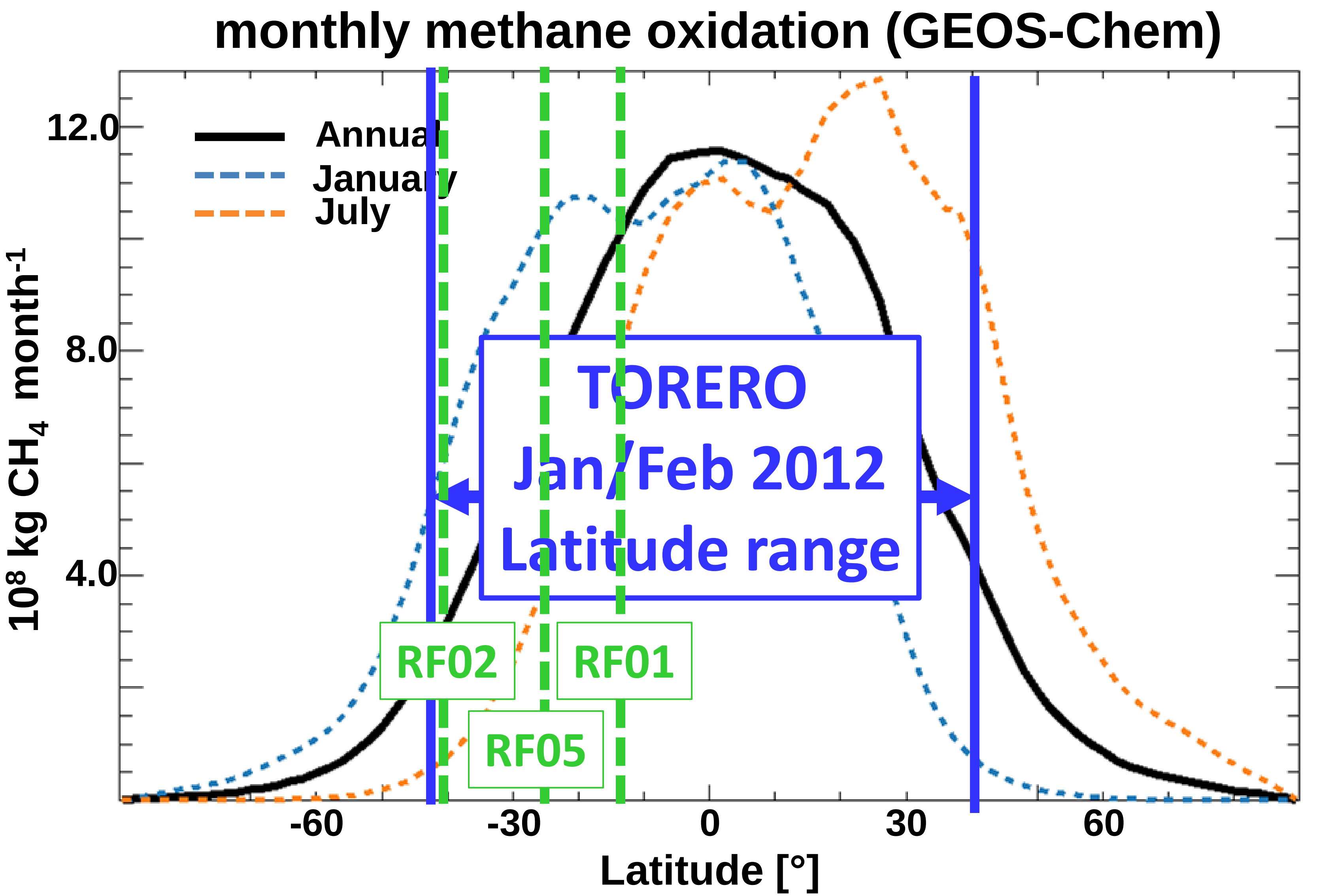


CIRES
Cooperative Institute for Research in Environmental Sciences
University of Colorado Boulder

Halogens destroy tropospheric ozone, and thus OH
How relevant is halogen chemistry?



Oxidation of long-lived gases by OH is mostly in tropics



Kevin Wecht, Harvard

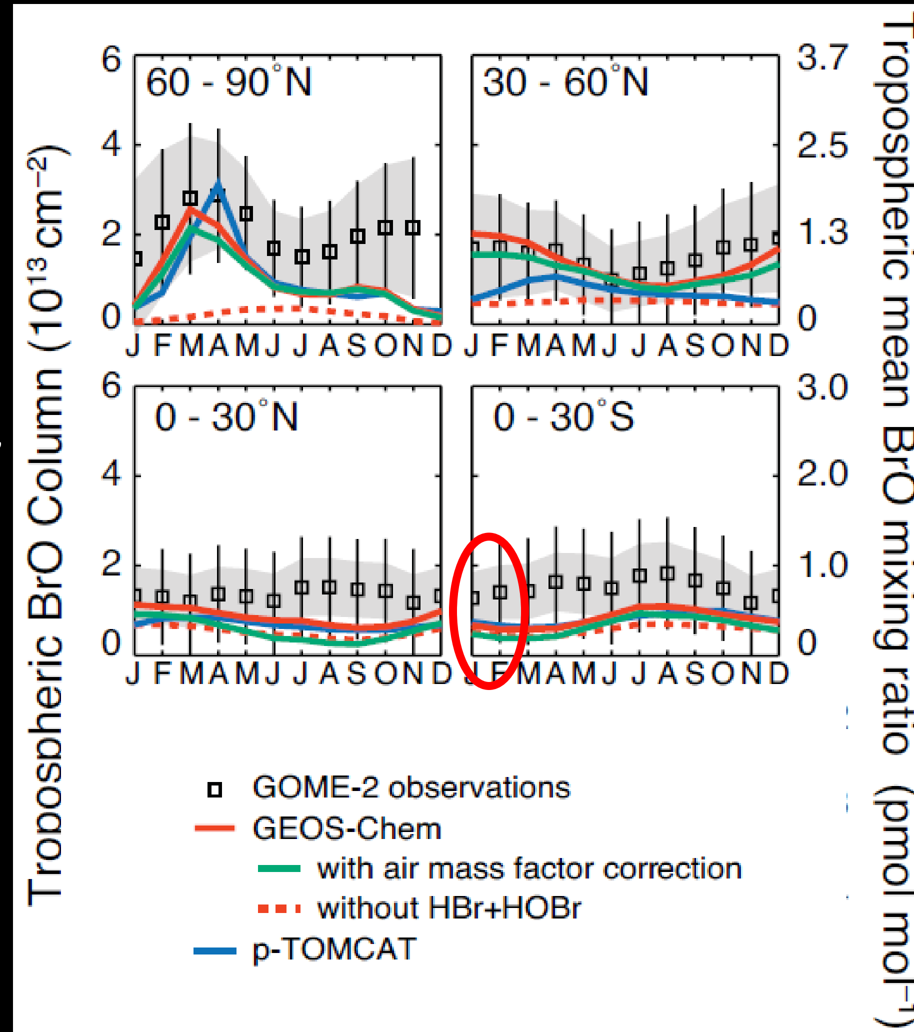
BrO comparison: GOME-2 with GEOS-Chem, p-TOMCAT

Satellite: 1-3 x10^{13} molec cm^{-2}
(Chance et al., 1998; Wagner et al., 2001; Richter et al., 2002; Van Roozendael et al., 2002; Theys et al., 2011)

Ground : 1-3 x10^{13} molec cm^{-2}
(Hendrick et al., 2007; Theys et al., 2007; Coburn et al., 2011; Coburn et al., 2014, in prep.)

