CU AMAX-DOAS measurements of BrO, IO and OVOC

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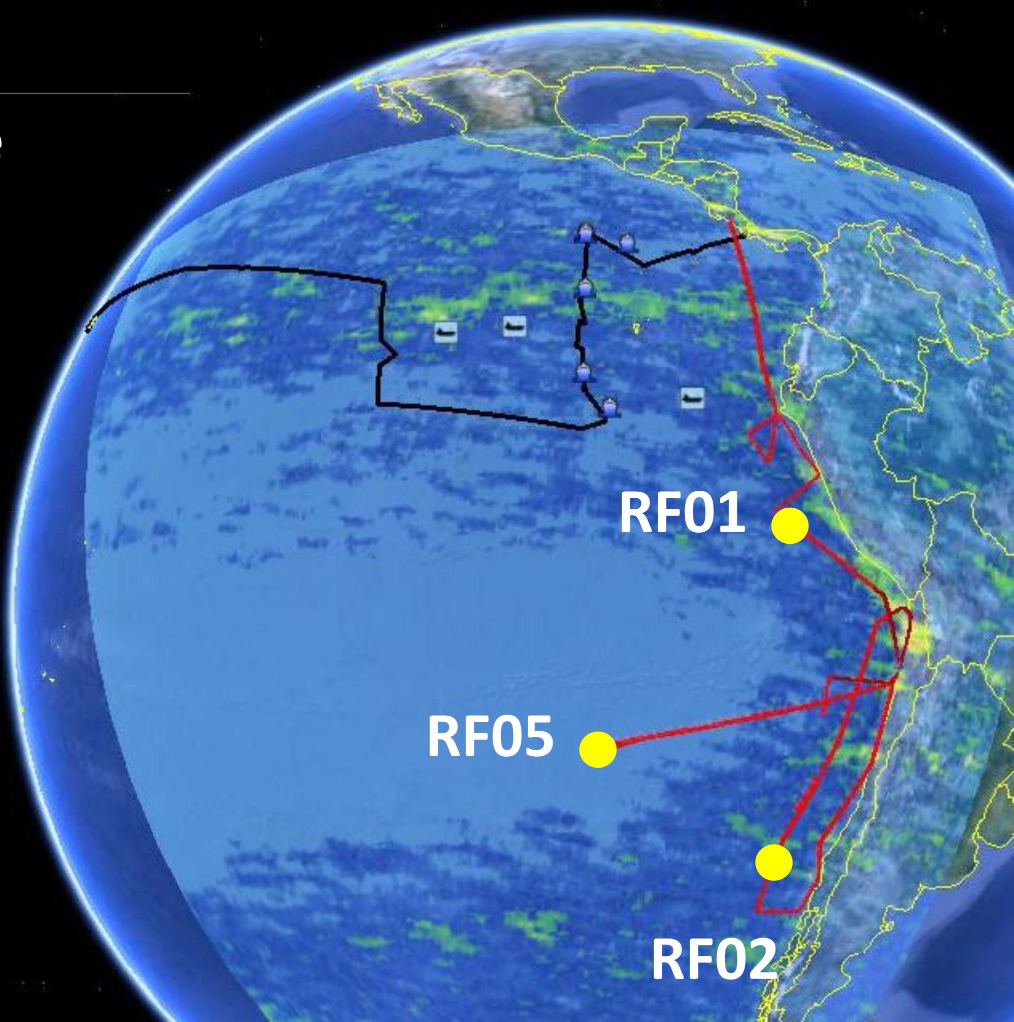
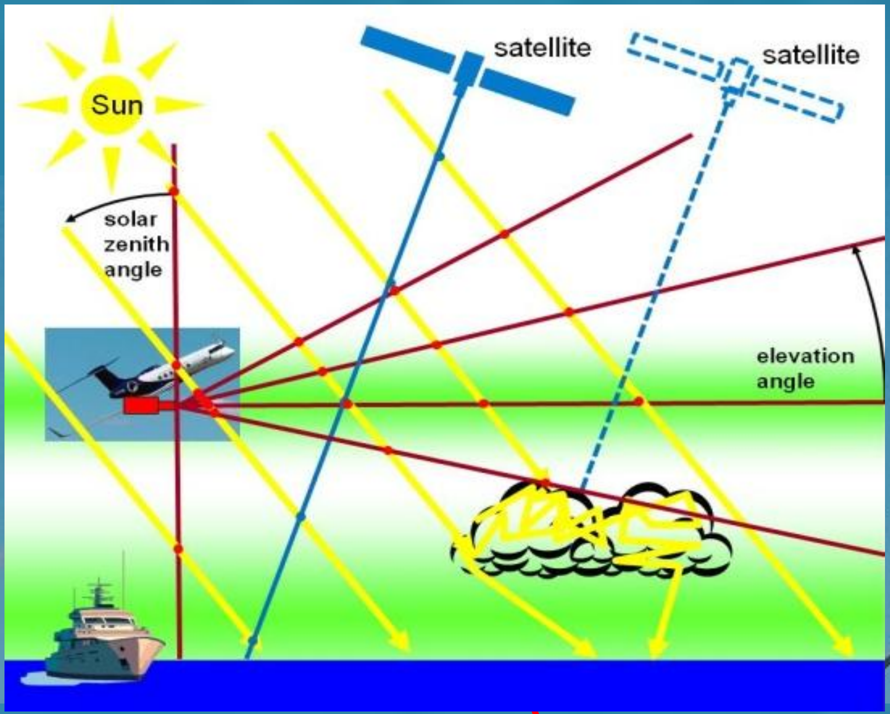
- CU AMAX-DOAS
  - Maximizing Signal-to-Noise
  - Real-time Motion Control
- Case studies: RF05, RF01, RF02
  - BrO / RAQMS
  - IO / Organohalides
  - CHOCHO / OVOC
- Relevance
  - OH- and Br-lifetime, Br recycling
  - Ozone, Mercury



CU Airborne Multi AXis-DOAS



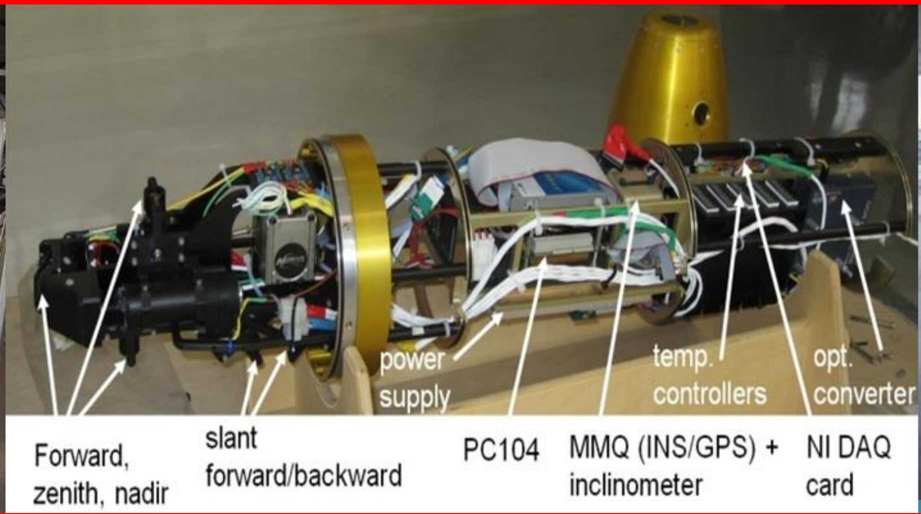
MAX-DOAS observations from ground, ship, and research aircraft: maximizing signal-to-noise to measure 'weak' absorbers

Rainer Volkamer*[ab], Sean Coburn[a], Barbara Dix[a], Roman Sinreich[a]

Volkamer et al., 2009, SPIE

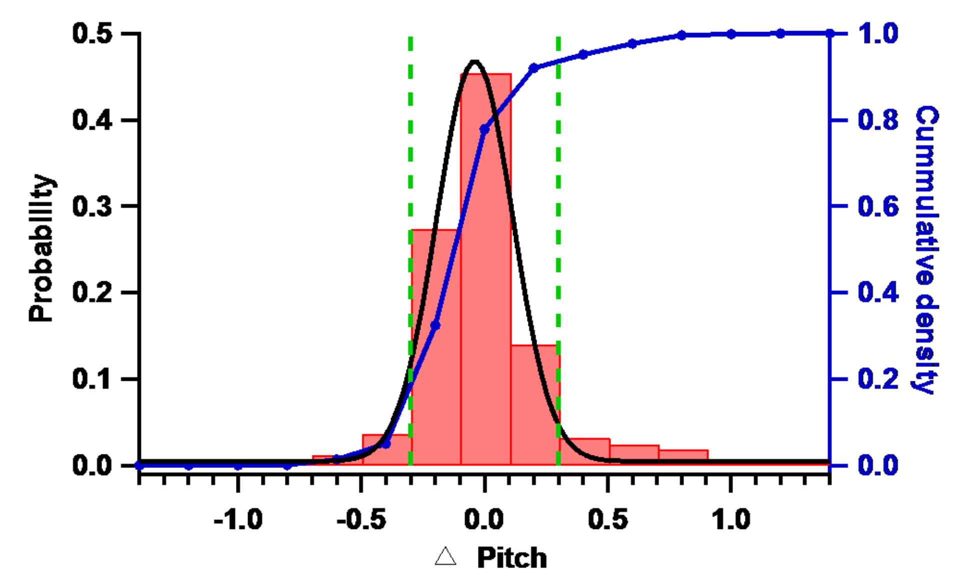
Parameters measured by CU AMAX-DOAS	Detection limit / Accuracy under FT conditions	Temporal / Spatial resolution
HCHO CHOCHO NO_2 HONO BrO IO OClO H_2O Aerosol extinction from O_4 at 360, 477, and 577nm	120 ppt 3 ppt 10 ppt 15 ppt 1 ppt 0.1 ppt 0.7 ppt 2 ppm 0.01 - 0.03 km^{-1}	Acquisition time: 2-30 sec Profile scan: 1-5 mins Vertical resolution: ~few 100m during ascent/descent; increases with distance from the plane at constant flight altitude. Horizontal fetch: UV: ~ 20km Vis: ~ 40km NIR: ~ 70km

CU AMAX-DOAS on NSF/NCAR GV during HEFT-10 RF#1 (29 Jan 2010)



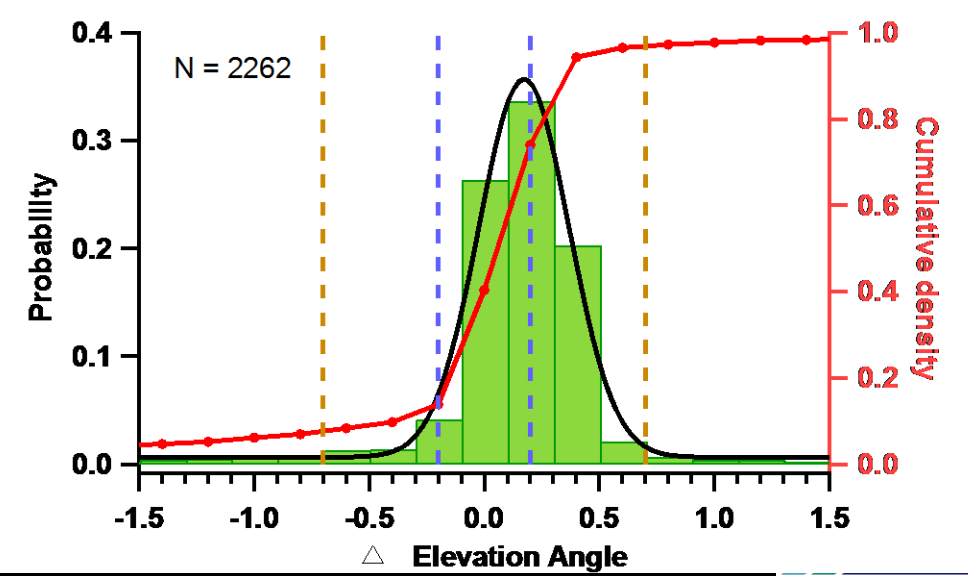
Technical Innovation

1 σ (0.16 degrees) < angle sensor accuracy (< 0.3 degrees)



1 σ (0.19 degrees) < motor encoder resolution (0.2 degrees)

