Recent observations of tropospheric BrO and IO profiles: implications for CONTRAST

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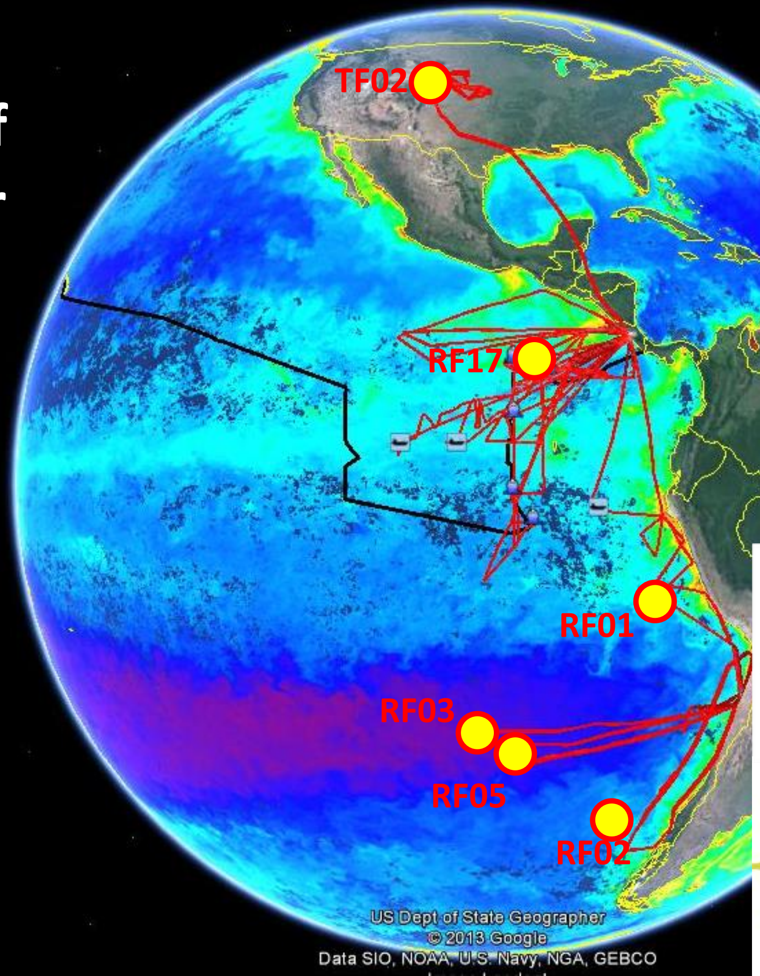
Brad Pierce, Eric Apel, Ru-Shan Gao, Julie Haggerty, and Team TORERO

TORERO : study air-sea exchange of oxygenated VOC and halogens over the full tropospheric air column

→ Bromine and iodine sources

→ What information/support do we need that is relevant for flight planning, model support



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

Most of the Earth's surface looks like this!

Hypothesis #1: Marine sources of halogens affect the lifetime of climate active gases (O_3, CH_4, DMS) and oxidize atmospheric mercury over much of the tropical air column.

How abundant are halogen oxide radicals (BrO, IO)?
Do we understand their sources?

Hypothesis #2: Glyoxal over oceans is a smoking gun for other oxygenated VOC and 'missing' sources from ocean biology.

Where does it come from, and what comes with it?
What do 4D measurements reveal about the source mechanism?

Myriokefalitakis et al., 2008; Sinreich et al., 2010; Coburn et al., 2011; Dix et al., 2013
Wang et al., 2013 in prep.; Volkamer et al., 2013 in prep.