Balloon: 0.2-0.3 x10^{13} molec cm^{-2}
(Pundt et al., 2002; Schofield et al., 2004, 2006; Dorf et al., 2008)

Models: 0.2-1.0 x10^{13} molec cm^{-2}
(Saiz Lopez et al., 2012; Parrella et al., 2012) – in the tropics



Theys et al. [2011]

Halogens deplete the O_3 column by ~10% in the tropics (Saiz-Lopez et al., 2012)

~0.2-0.5 ppt BrO, and <0.1 ppt IO **Parrella et al. [2012]**

Trace Organic Gas Analyzer (TOGA)

VOCs: NMHCs (C3-C10), OVOCs (C2-C9), HVOCs

High selectivity GC/MS
2 minute continuous analyses of 50 VOCs
Semi-autonomous operation up to 50,000 ft
TORERO, DC3

TOGA on GV aircraft

Eric Apel
Alan Hills
Becky Hornbrook
Dan Riemer (U Miami)

Instrument designed to have very low limits of detection (low – sub pptv)

CU AMAX - DOAS

Volkamer group

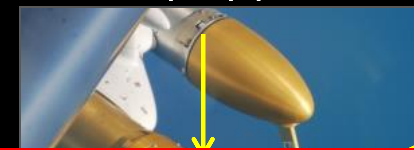
Parameters measured by CU AMAX-DOAS	Detection limit* / Accuracy
BrO	0.3 ppt **
IO	0.05 ppt
HCHO	100 ppt
CHOCHO	3 ppt
H_2O	5 ppm (590nm)
NO_2	10 ppt
OClO	0.7 ppt
HONO	12 ppt
Aerosol extinction from O_4 at 360, 477, and 577nm	0.01 - 0.03 km^{-1}

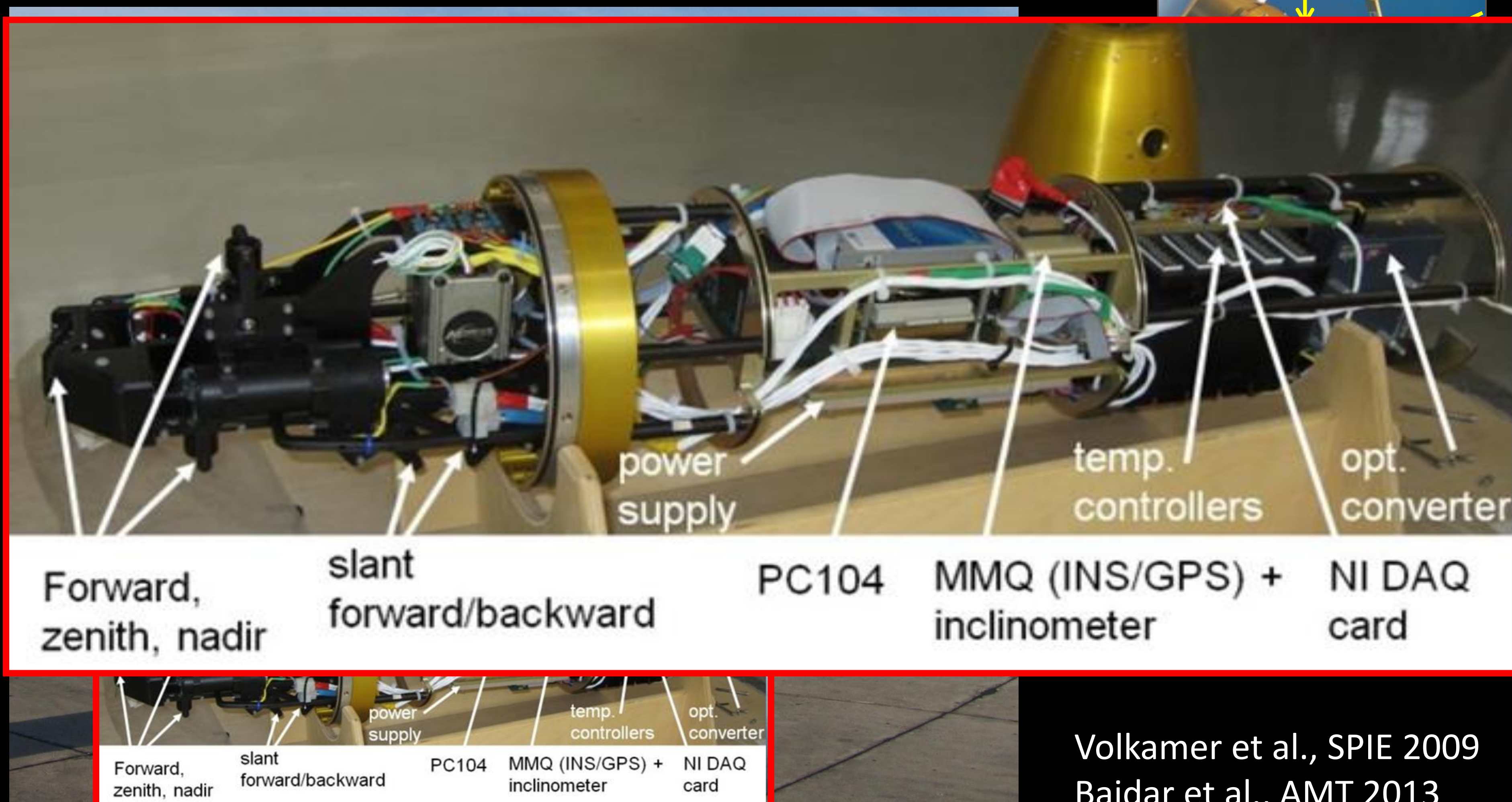
* 30 sec; ** 60 sec integration time

CU-AMAX-DOAS instrument aboard NSF/NCAR GV

University of Colorado Airborne Multi-AXis Differential Optical Absorption Spectroscopy

Telescope pylon

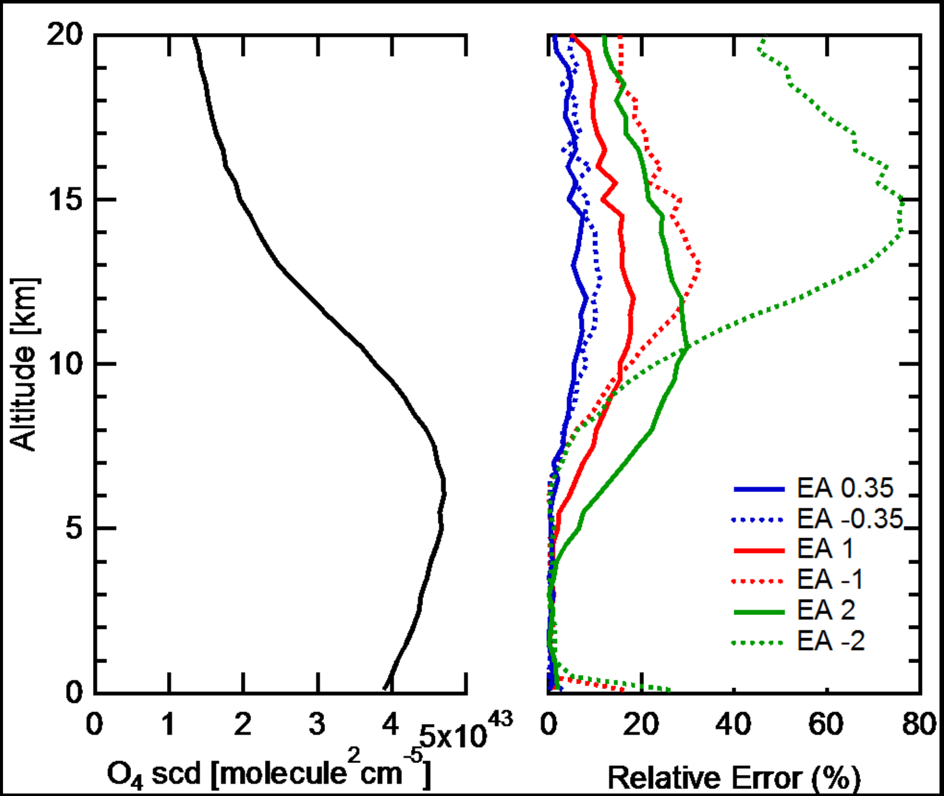


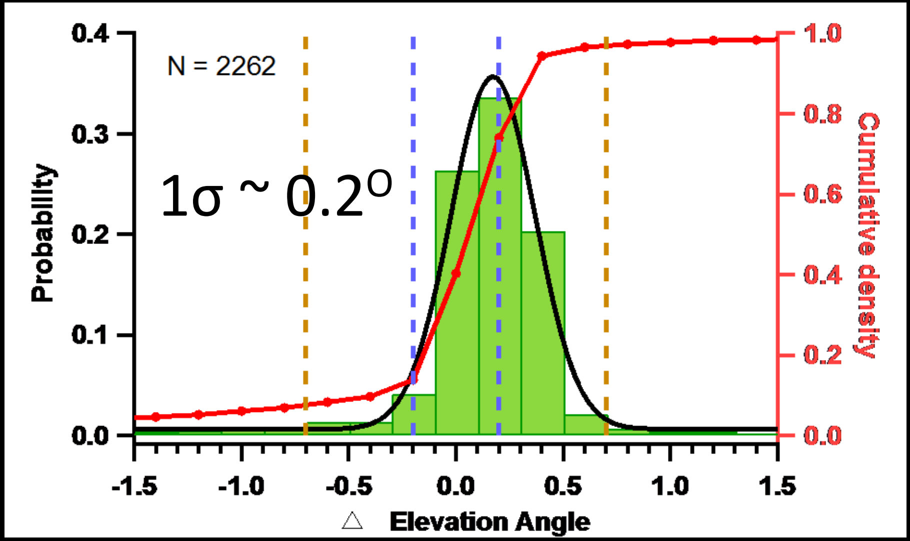


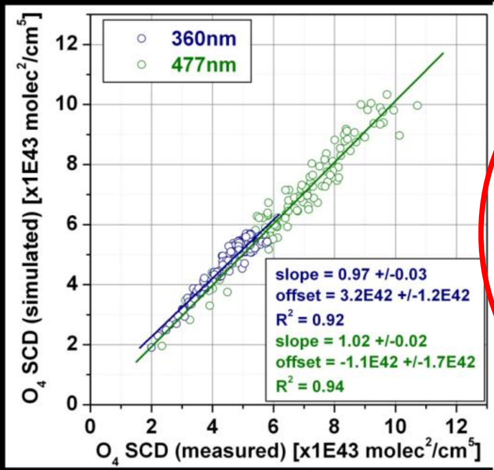
Volkamer et al., SPIE 2009
Baidar et al., AMT 2013