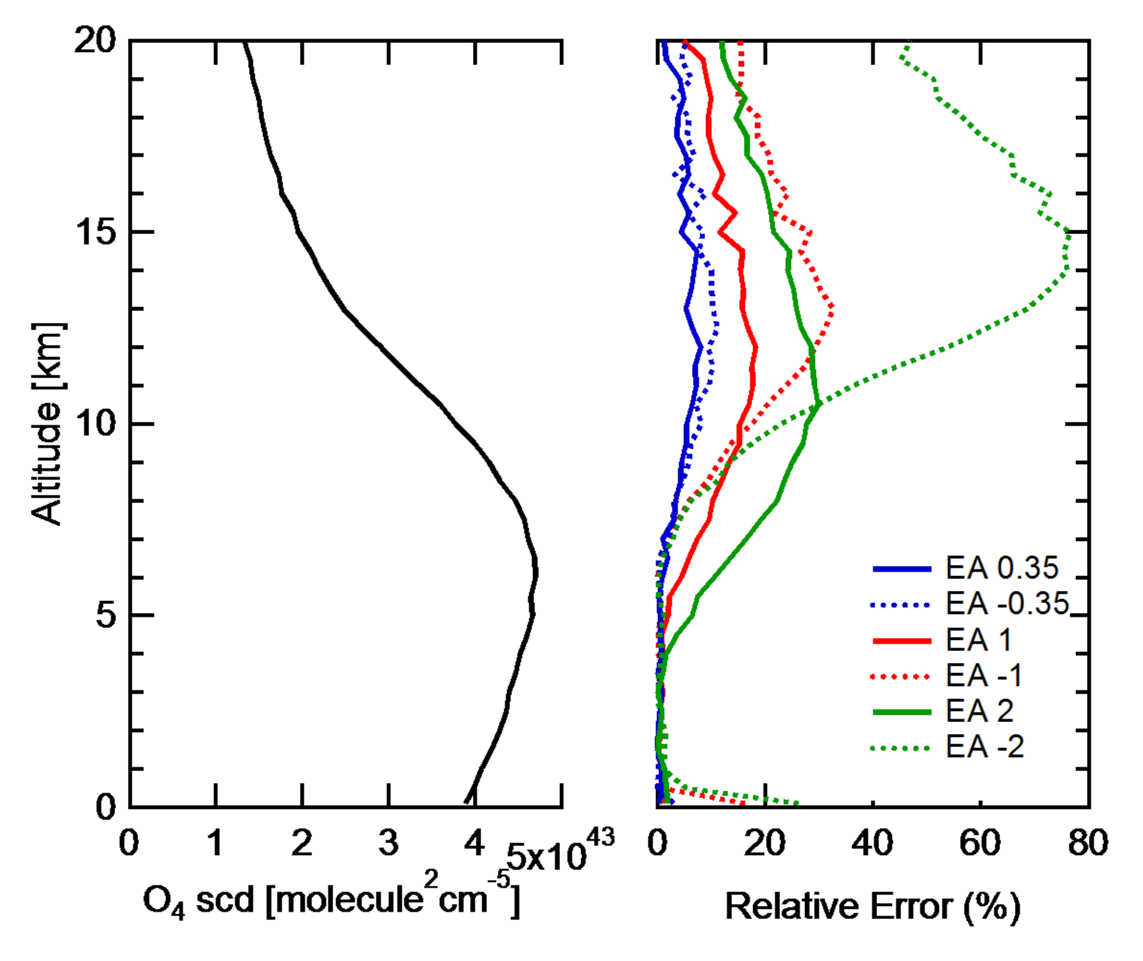
Overall angle accuracy < 0.35 degrees



University of Colorado
Boulder

CIRES

Relevance of angle uncertainty

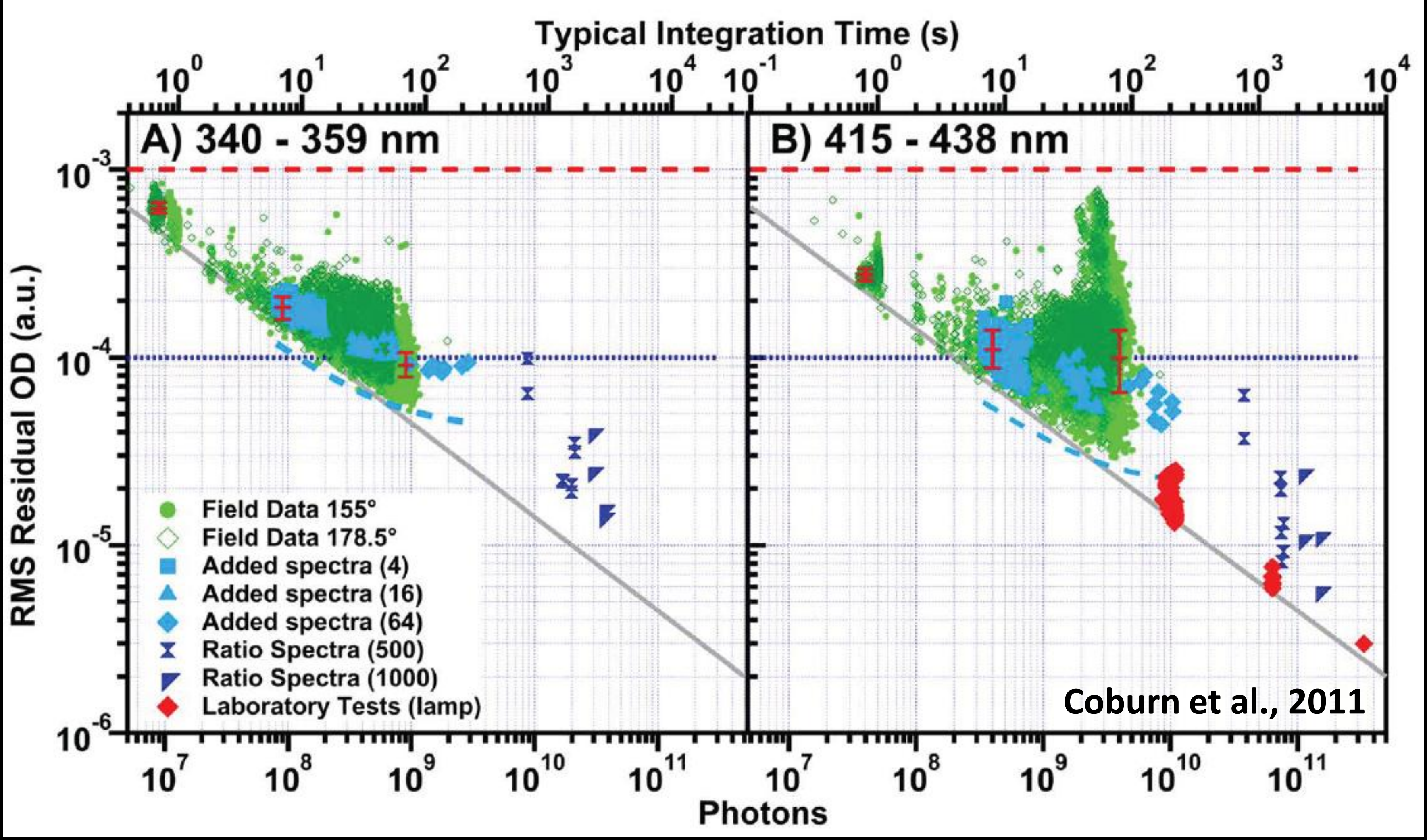


University of Colorado Boulder

Baidar et al., 2012, in prep.

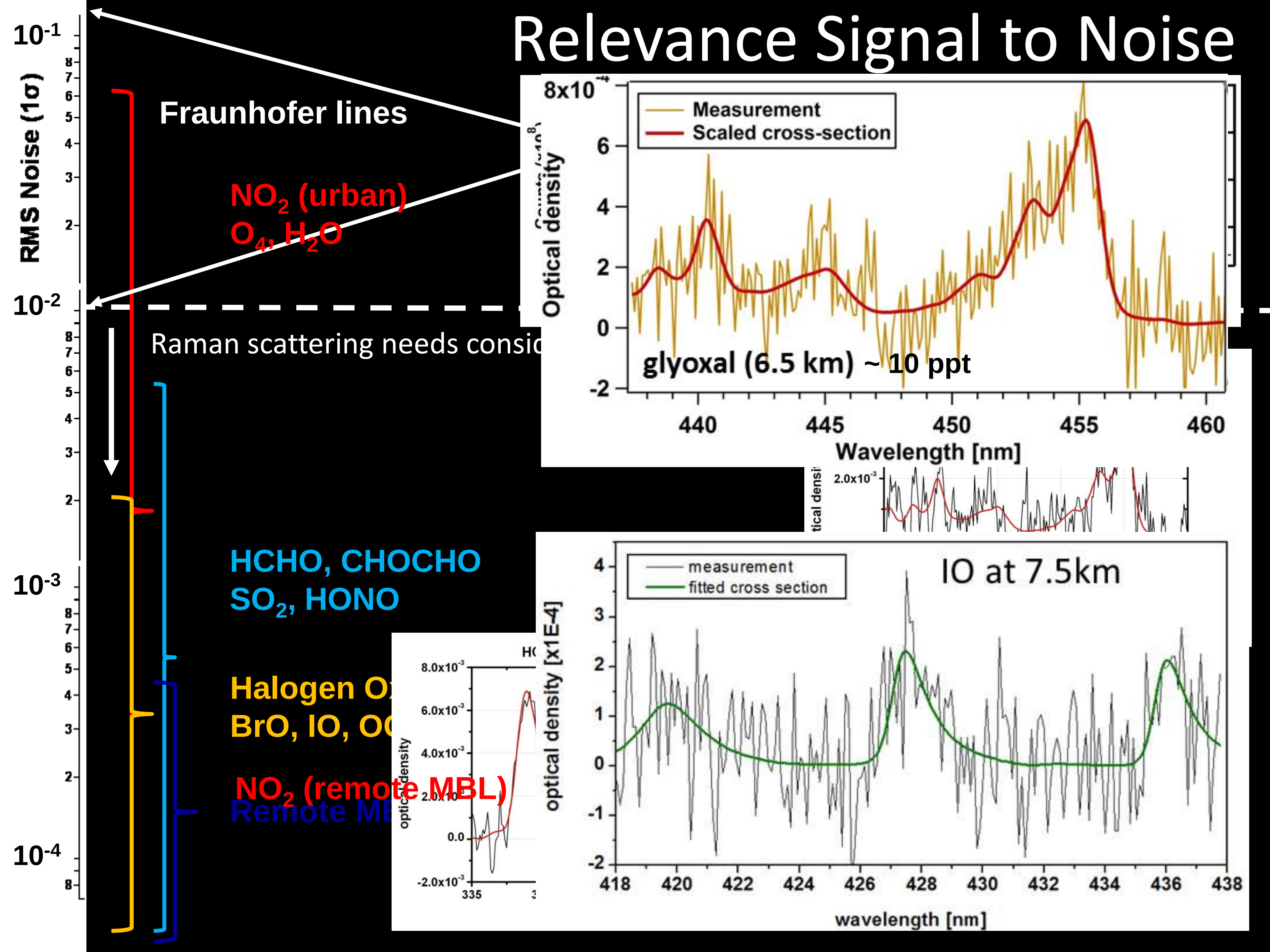
CIRES

Statistical Noise limit

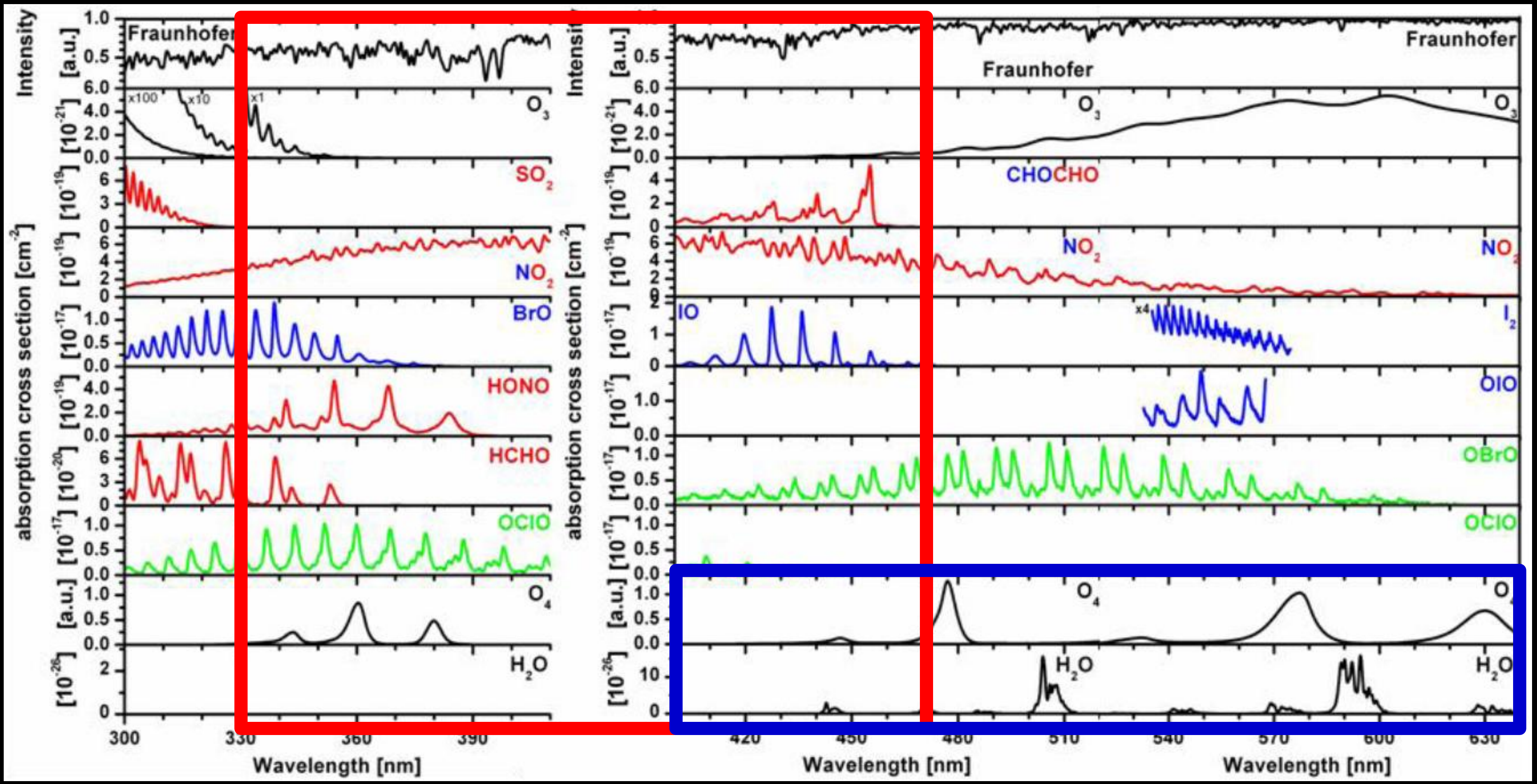


Photon shot noise limited RMS = 10^{-4} in ~10 sec @ 440nm

Relevance Signal to Noise

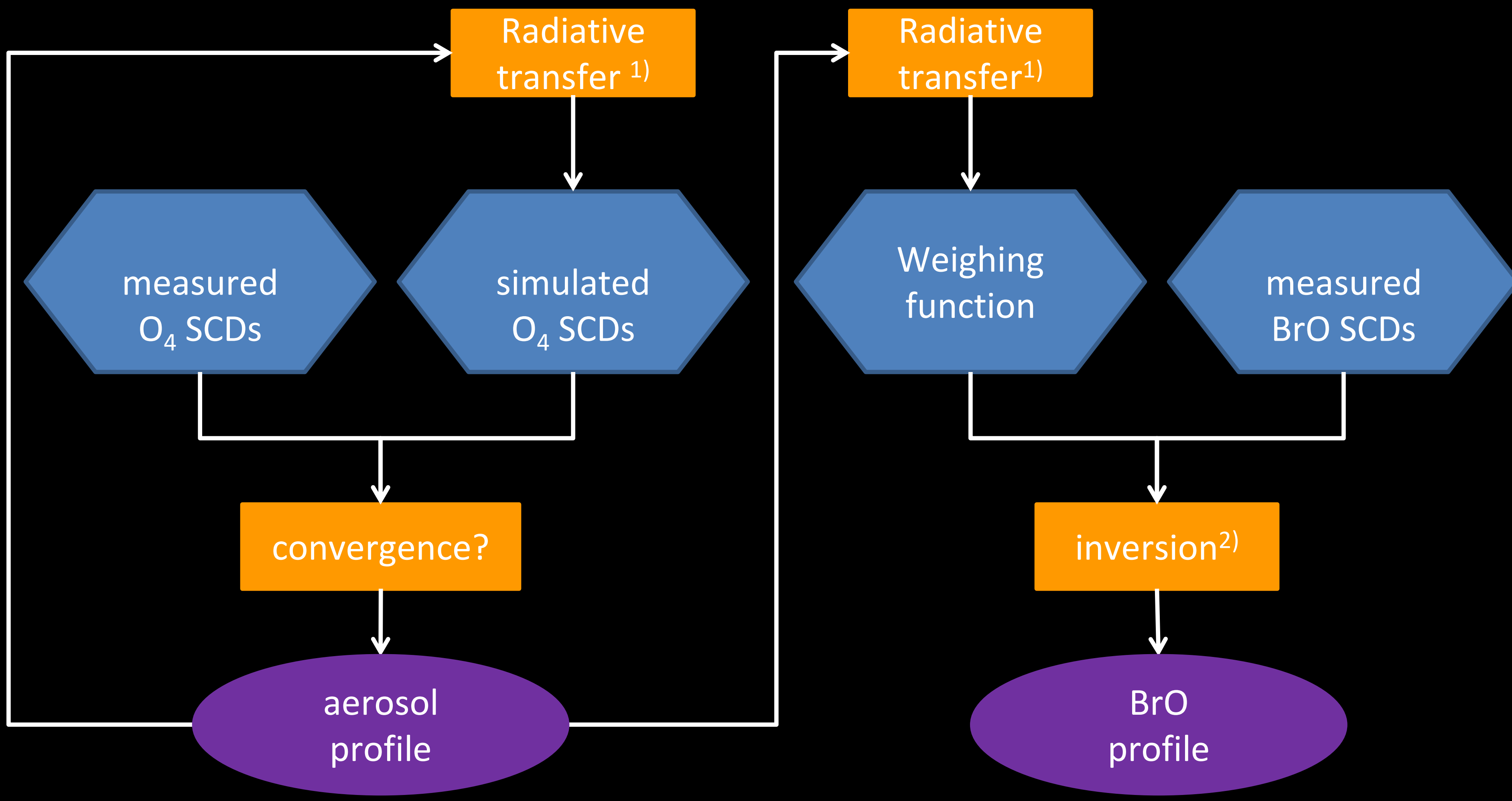


Trace gases and Aerosols simultaneously



- two synchronized CCDs; same telescope; narrow FoV;
- Vertical resolution limited by FoV to few 100m