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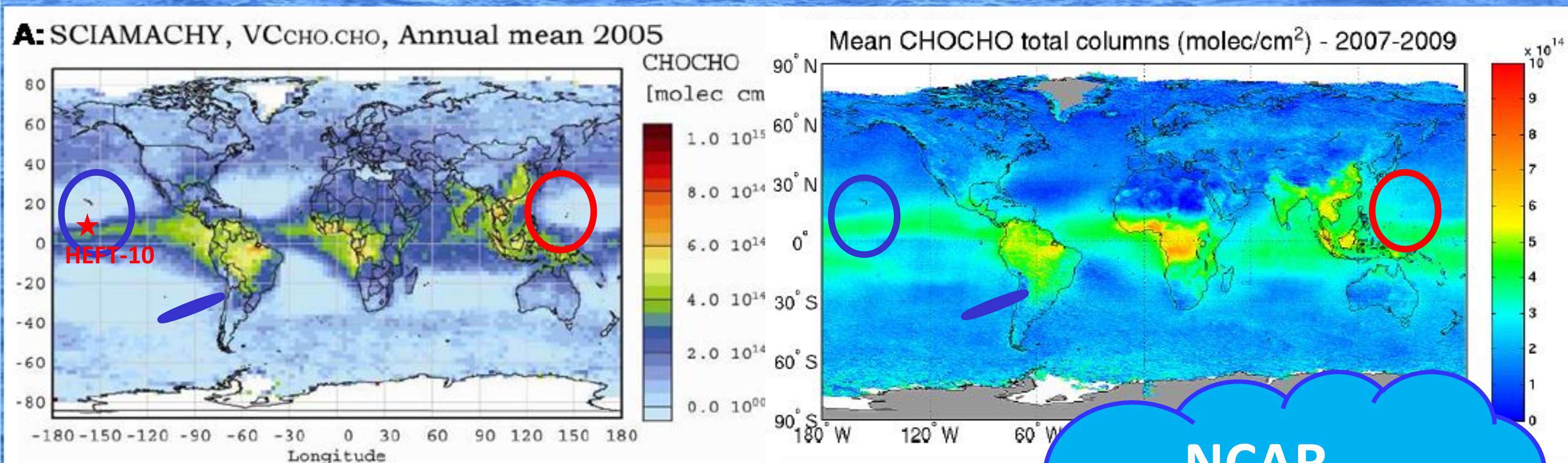


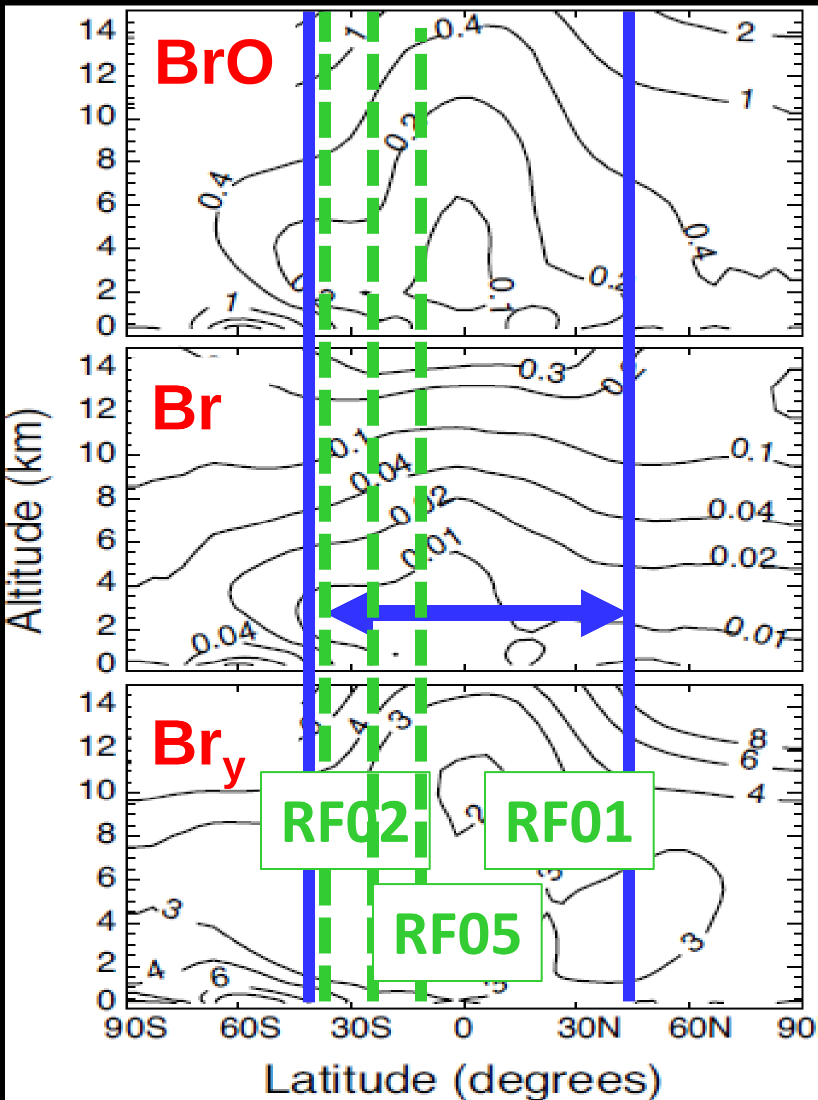
Wittrock et al., 2006; Myriokefalitakis et al., 2008; Sin