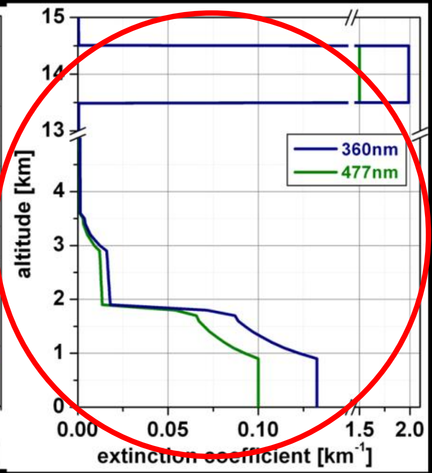
Confirmation of excellent motion control

Technological innovation:
Motion stabilization & low RMS





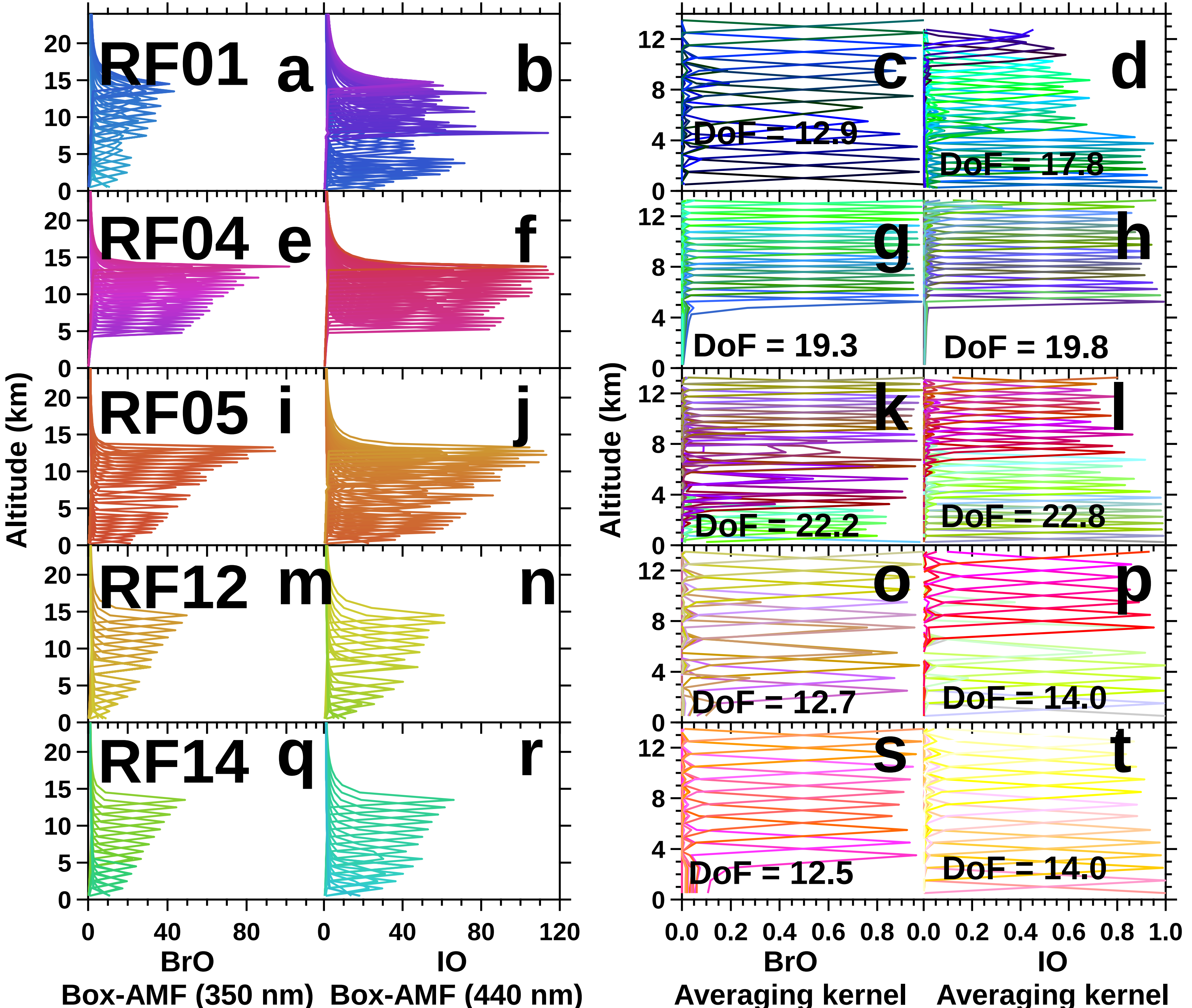




⇒ O_4 observations in a Rayleigh atmosphere & GV C-migit sensor
⇒ Trace gases and aerosol extinction profiles