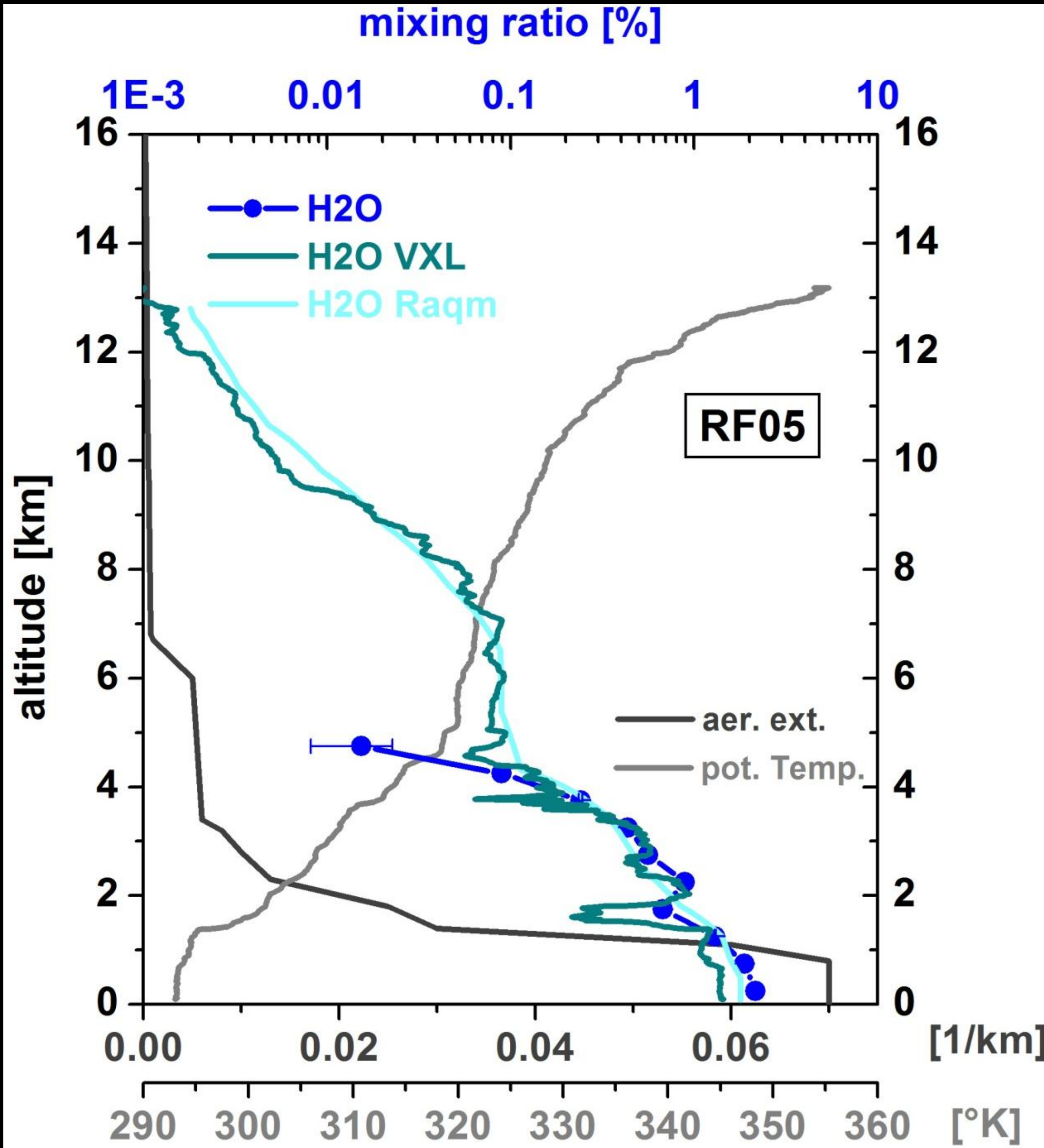
Vertical profiles: Non-linear Optimal Estimation



[1)] http://rtm.iup.uni-heidelberg.de/McArtim

[2)] Rodgers (2000)

Example: Inversion of water vapour

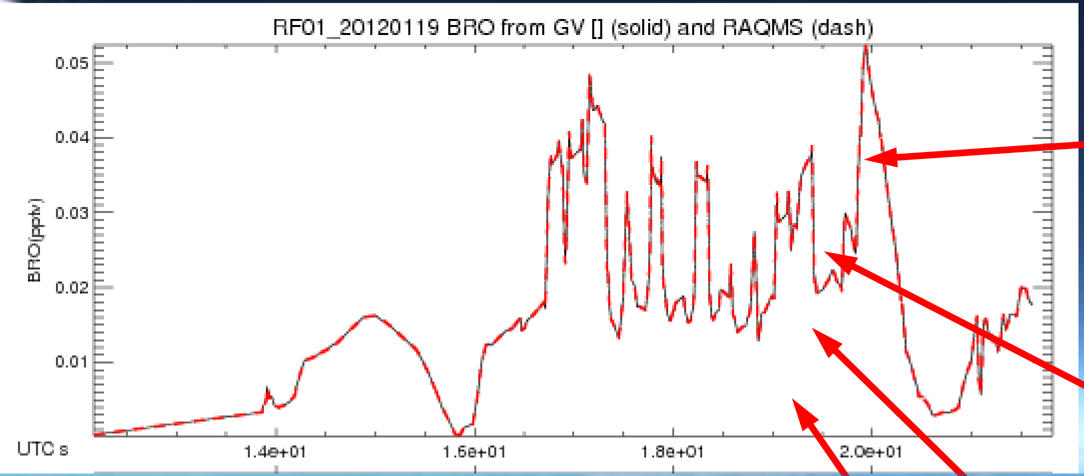


- Water @ 442nm
- Good agreement below 4km:
  - RAQMS
  - VCSEL
- Above 4km, use of a stronger water band, and refined a-priori estimates have unexplored potential

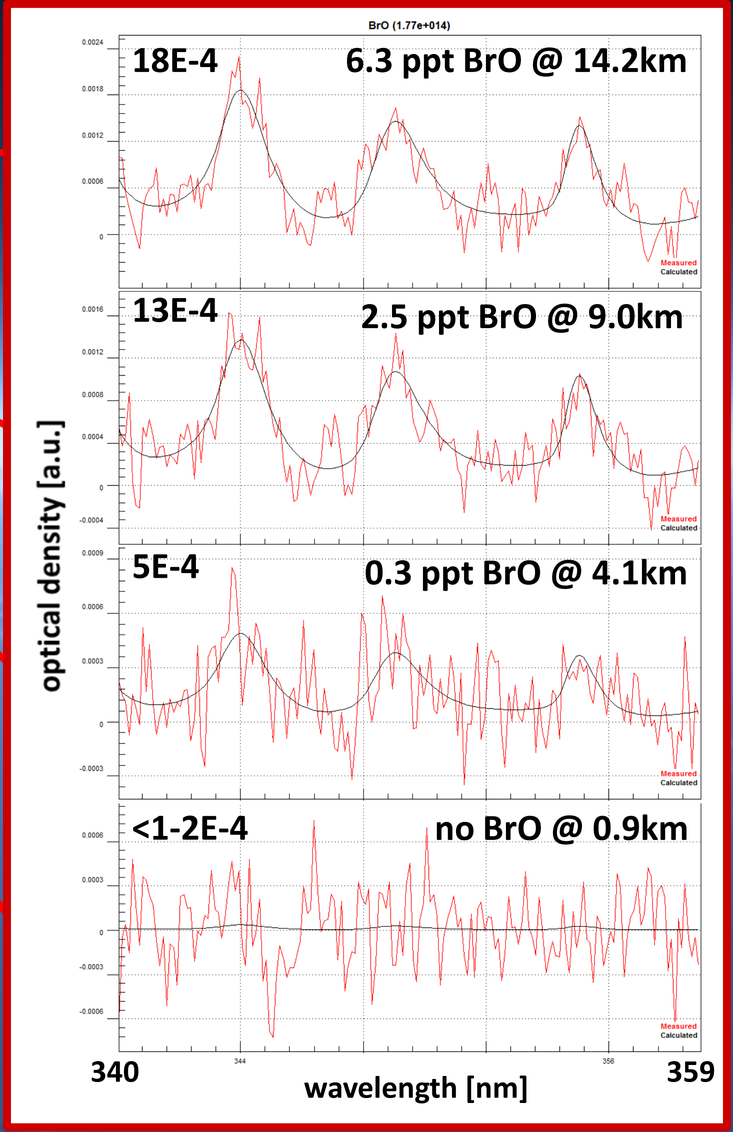
Picture break

Detection of BrO in the tropical FT

BrO predicted along RF01 flight track (RAQMS)



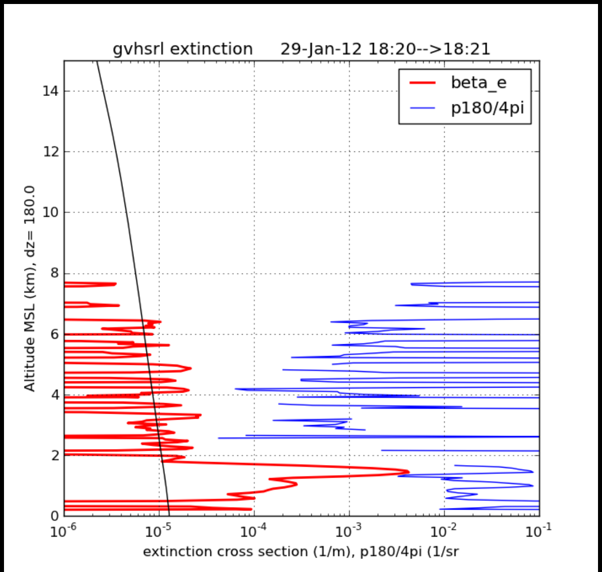
BrO measured by CU AMAX-DOAS

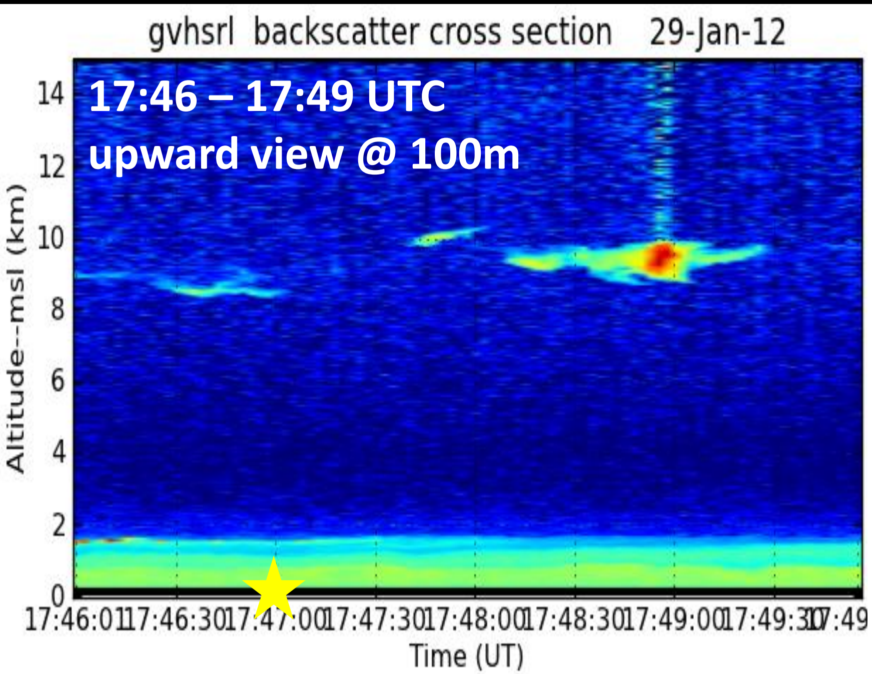


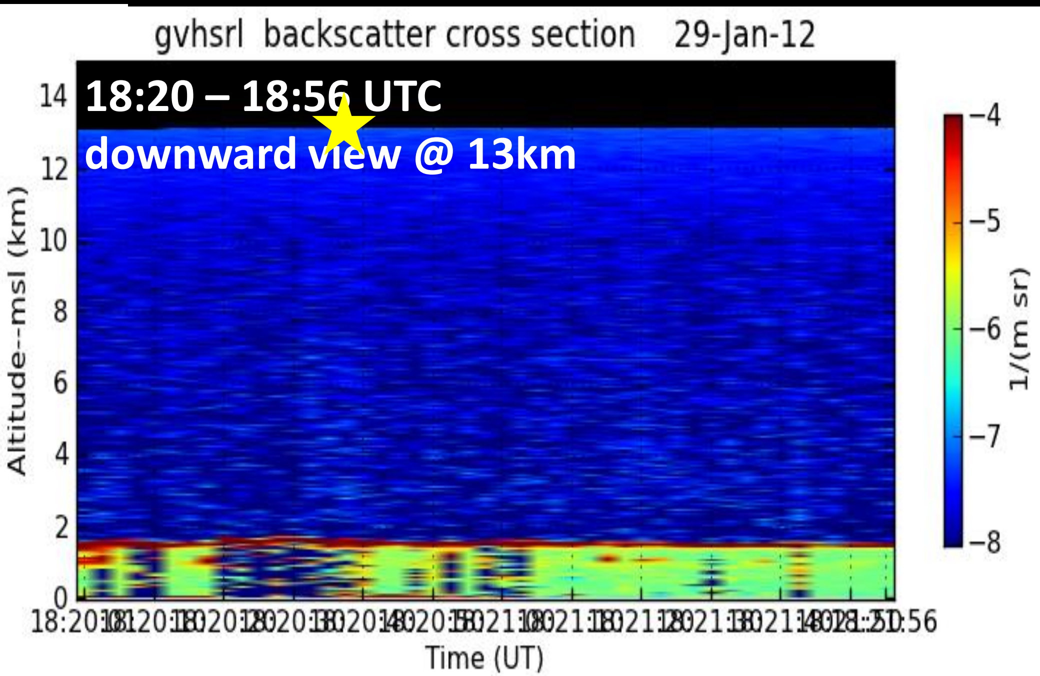
- BrO is detectable over most of the tropospheric air column
  - ~ 0.3 ppt BrO in lower FT (4.1km)
  - ~ 6.3 ppt BrO above 14km
- RAQMS predicted BrO < 0.05 ppt over the entire flight
- Timing of RAQMS BrO peak corresponds to peak BrO at altitude