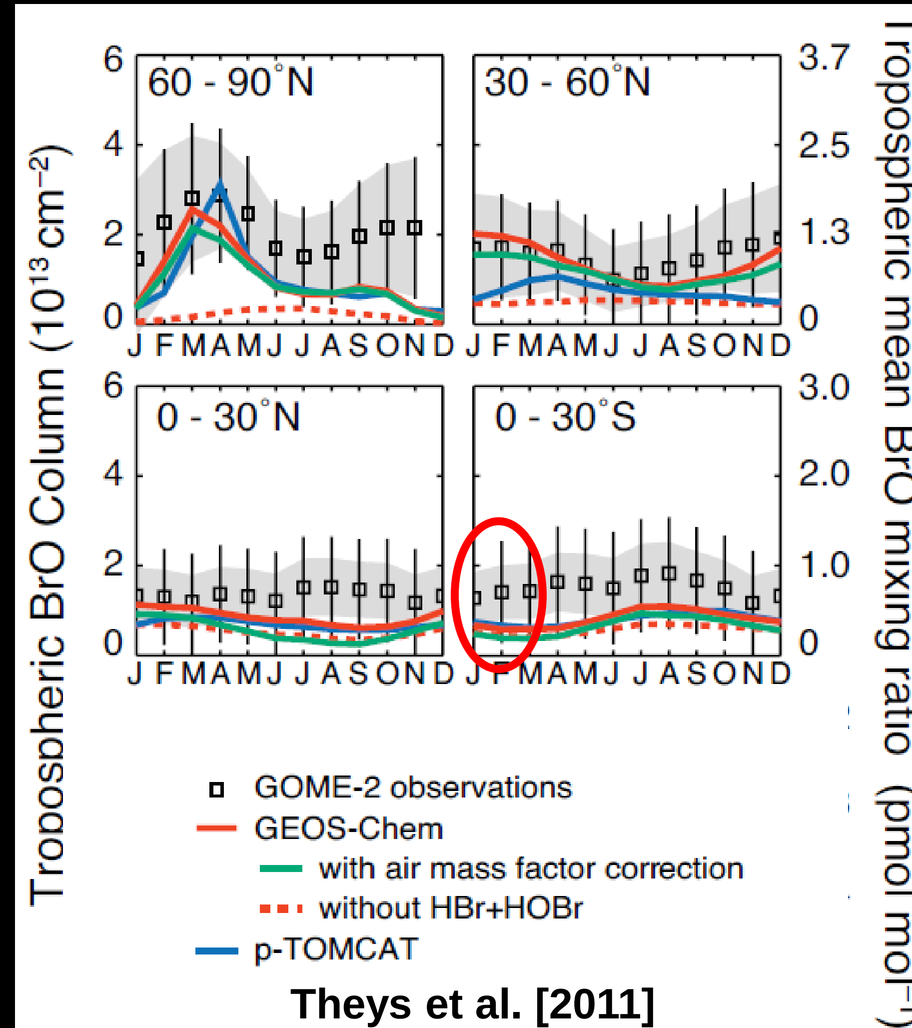
Atmospheric models do not predict any

… an unknown unknow

NCAR Seminar 28 Oct, 3pm

BrO comparison GEOS-Chem with GOME-2 satellite data





Parrella et al., 2012; Saiz-Lopez et al., 2012