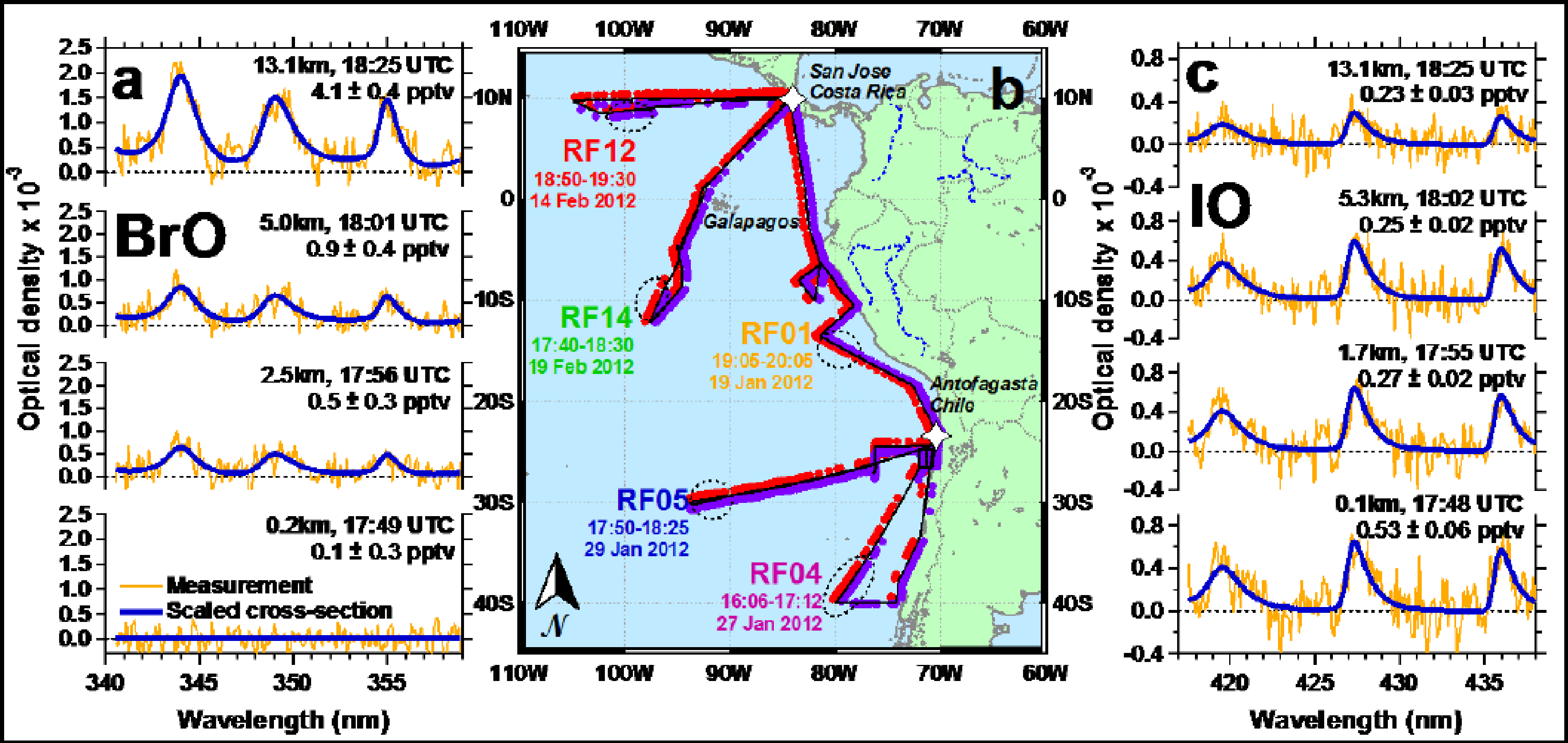
Baidar et al., 2013 AMT

Dix et al., 2013 PNAS



RF01
a
b
c
d
DoF = 12.9
DoF = 17.8
RF04
e
f
g
h
DoF = 19.3
DoF = 19.8
RF05
i
j
k
l
DoF = 22.2
DoF = 22.8
RF12
m
n
o
p
DoF = 12.7
DoF = 14.0
RF14
q
r
s
t
DoF = 12.5
DoF = 14.0
Altitude (km)
Altitude (km)
BrO
Box-AMF (350 nm)
IO
Box-AMF (440 nm)
BrO
Averaging kernel
IO
Averaging kernel

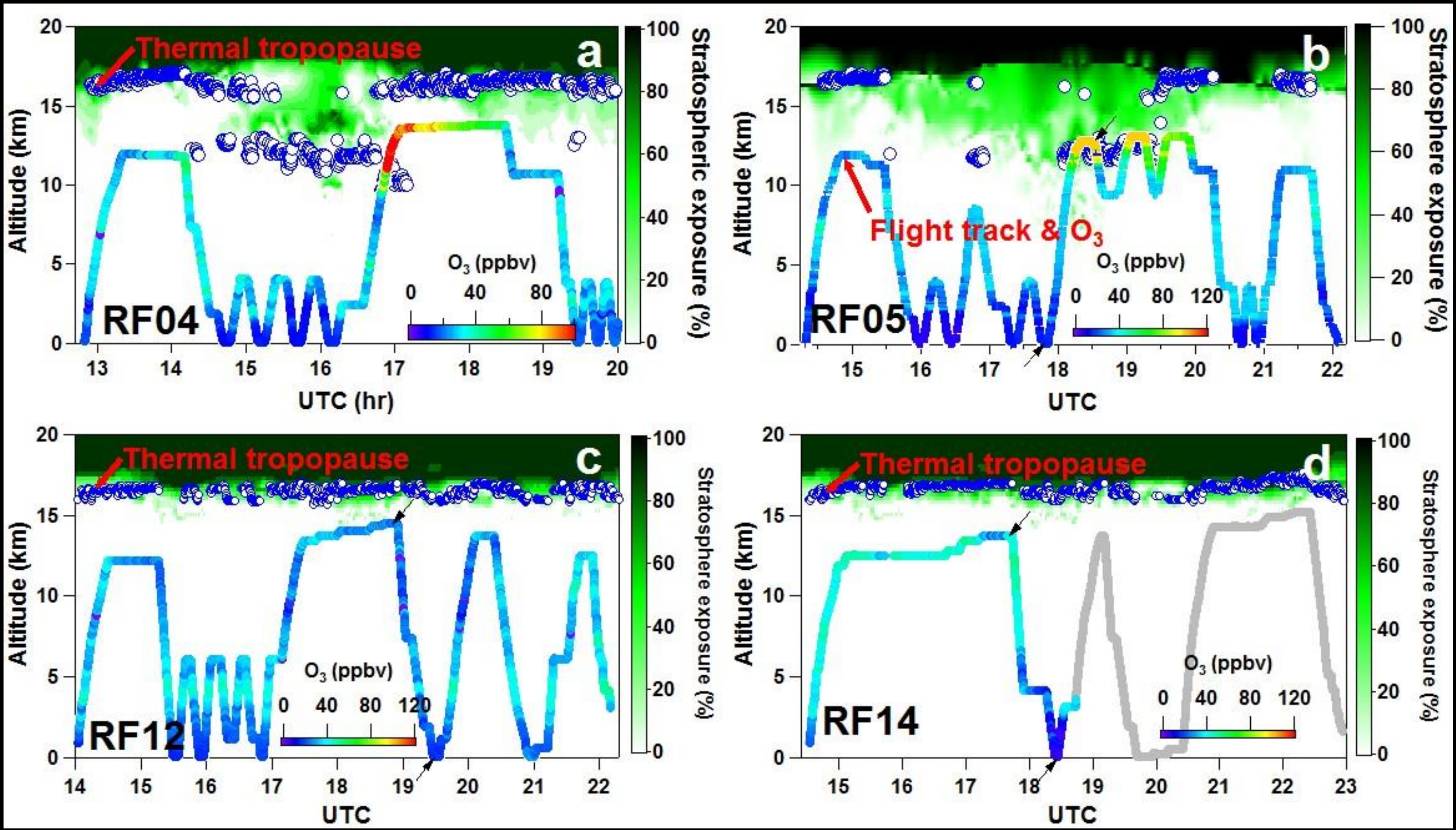
BrO and IO detection SH tropical troposphere



- NH/SH tropics: $(1.5 \pm 0.3)\ x10^{13}$ molec cm^{-2}
- SH sub-tropics: $(1.7 \pm 0.3)\ x10^{13}$ molec cm^{-2}
- SH mid-latitudes: $(1.0 \pm 0.3)\ x10^{13}$ molec cm^{-2}