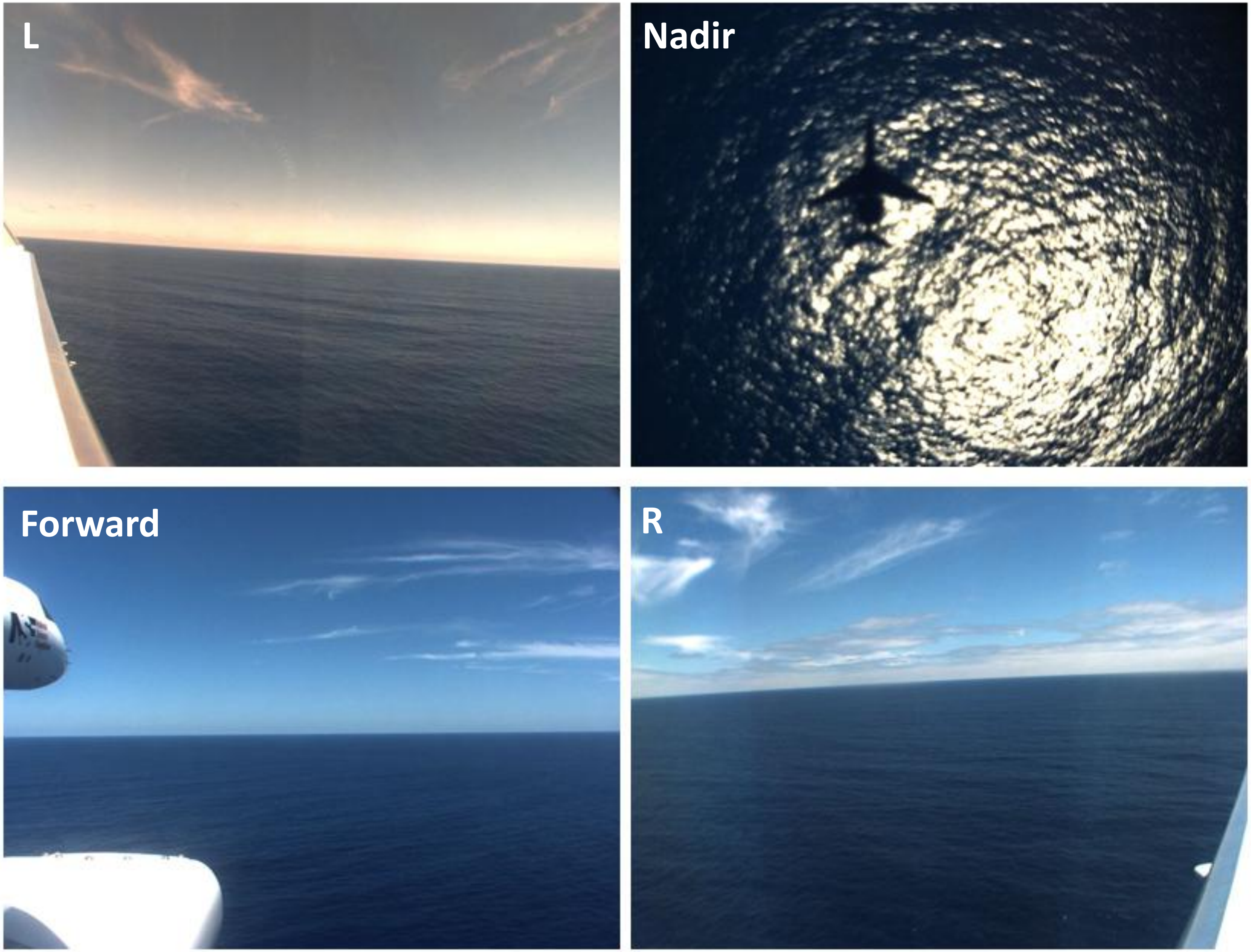
RF05, profile E: 1745-1829 UTC

- Aerosols:
  - below 1.8 km:
  - 2-6 km: near Rayleigh extinction
  - above 6km: << Rayleigh extinction
- Clouds: mostly cloud free

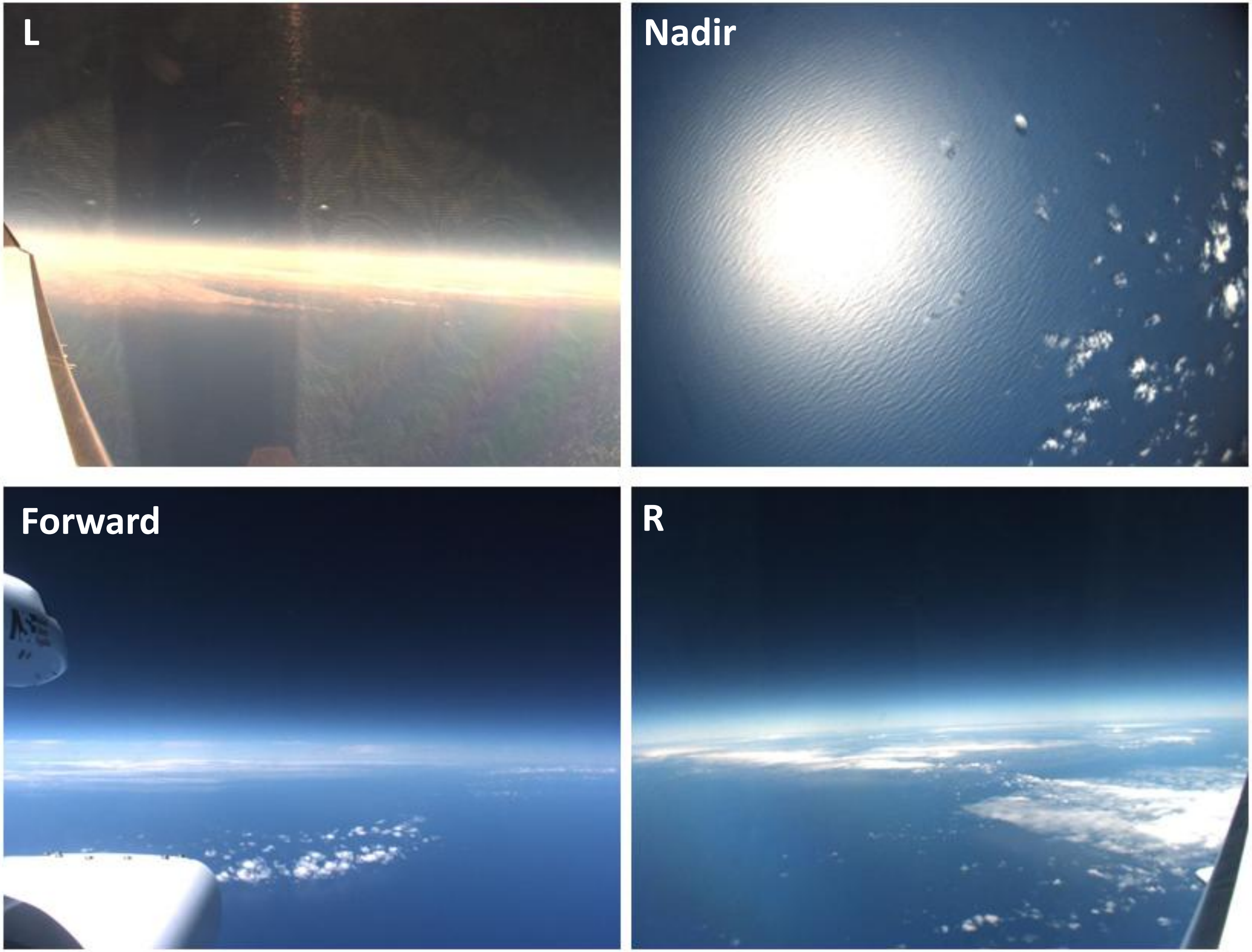






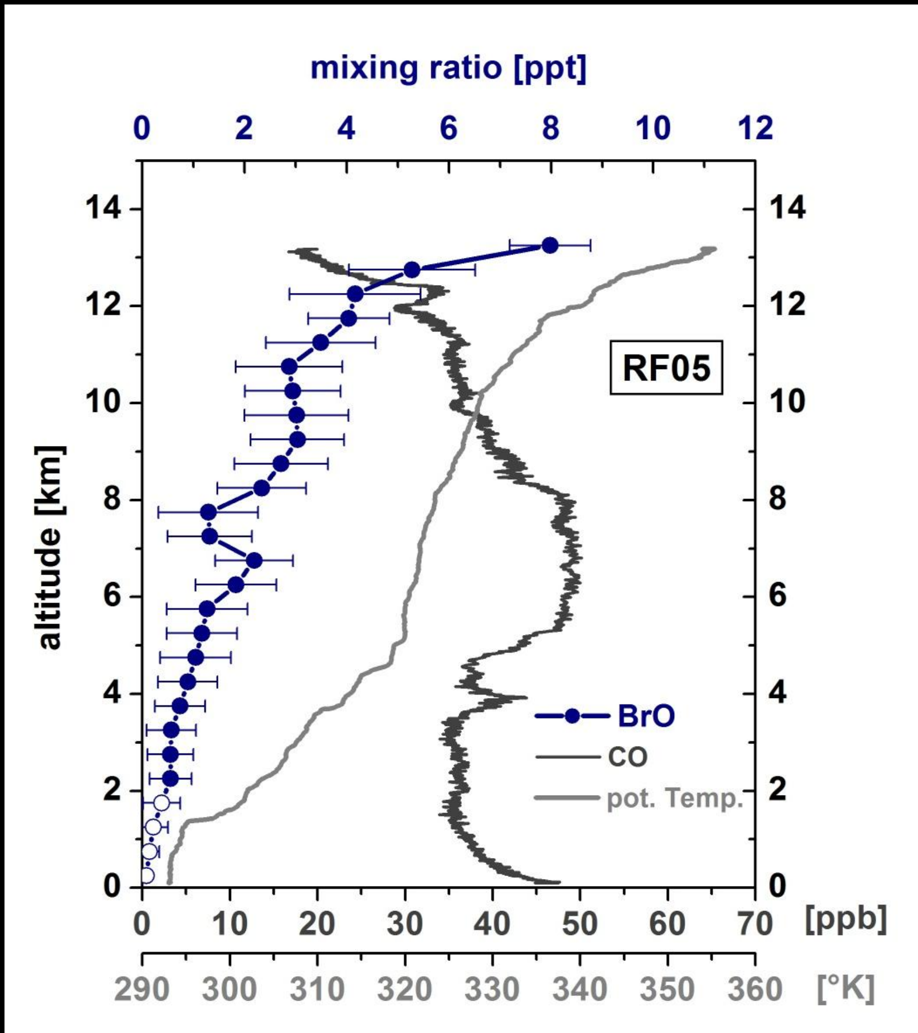


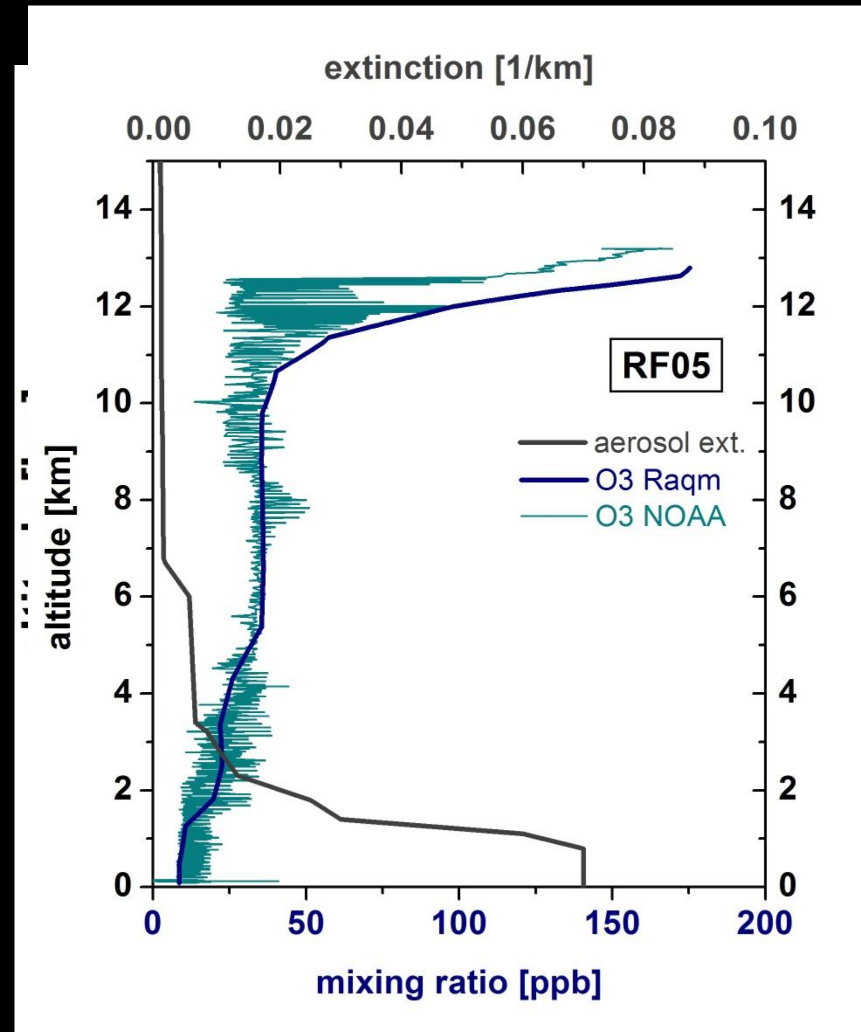
17:47 UTC @ 100m (in MBL)