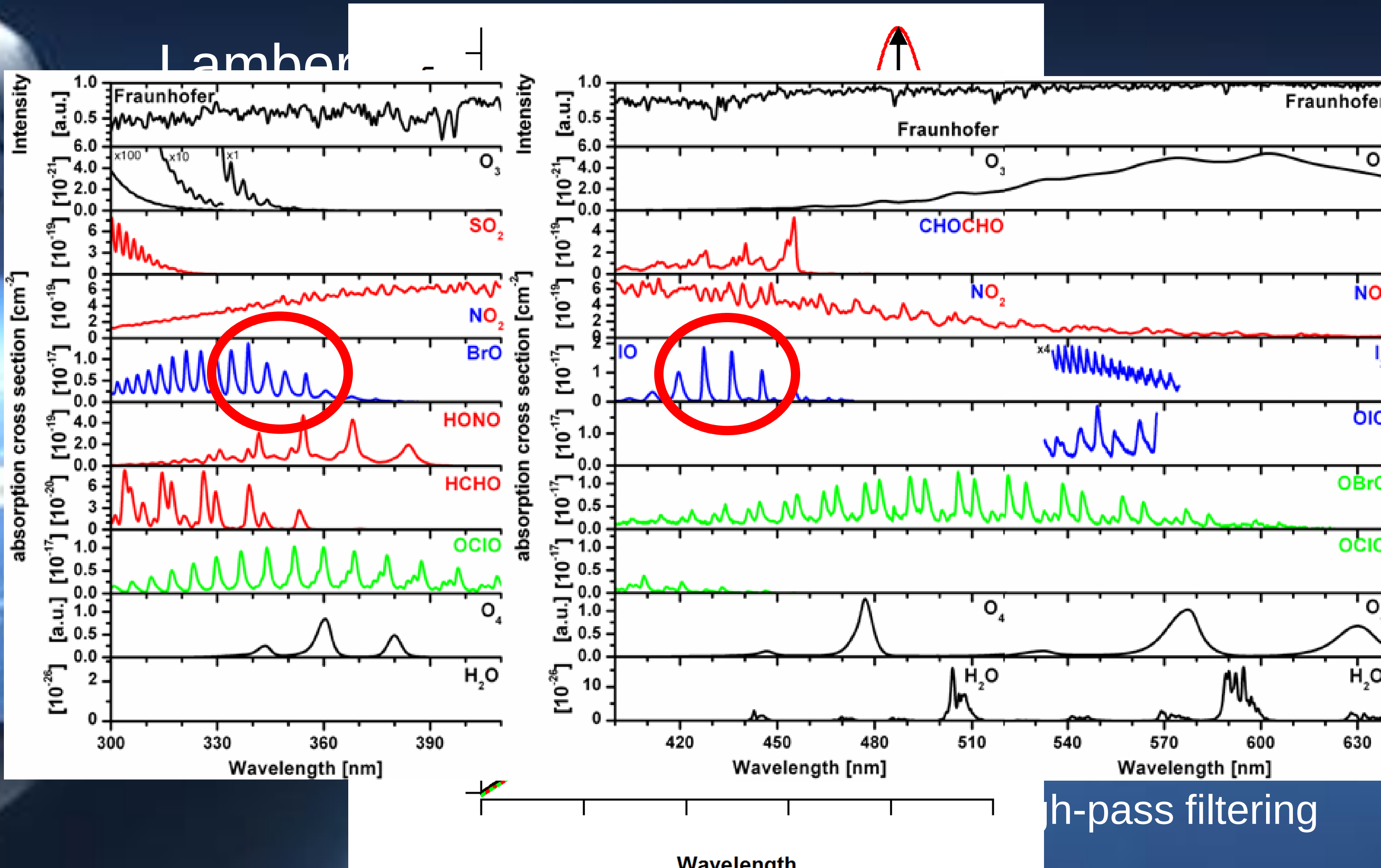
Halogens deplete the O_3 column by ~10% in the tropics

GEOS-Chem: ~0.2-0.5 ppt BrO, no IO; CAM-Chem: 0.2 ppt BrO, ~0.1 ppt IO

Atmospheric models remain untested in the FT !