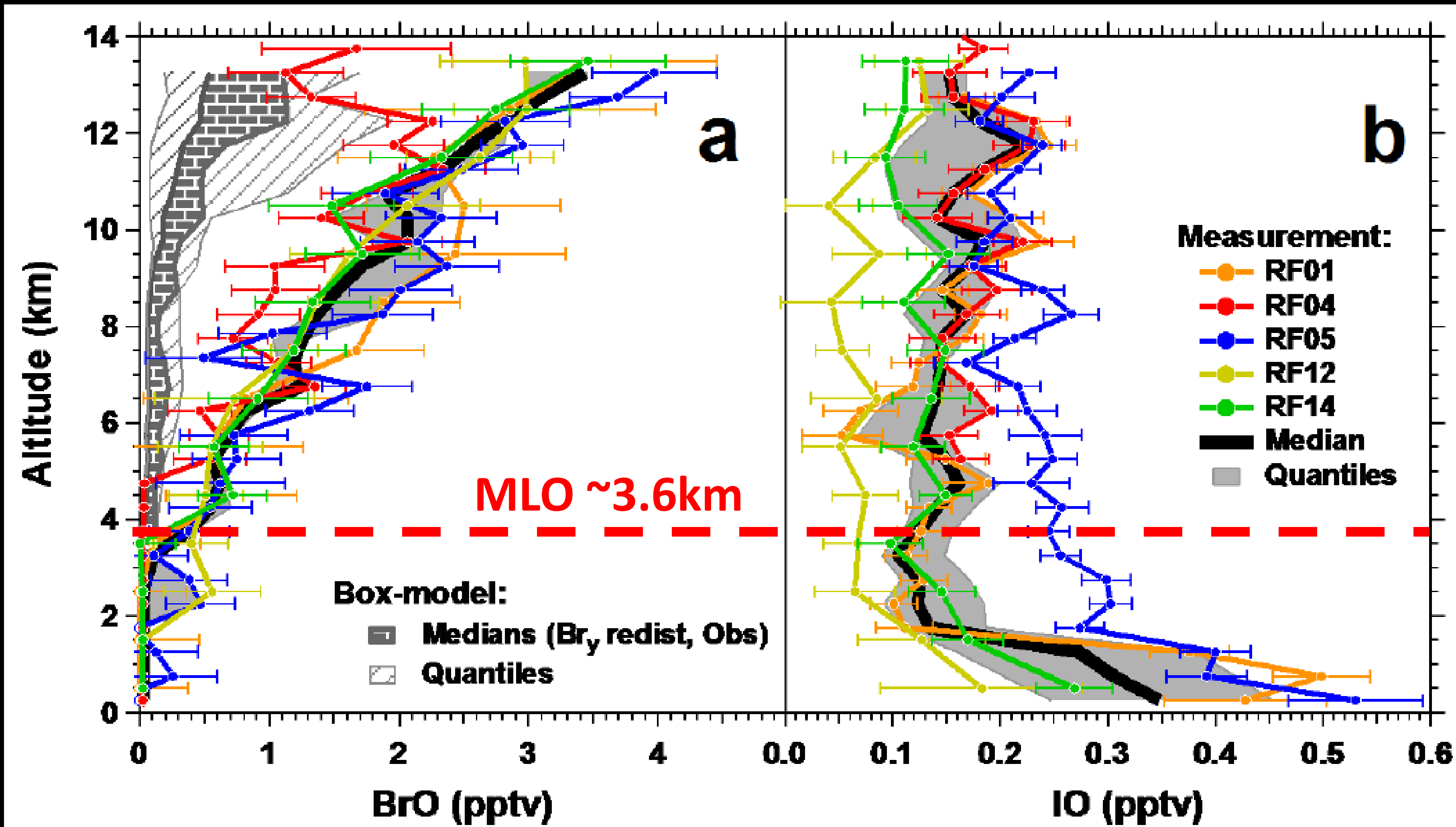
Double tropopause & tropical flights

SH mid-latitudes | SH subtropics



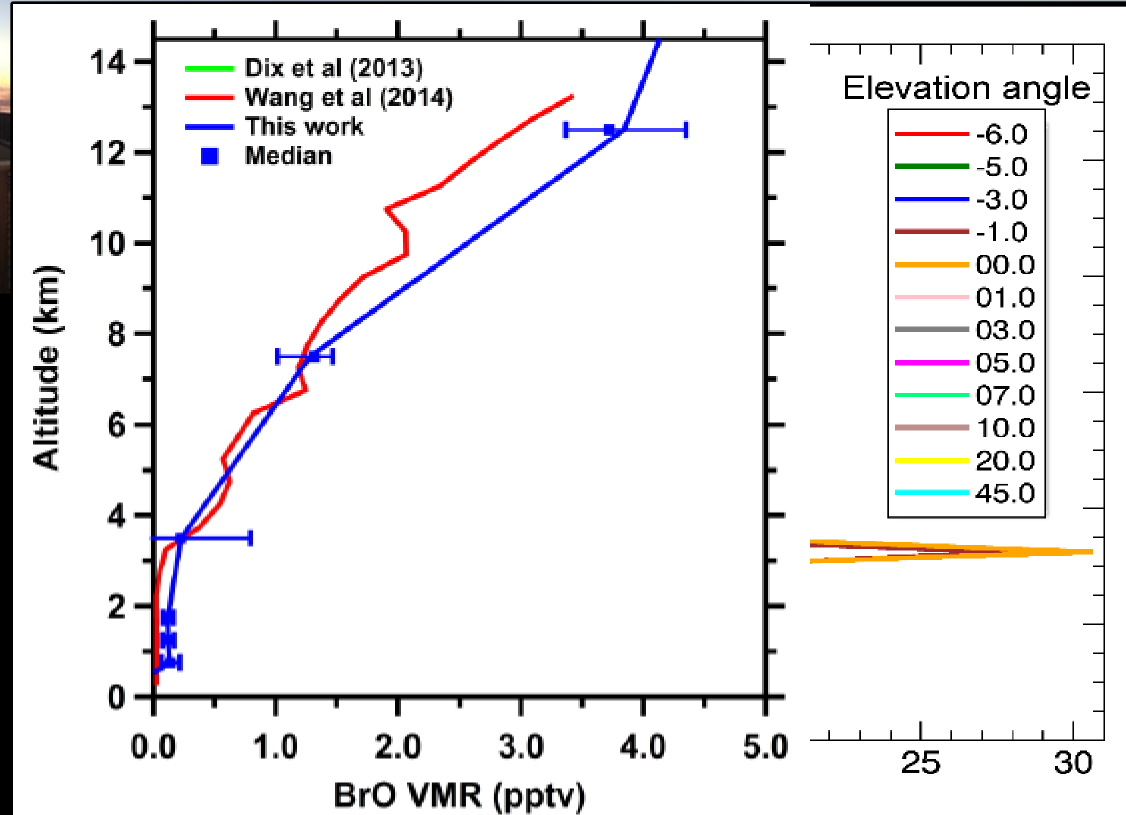
SH tropics | SH tropics

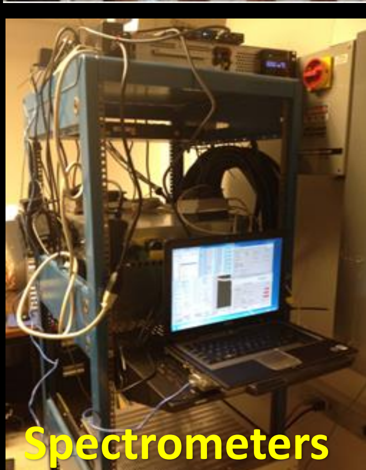
Vertical profiles & comparison with models



- GEOS-Chem: underestimates BrO by a factor 2-4
- Box-model (organohalogens, aerosol SA) -> even less BrO