18:30UTC @ 13.4km – return leg – clear above

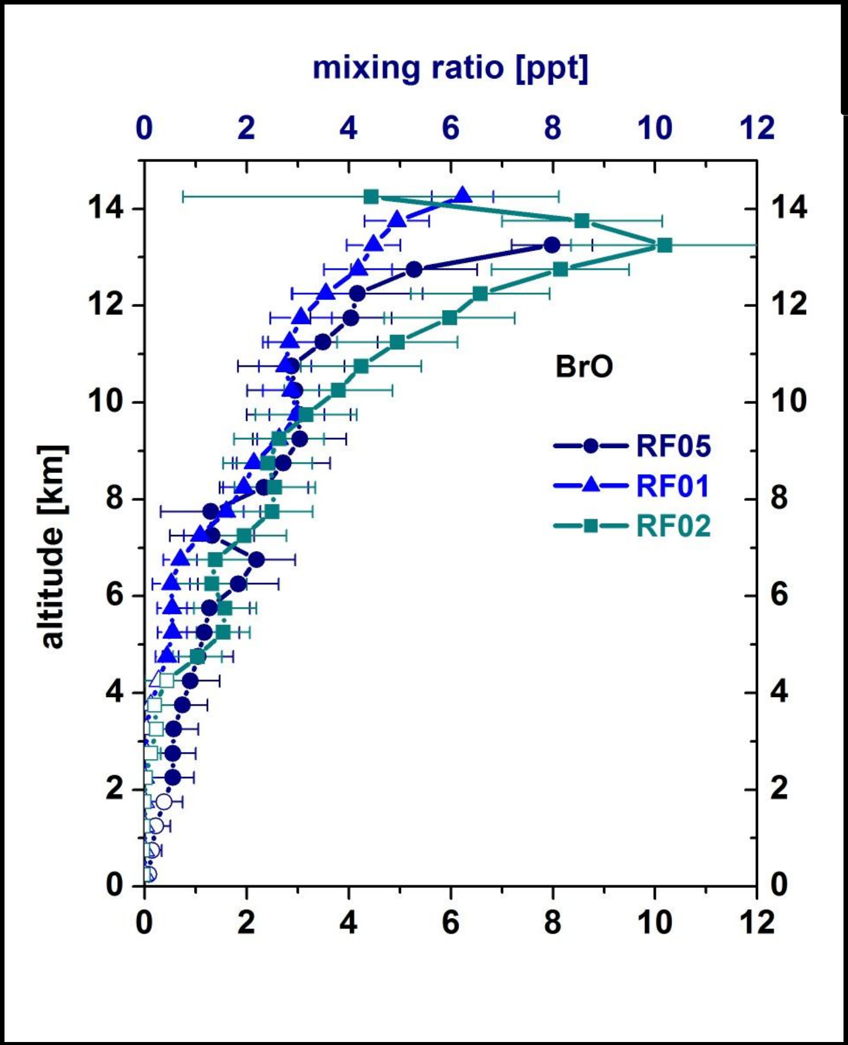
BrO vertical profile E, RF05, 29 Jan 2012

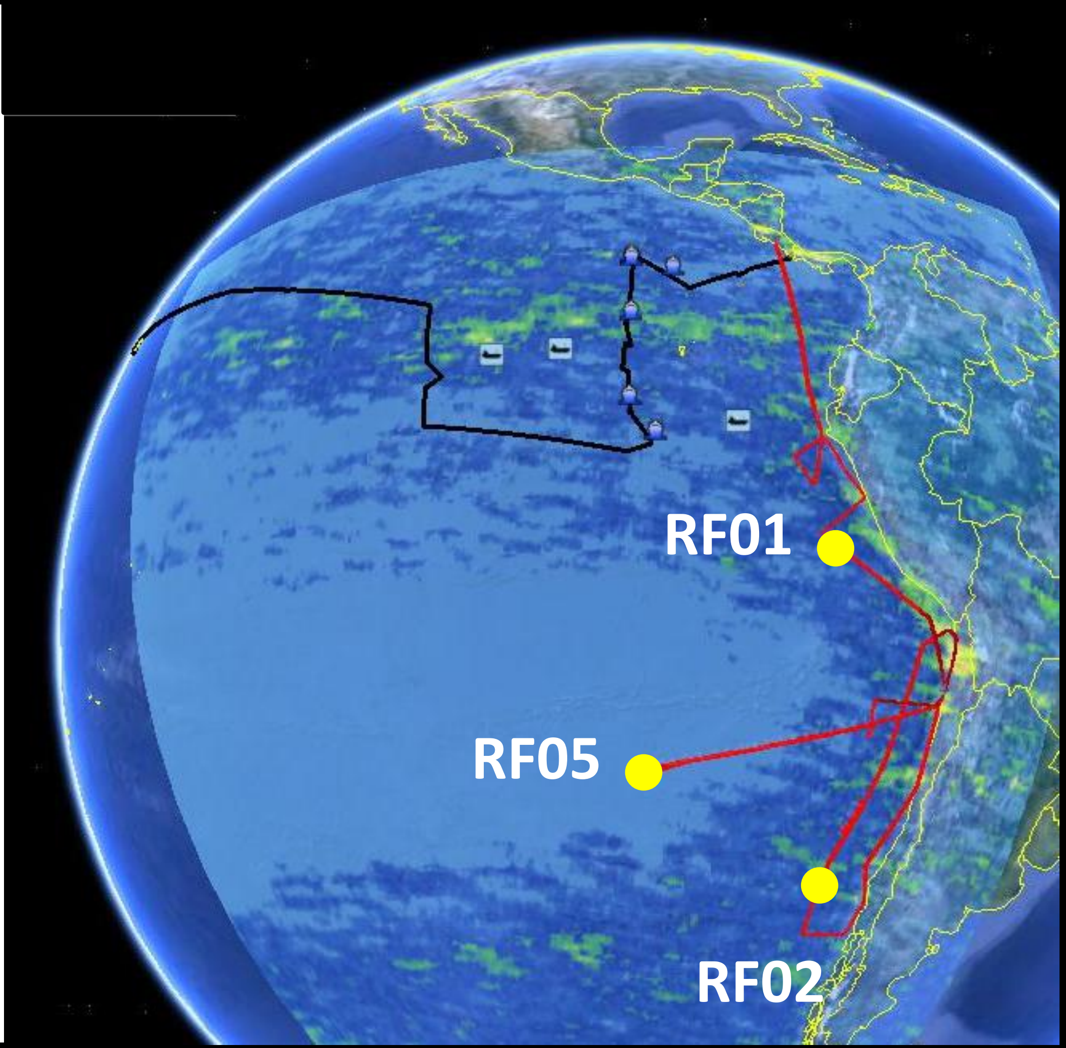




- BrO was detected above 2km; visible through most of the air column
- No BrO was observed in the MBL; consistent with our ship data

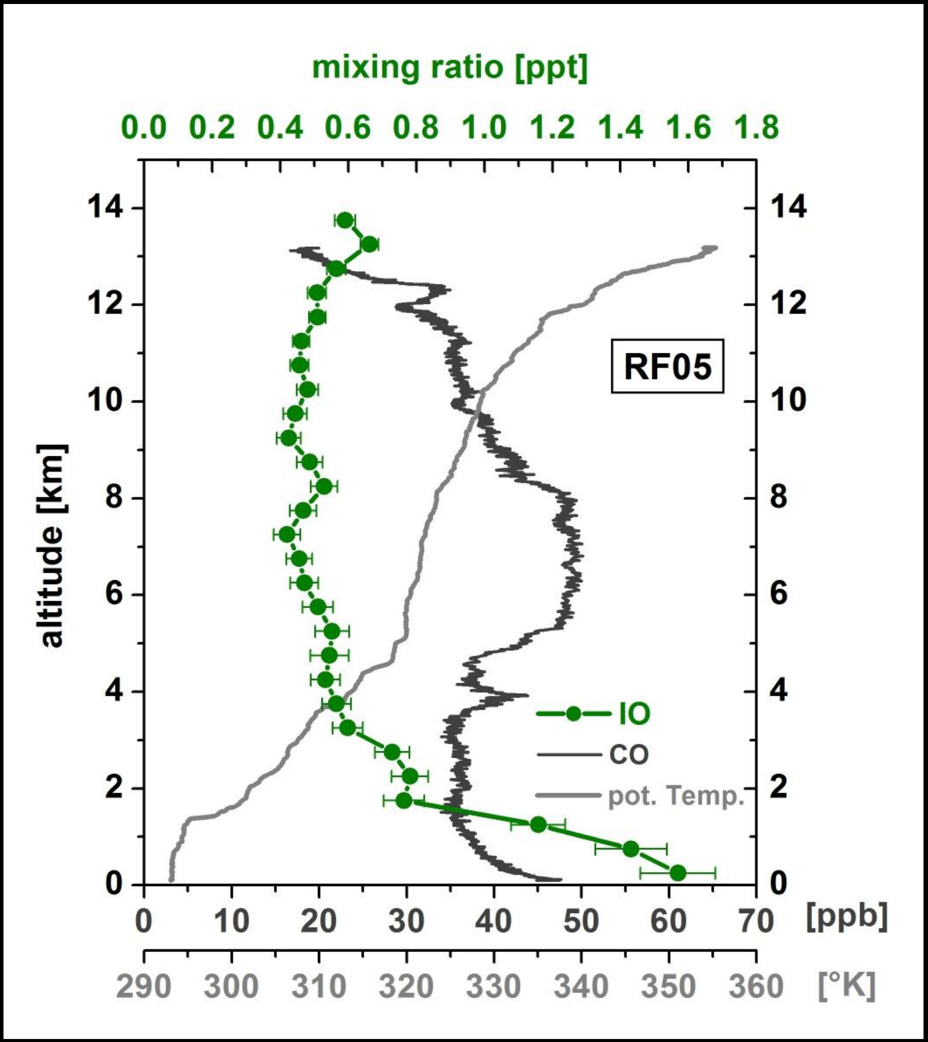
Comparison of BrO: RF01, RF02, RF05

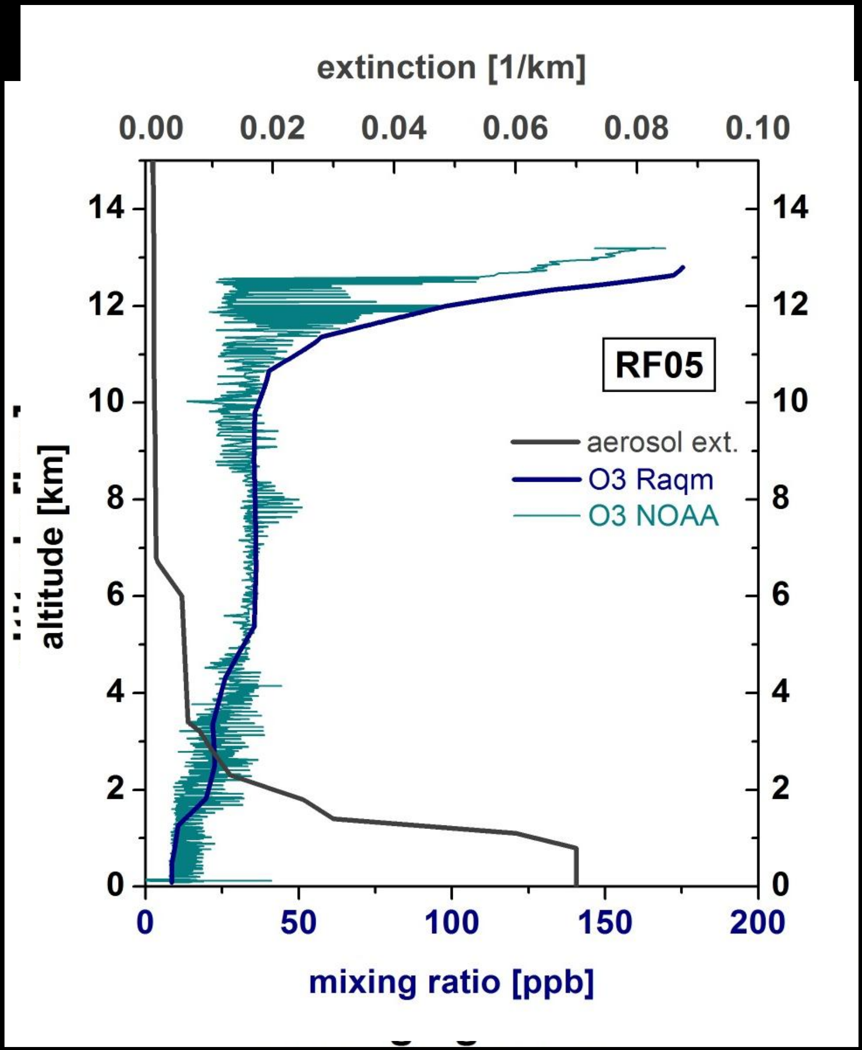




- Confirms RF05 case study over a wider spatial range
- BrO increases with altitude; No BrO was observed in the MBL