Differential Optical Absorption Spectroscopy (DOAS)

Lamber

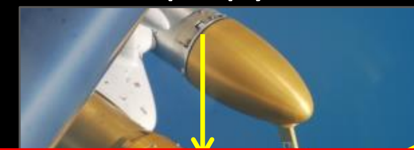


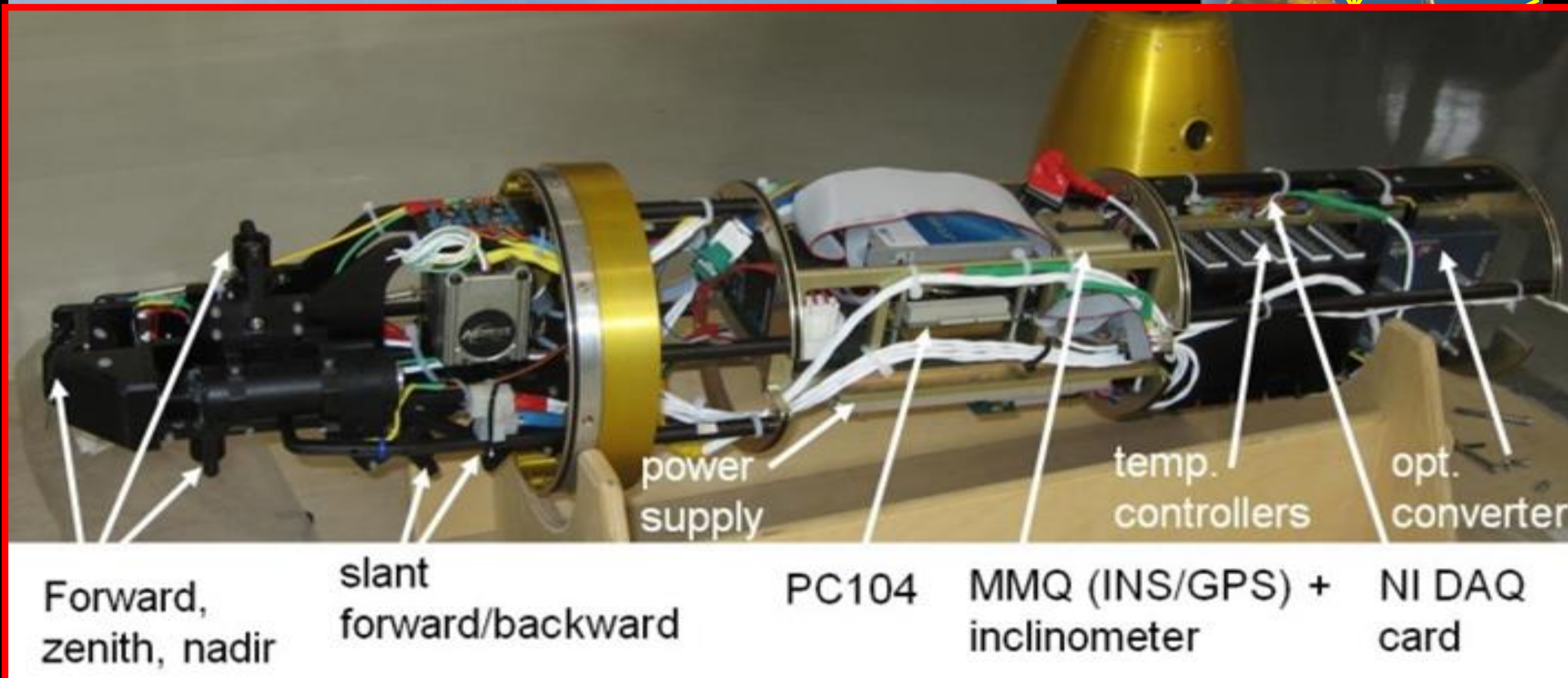
h-pass filtering

CU-AMAX-DOAS instrument aboard NSF/NCAR GV

University of Colorado Airborne Multi-AXis Differential Optical Absorption Spectroscopy