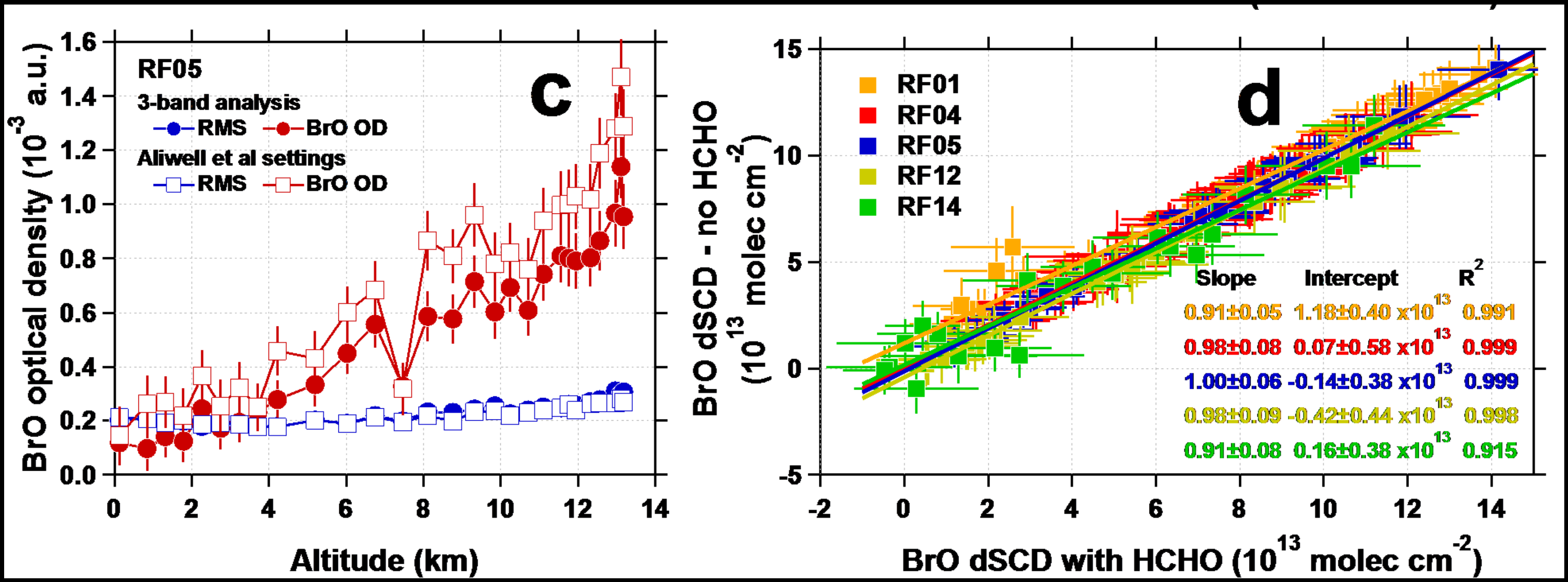
Mauna Loa Observatory, Hawaii





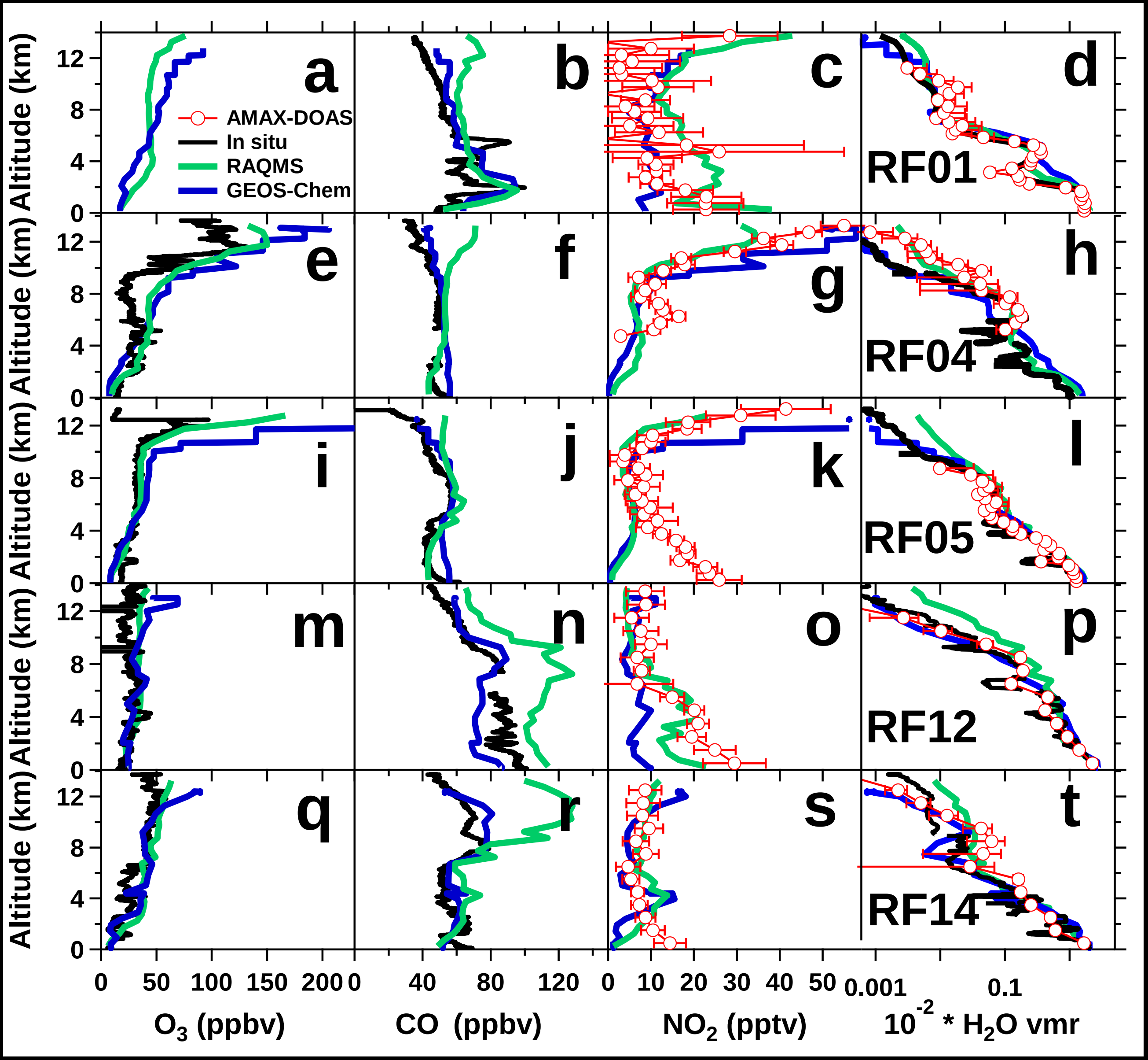
Parameters	Detection Limit	Figures of Merit
BrO IO HCHO CHOCHO NO_2 Extinction (360, 477, and 560nm)	0.3 ppt 0.05 ppt 100 ppt 3 ppt 10 ppt 0.01-0.03 km^{-1}	• 60s integration time • Full scan: 27 min • Footprint: 20-80km depending on aerosol load and wavelength • Vertical profiles: ~3DoF

Robustness of the BrO dSCD retrievals

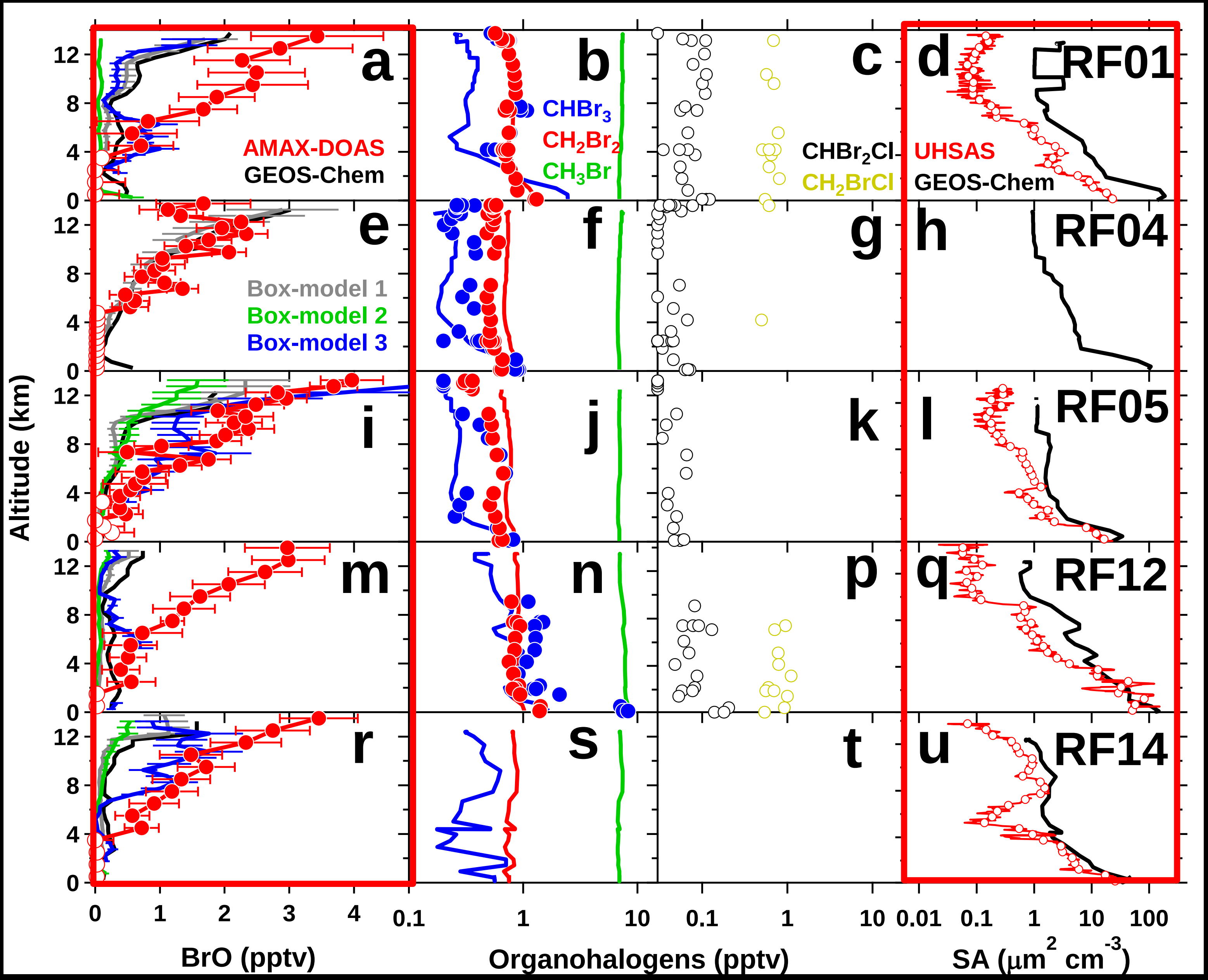


- References: consistent dSCD offset between different geometries
- MBL limb, zenith, -10EA reference contain variable amount of Ring
- BrO in MBL: no evidence in our spectra (upper limit ~ 0.5 pptv)
- BrO fit settings: 3-band analysis; BrO is conservatively bound
- Including/excluding HCHO has no effect on BrO dSCDs