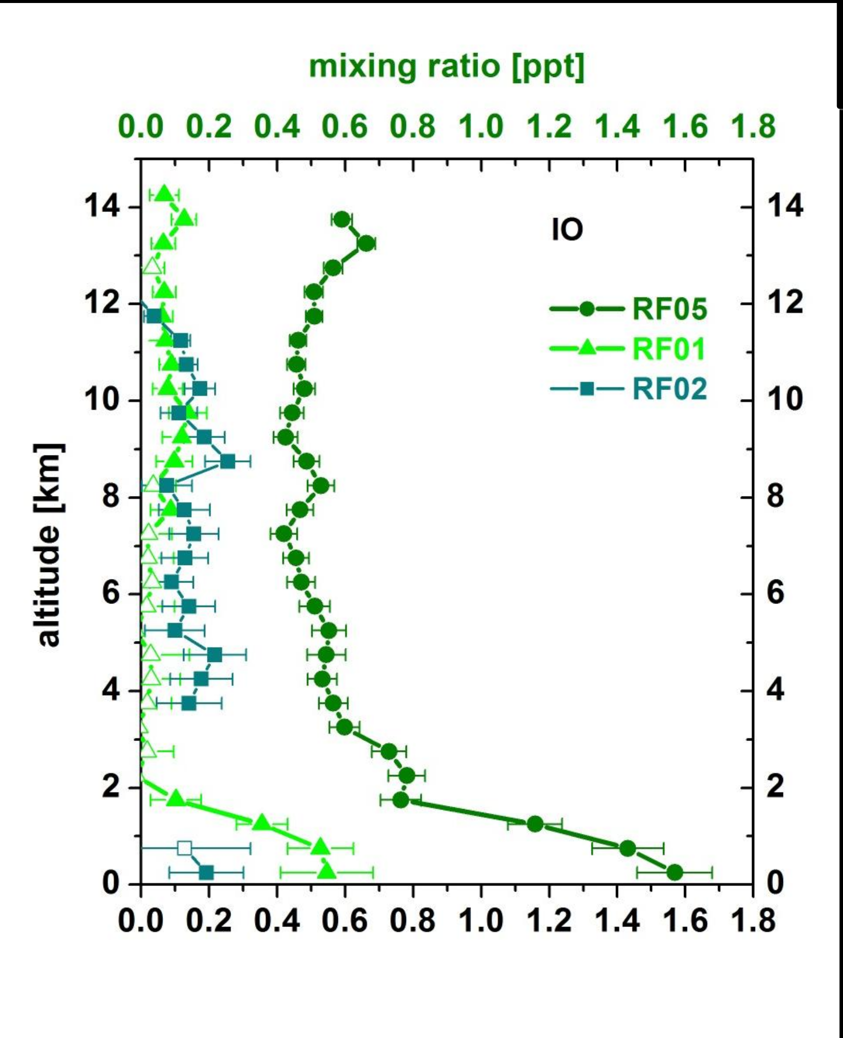
IO vertical profile E, RF05, 29 Jan 2012

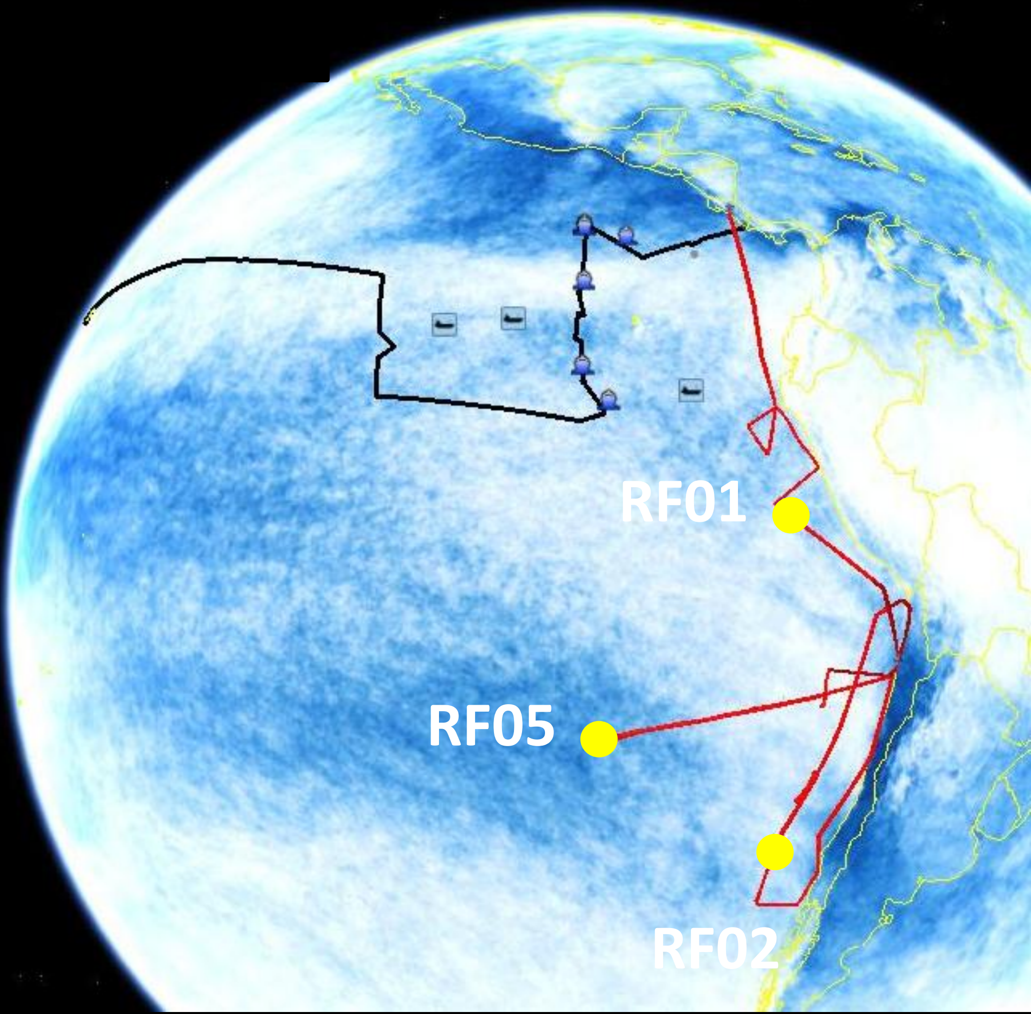




IO detected over the entire air column

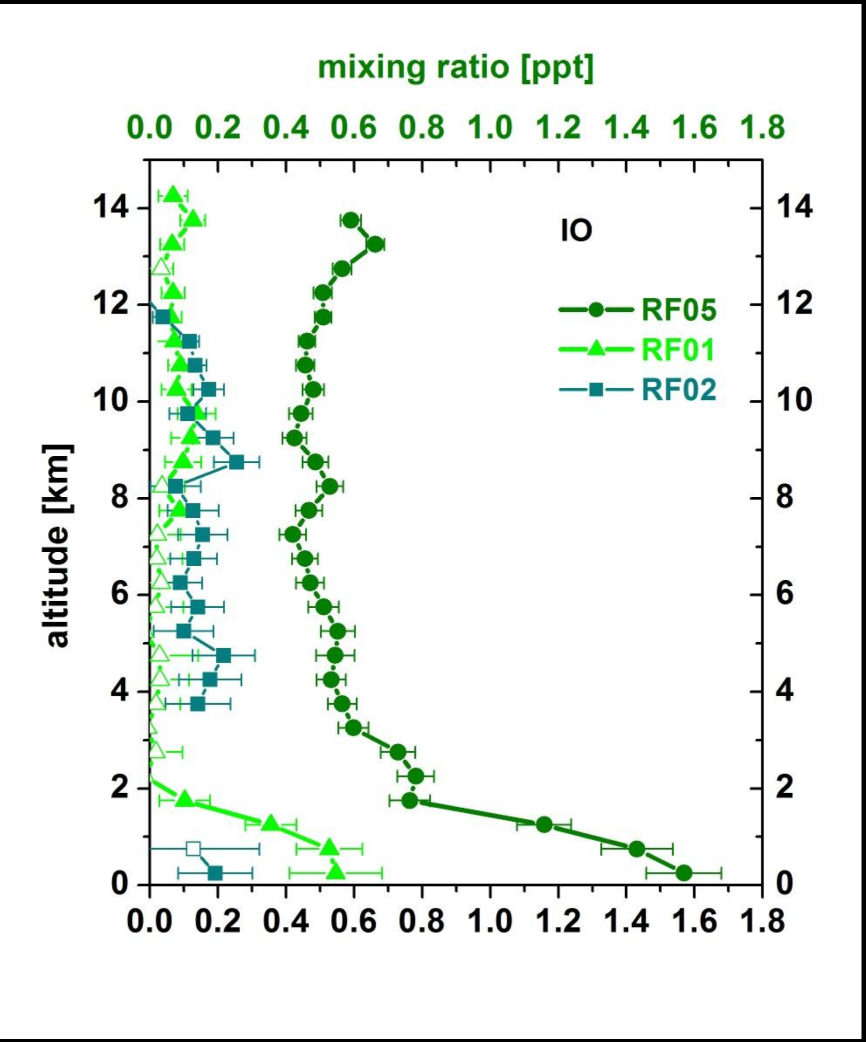
Comparison of IO: RF01, RF02, RF05

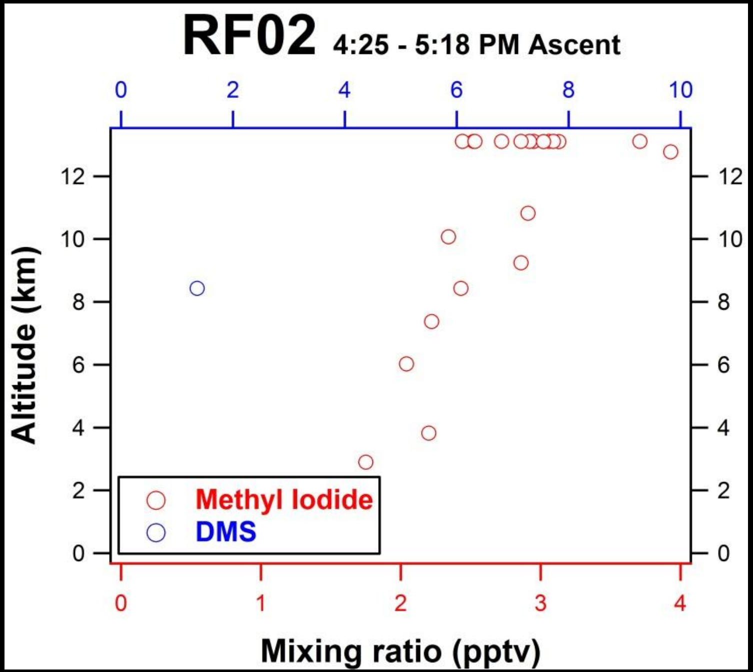


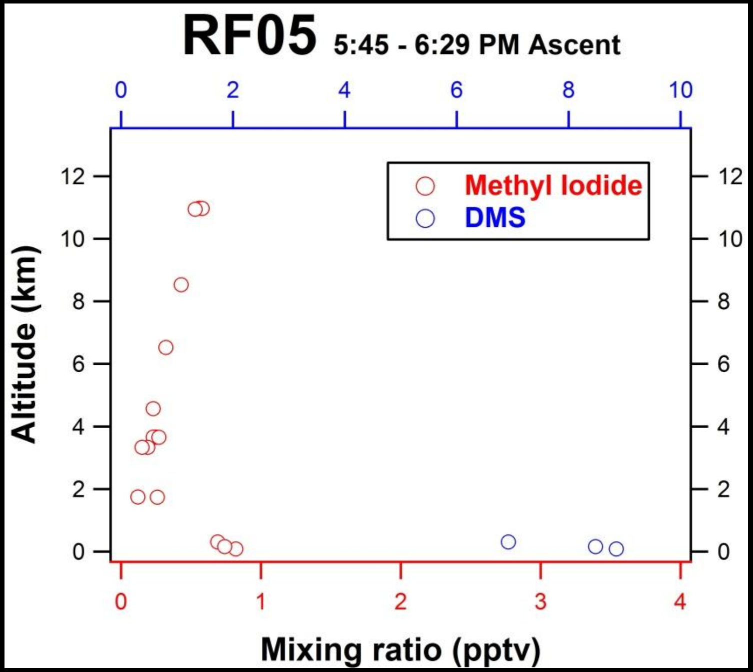


Satellite bias due to clouds? -> Dix et al.

Conundrum: CH_3I?

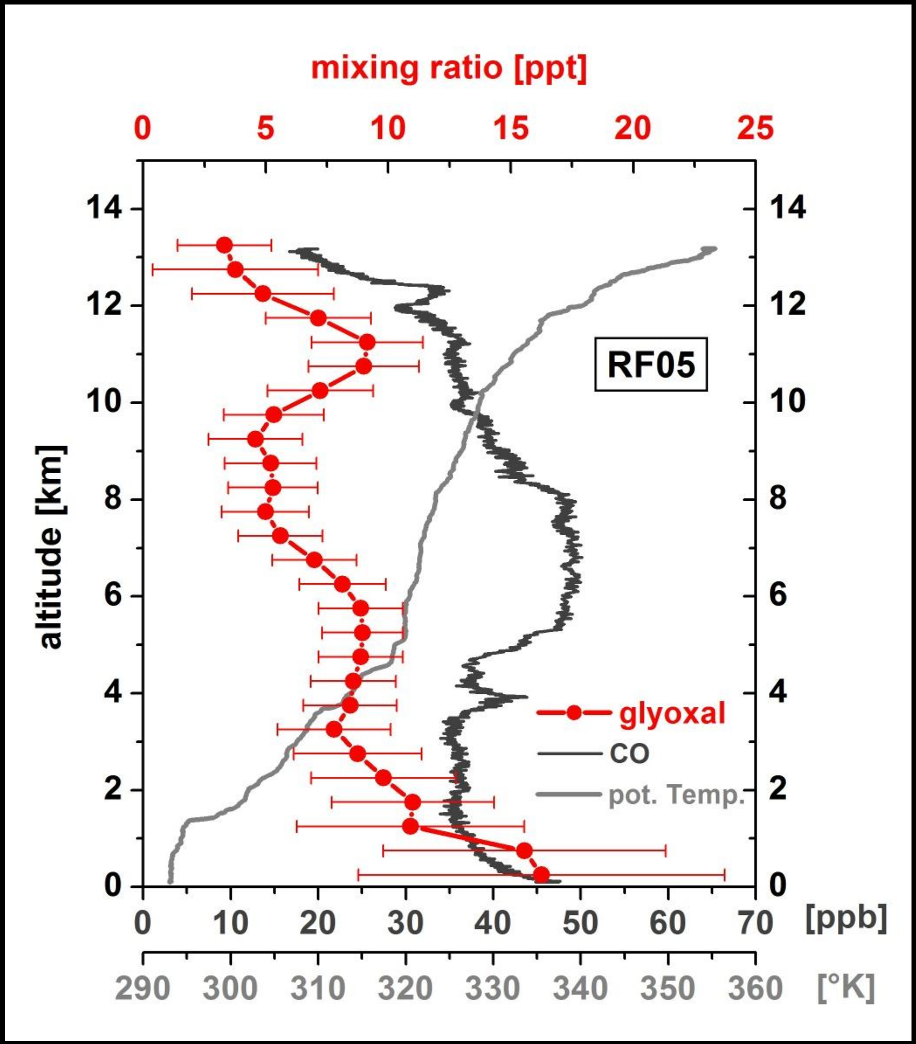


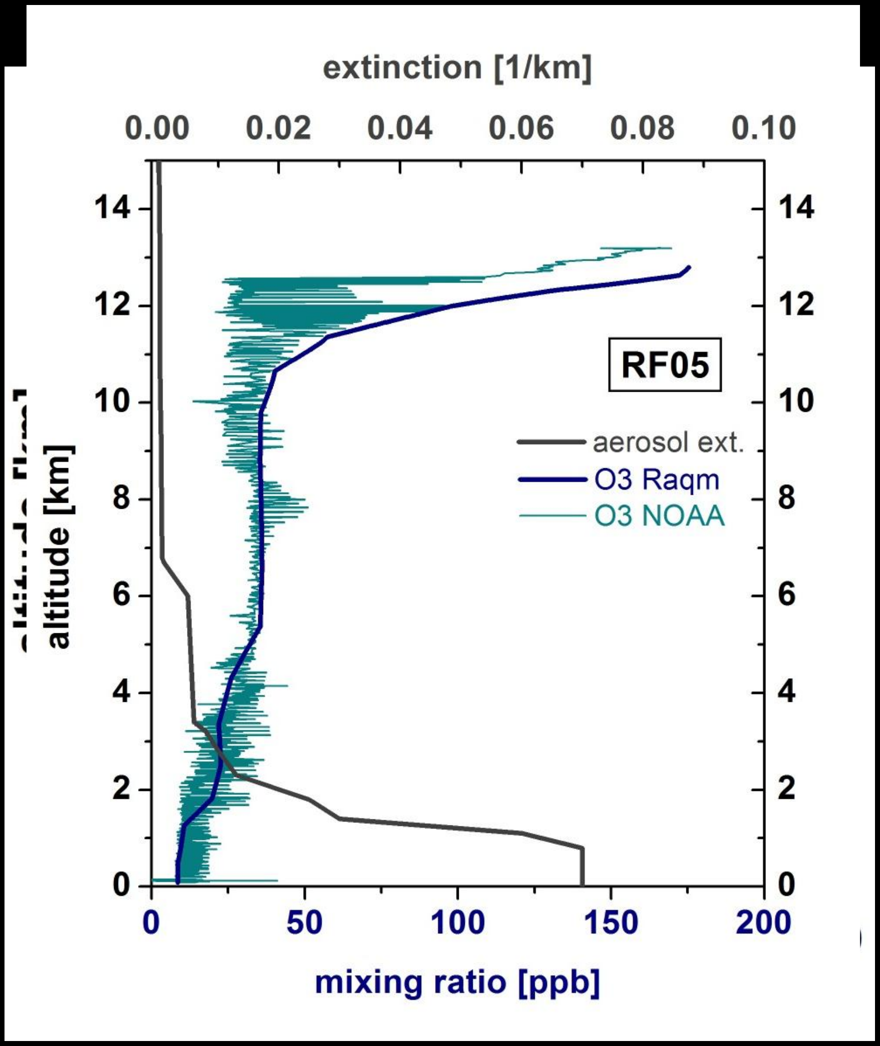




High IO ⇔ low CH_3I, really?

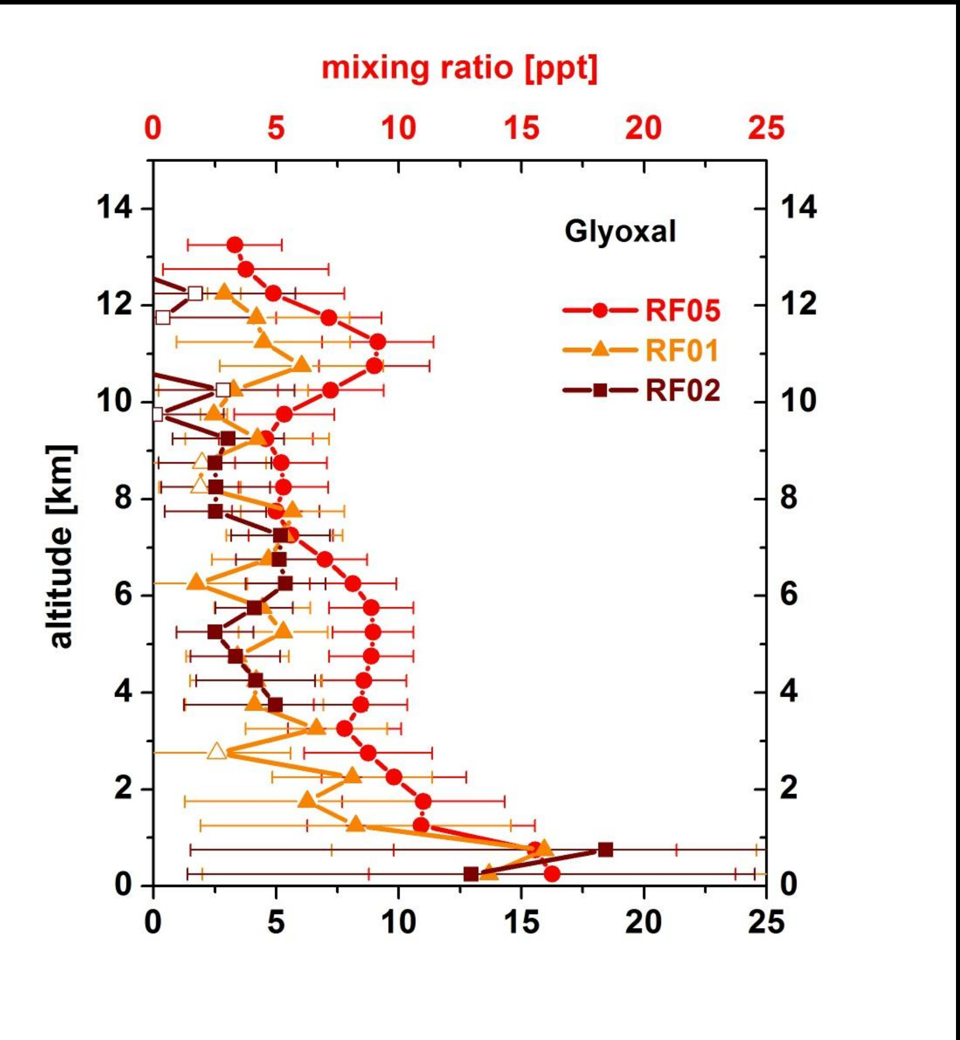
CHOCHO vertical profile E, RF05

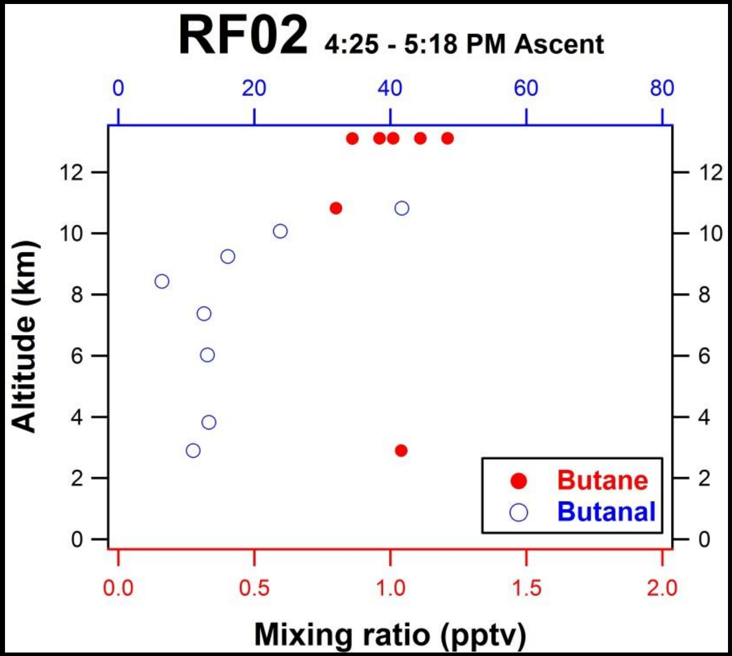


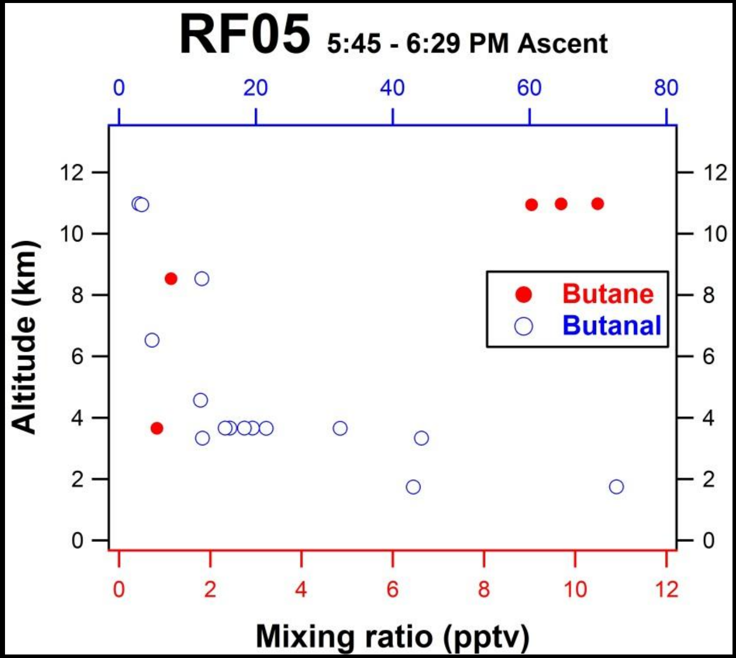


CHOCHO detected over the entire air column

OVOC artifacts?