Decoupling the stratosphere & RTM

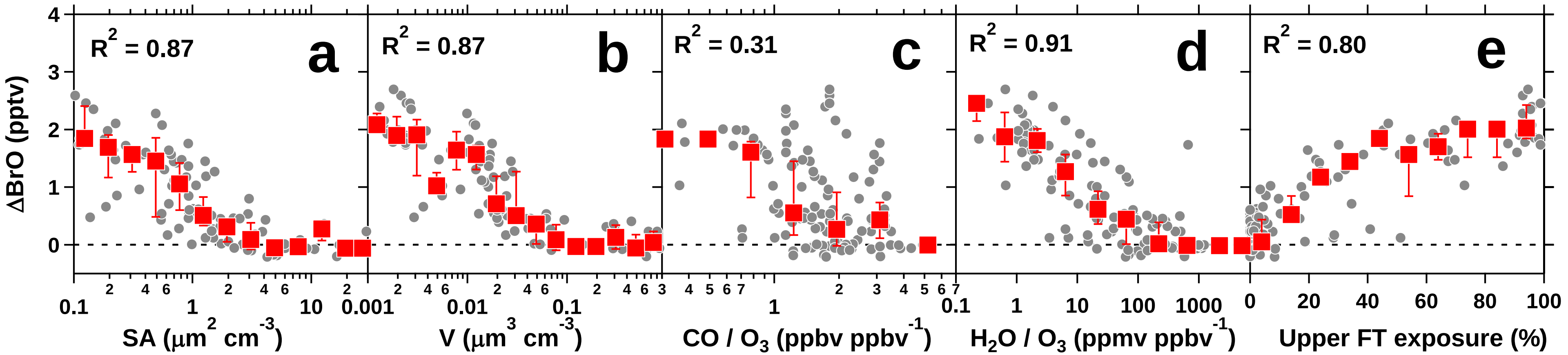


Sources from multiphase chemistry, organo halogens

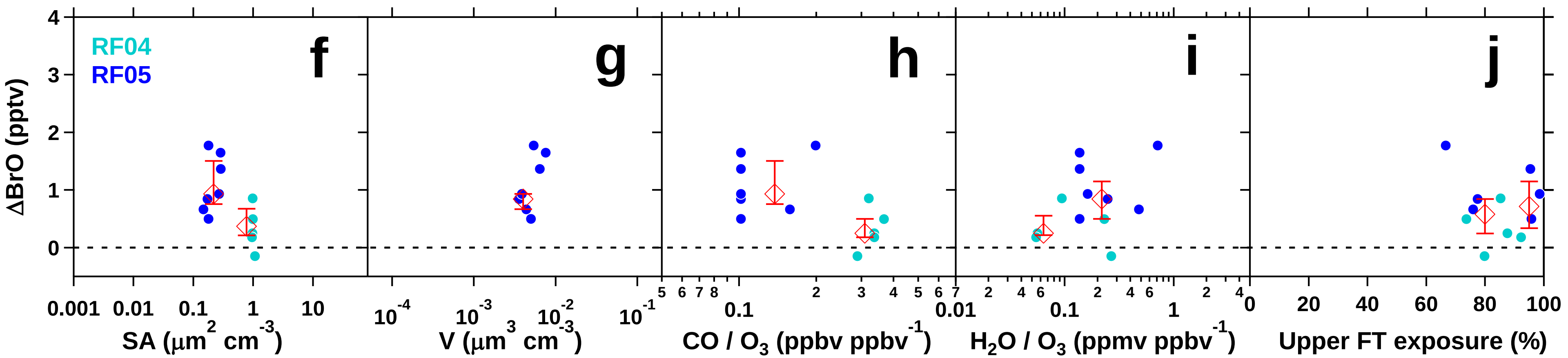


ΔBrO (unexplained BrO) – correlations

Tropospheric air

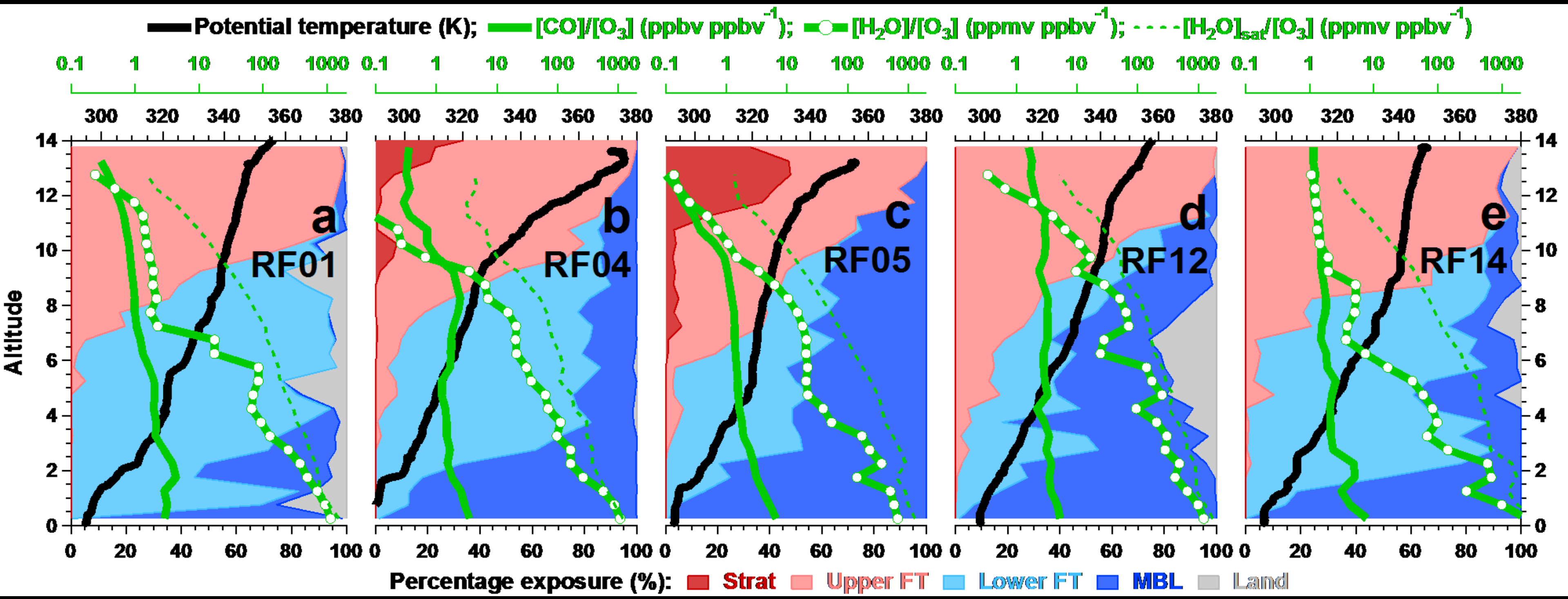


Lower stratospheric air



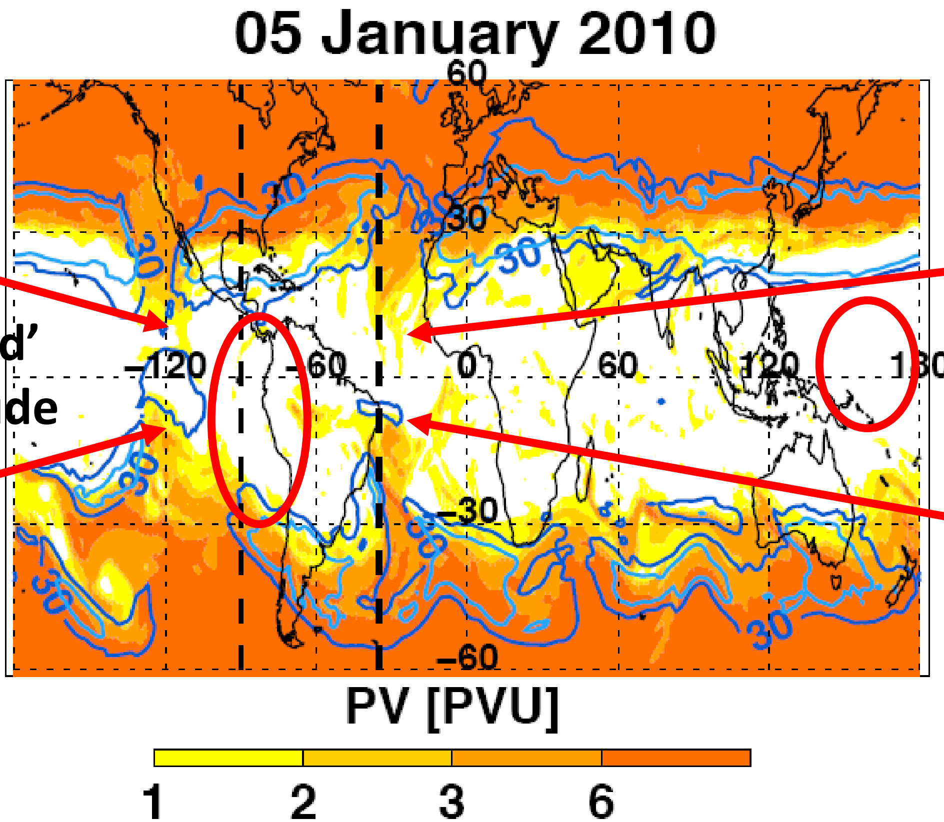
- Unexplained BrO in the upper tropical FT:
  - correlates with uFT exposure, decreasing H_2O/O_3 ratios (stratospheric tracer)
  - Is anticorrelated with aerosol SA
  - BrO in the lower stratosphere seems further to be underestimated

Influences from mid-latitude lower stratosphere on the tropical upper free troposphere?