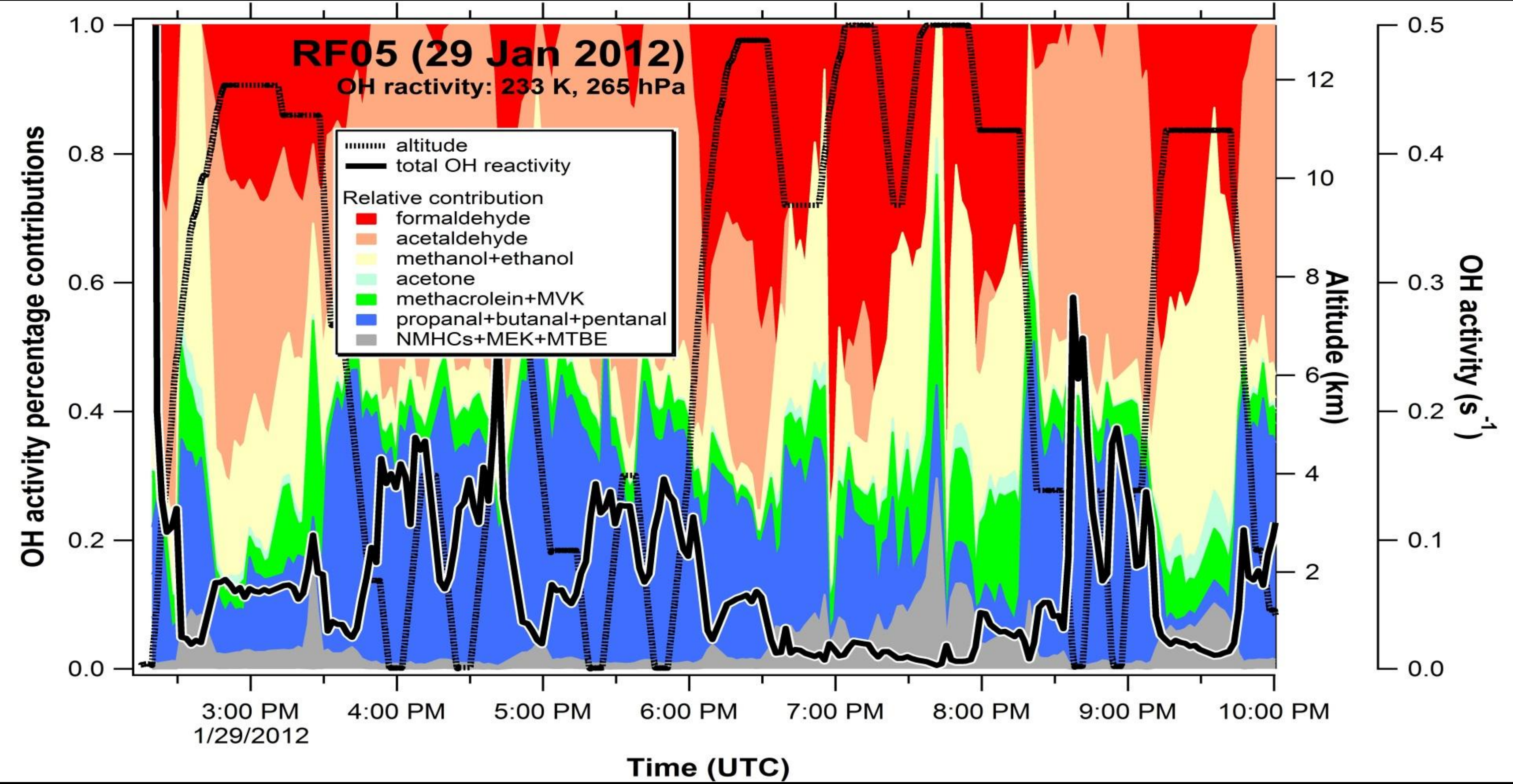






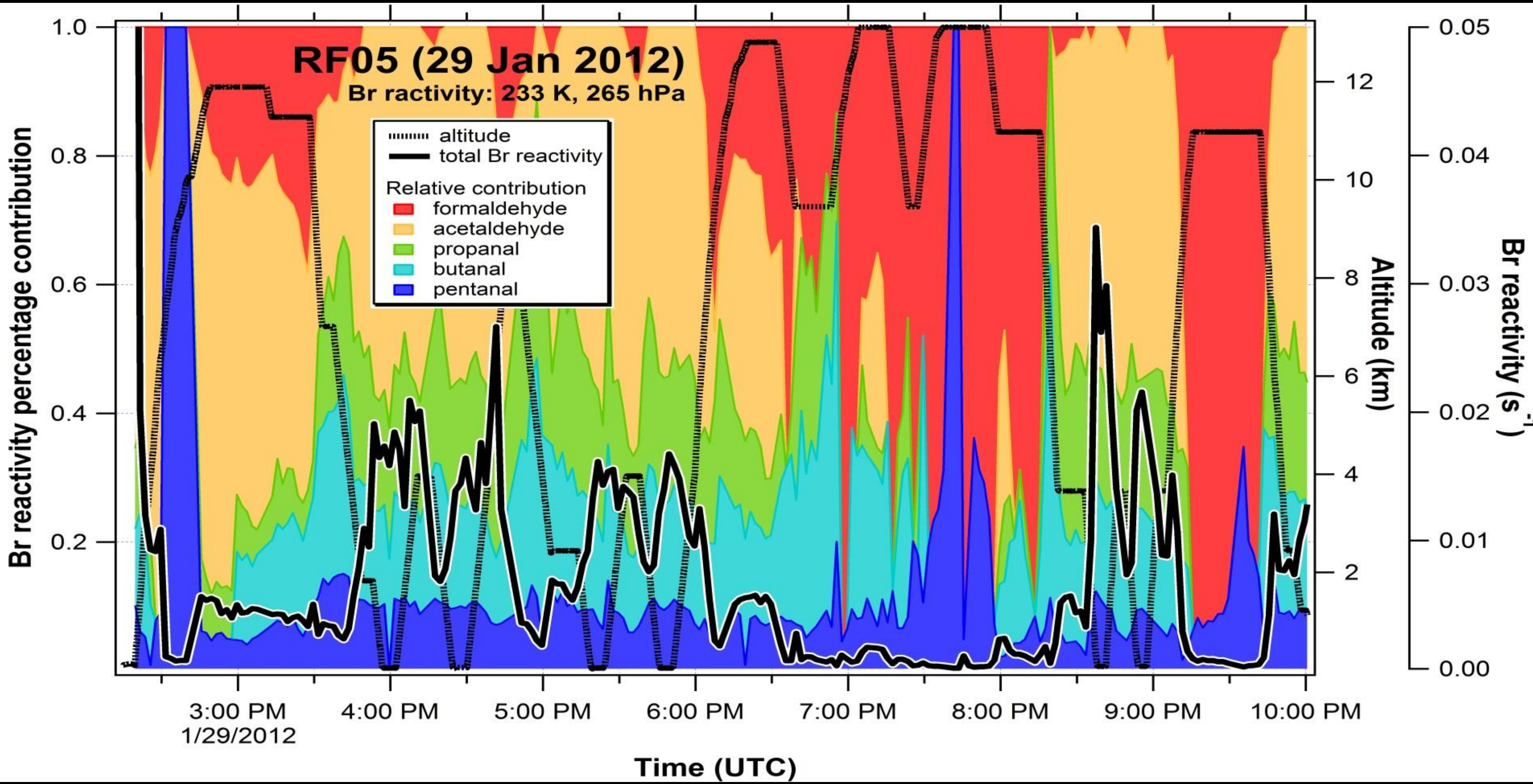
No CHOCHO during RF02 in air influenced by the stratosphere

Effect of organic carbon on OH reactivity



- OH reactivity = $\Sigma\, k_{i,OH}\, [VOC_i]$
- OVOC account for major share of OH reactivity

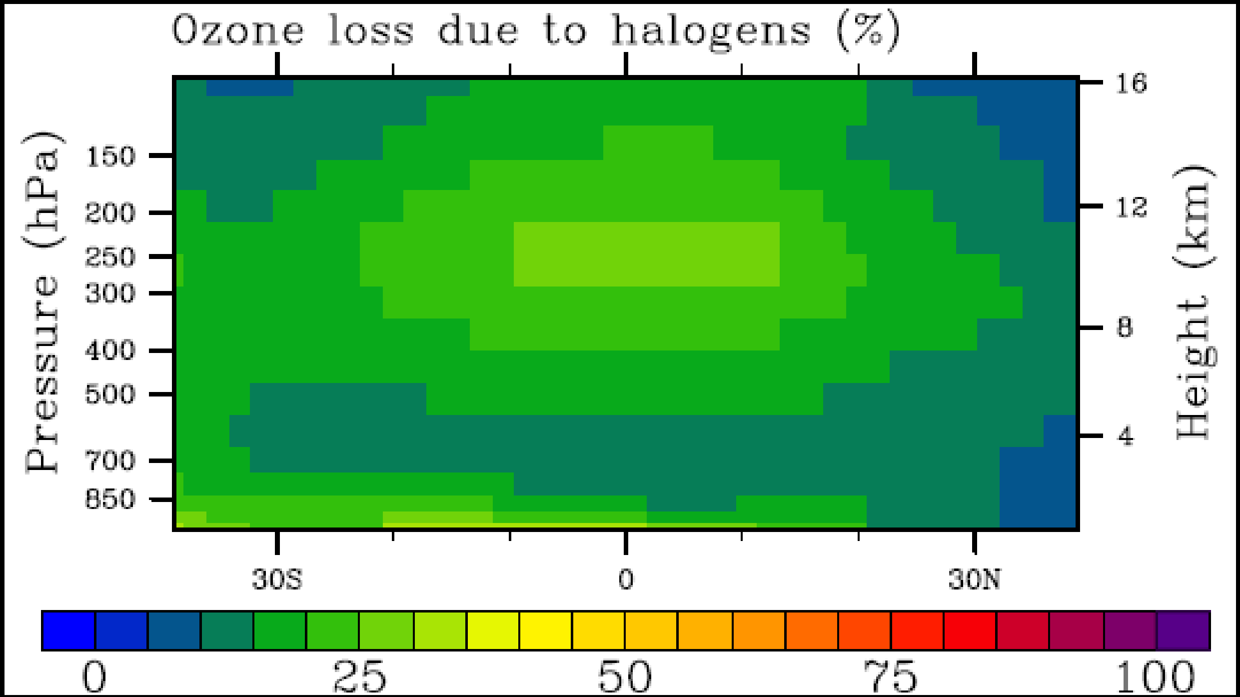
Effect of OVOC on Br reactivity



- Br reactivity = $\Sigma\ k_{i,Br}\ [OVOC_i]$
- What species are missing?

Relevance of bromine and iodine ?

- Reaction: $BrO + IO \rightarrow Br + I + O_2$
  - – > IO shifts the Br/BrO ratio towards Br atoms
  - – > accelerates the rate of mercury oxidation
  - – > accelerates the rate of ozone destruction
  - – > effects on HOx



Assumes:

BrO ~ 1ppt

IO ~ 0.02 ppt ?

⇒ Current first estimates may be a lower limits

Saiz Lopez et al., 2012

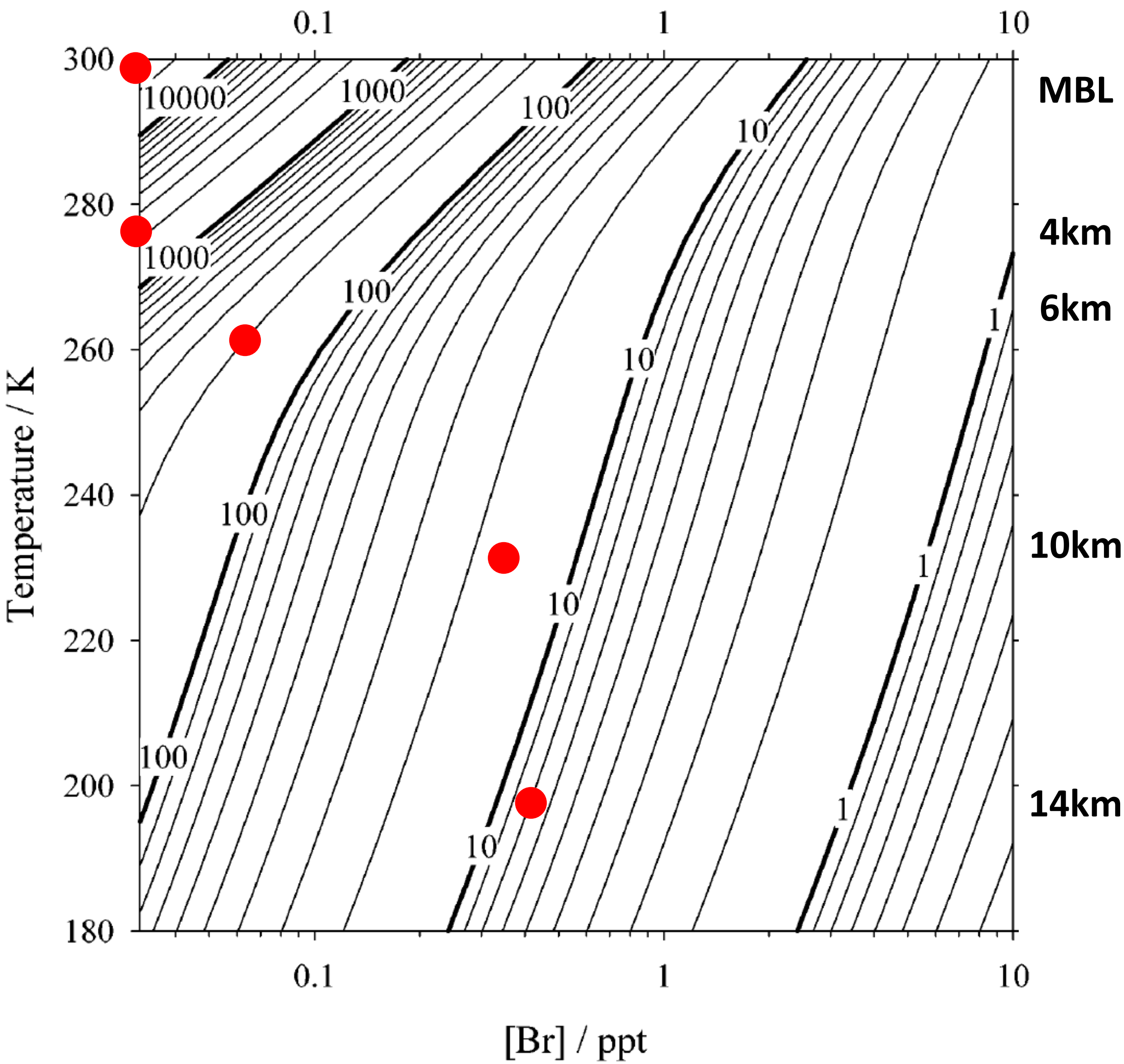


FIGURE 2. Contour plot of the lifetime in hours for Hg^0 oxidation to $HgBr_2$, plotted as a function of [Br] in parts per trillion and temperature in Kelvin.

Hg lifetime

Assumption:
[Br] ~ 0.1 [BrO]

⇒ τ_{Hg} < 10 days above 6 km

⇒ τ_{Hg} < 1 day above 10 km

⇒ τ_{Hg} < 8 hrs above 14 km

Hg + Br -> HgBr (1)
HgBr -> Hg + Br (2)
HgBr + Br -> $HgBr_2$ (3)

Goodsite et al., 2004

Rapid mercury oxidation in upper FT

PAMS field data tropical UTLS

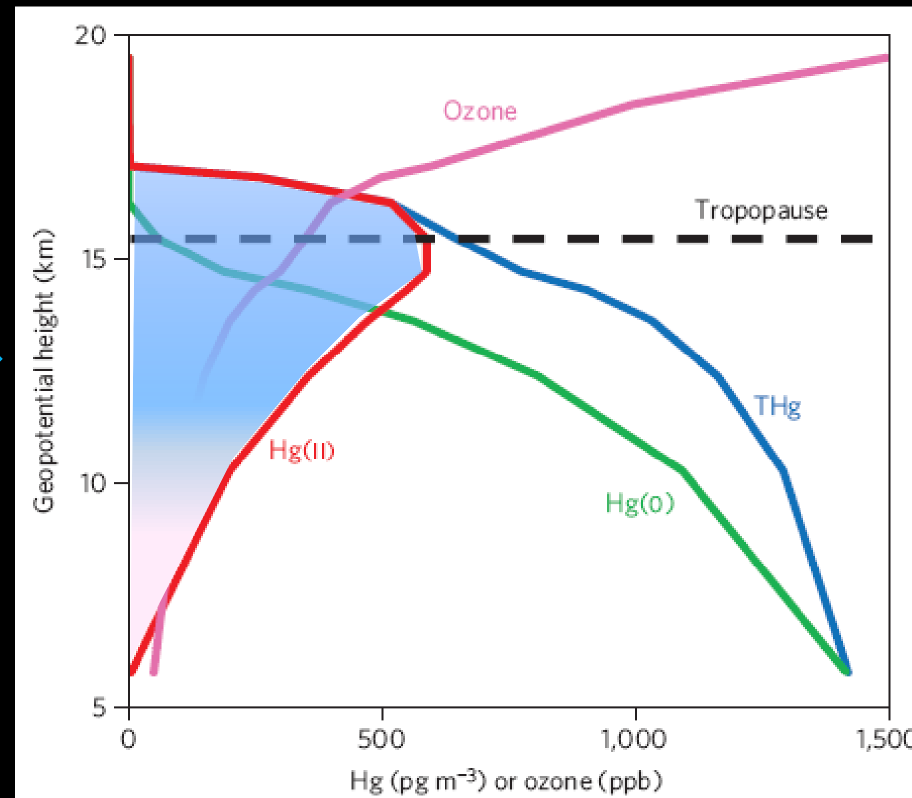
Quote: '[A **sharp gradient** is observed]... **just above the tropopause** small amounts of mercury were found in over half of the aerosol particles that were analyzed.'

- Condensation?
- Ionization efficiency?
- Calibration?
- Size bias (D_p > 200nm)?

Murphy et al., 1998

?

Empirical Hg-O3 relationships



Lyman and Jaffe, 2012; Rutter and Schauer, 2007

With τ_{Hg} < 1 day there is abundant semi-volatile mercury above 10 km,
Which exists mostly in the particulate phase @ -20 to -30 C (~ 9-10km)

Why is mercury not observed in particles already in the upper FT?

A missing piece… consistency with PAMS?

BrO constrains the rate of mercury oxidation

Efficient oxidation in FT (~10 days @ 6km;

Particles in lower stratosphere tend to be larger due to coagulation (Murphy et al., 1998)

TORERO: frequent nucleation mode in upper FT.

How much condensational sink surface area is due to particles with D_p < 200nm (invisible to PAMS)?

Action items:

$\Rightarrow$ Evaluate aerosol surface area distribution data [IO, Hg(II)]

$\Rightarrow$ Air mass back trajectories (Run Flexpart along GV tracks?)

$\Rightarrow$ More analysis…

Conclusions

- BrO, IO, and CHOCHO are measured over the entire air column
- The spatial variability needs more analysis…
  - HARP – J-values, and cloud OD
  - HSRL – data access currently via 'Bruce'
  - Aerosol size distribution data

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