- Potential temperature profiles
- CO/O_3 ratio profiles
- H_2O/O_3 ratio profiles

UTLS evidence for persistent forcing of mid-latitude lower stratopsheric air into the upper tropical troposphere



Tropics 'closed'
120W longitude

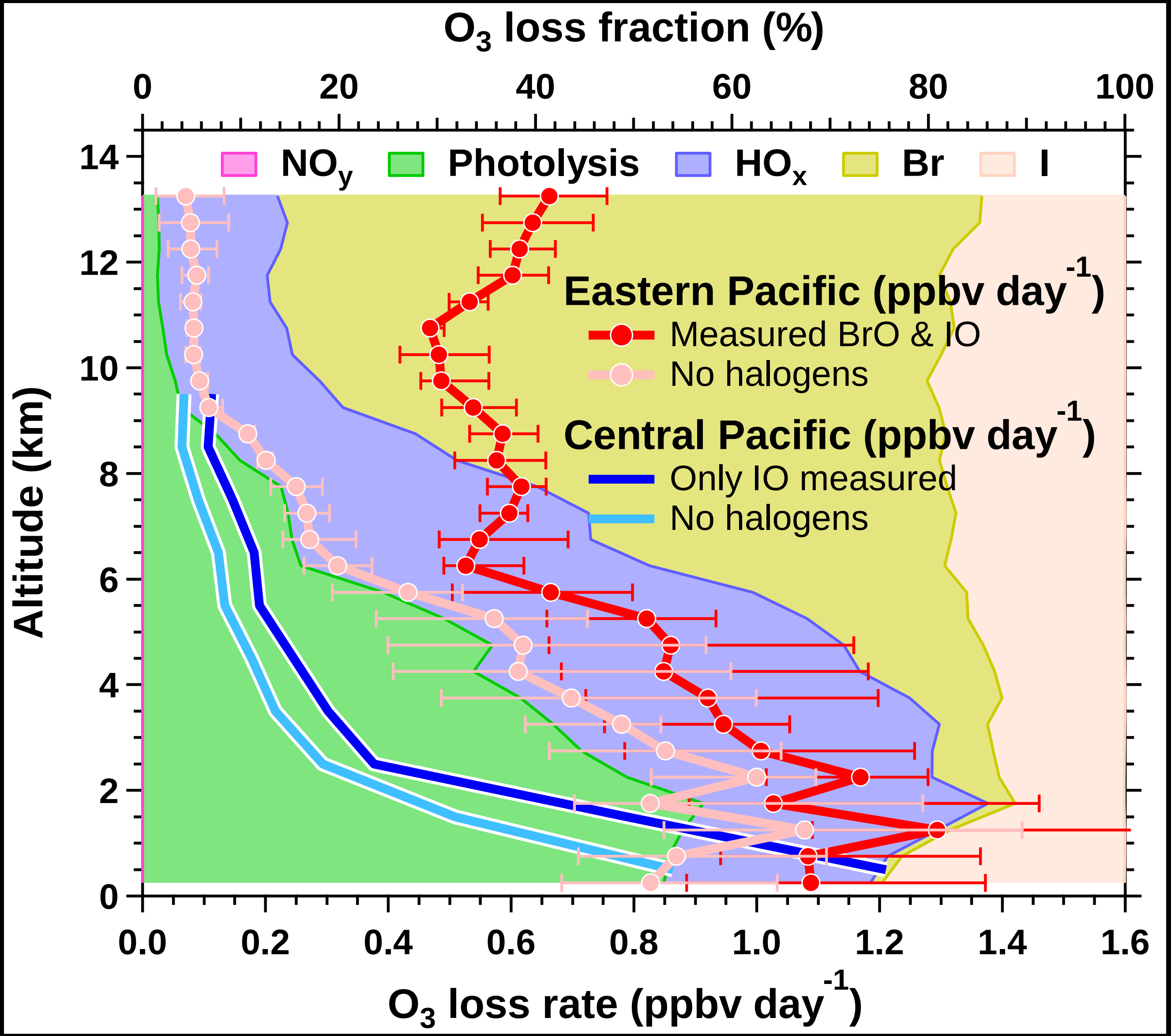
Tropics 'closed'
30W longitude

Figure 8: GFS model analysis of potential vorticity (orange filled contours) and wind speed (blue contours, 30 and 40 m/s) at 150 hPa on 5 January 2010 at 12 Z. Dashed lines indicate the locations of the cross sections shown in Figures 6 and 7.

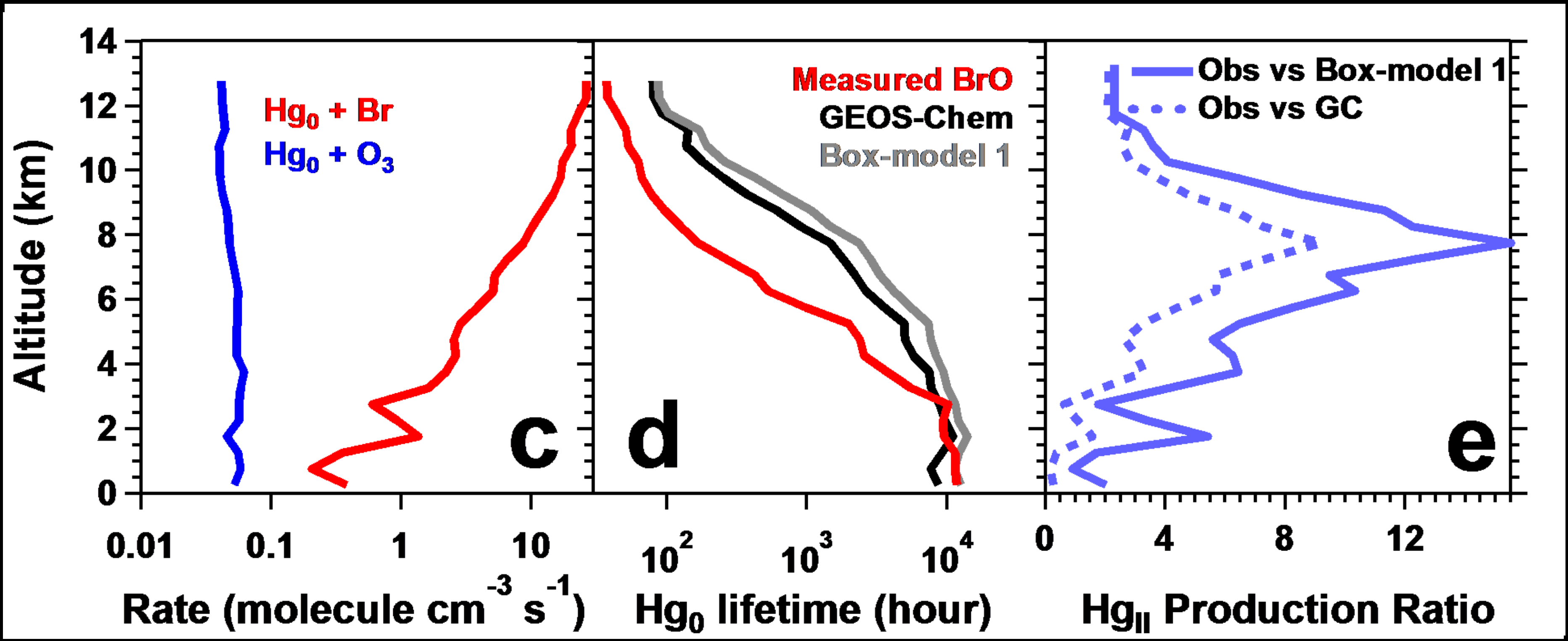
Waugh and Polvani, 2000, GRL

Munchak & Pan, 2014, JGR *in press*

Relevance for O_3 loss rates



Relevance for HO_x and mercury



- Halogen chemistry: reduction in O_3 is ~8 times stronger than secondary OH source → CH_4 lifetime?
- Our measurements constrain the mercury lifetime, and suggest mercury is oxidized faster, and at lower altitudes than current models suggest

Conclusions

- *First limb-observations of BrO and IO in the tropics*
- *BrO is detected regularly above 2-4 km; BrO and IO are abundant throughout the air column*
  - *Consistent with the GOME-2 satellite, ground-based MAX-DOAS data (Theys et al., 2011)*
  - *~8 times higher than direct-sun profiles (Dorf et al.)*
  - *~2-4 times more than predicted by models*
  - *BrO in the lower stratosphere seems slightly higher than predicted*
- *Measurements support ~6-10 pptv Br_y in the tropical UTLS*
- *Do global chemistry models accurately represent the persistent forcing of extratropical lower stratospheric air into the upper tropical free troposphere?*

Funding: NSF-CAREER award, NSF-AGS (TORERO)

Acknowledgements: NCAR/EOL, RAF, TORERO team