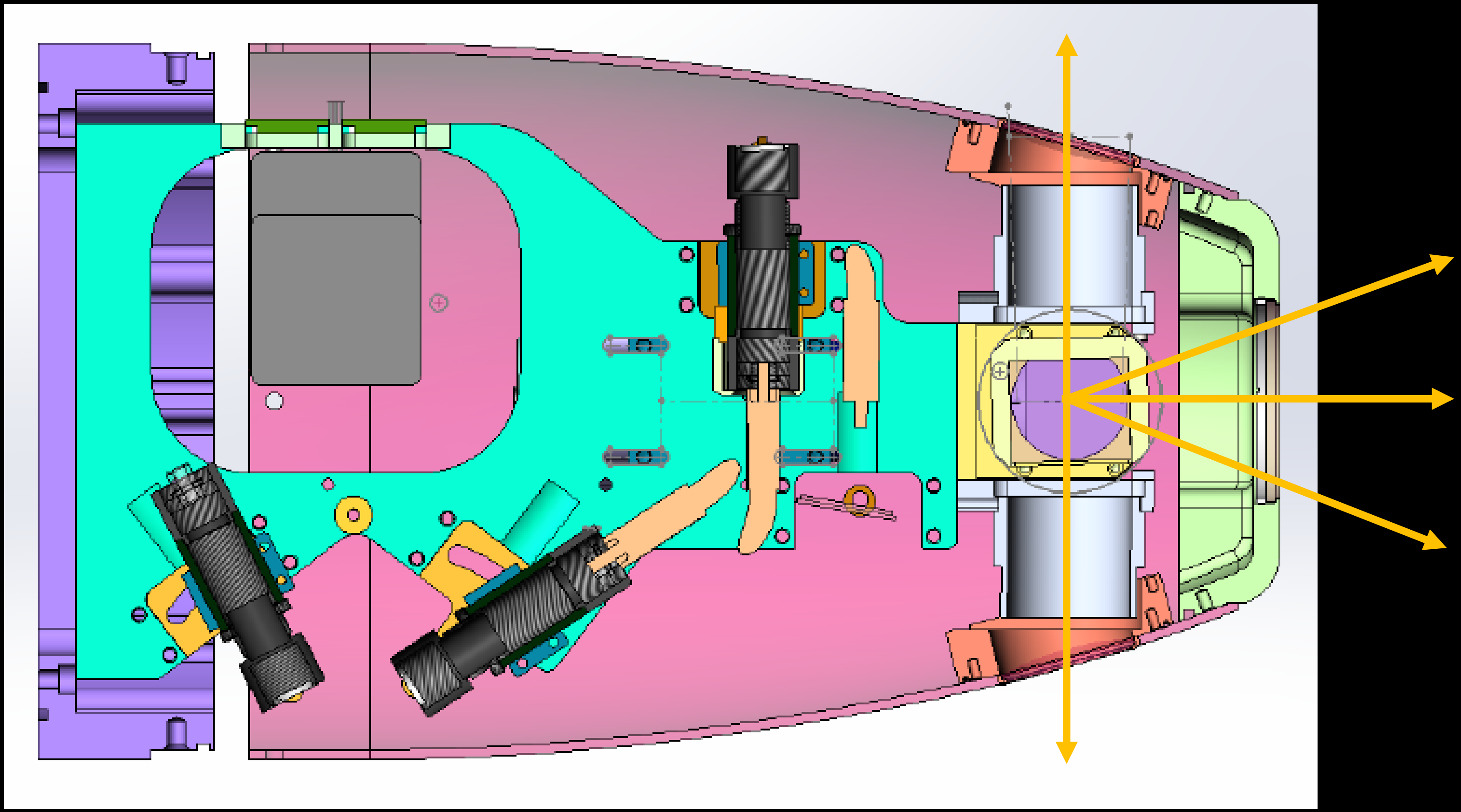
Telescope pylon





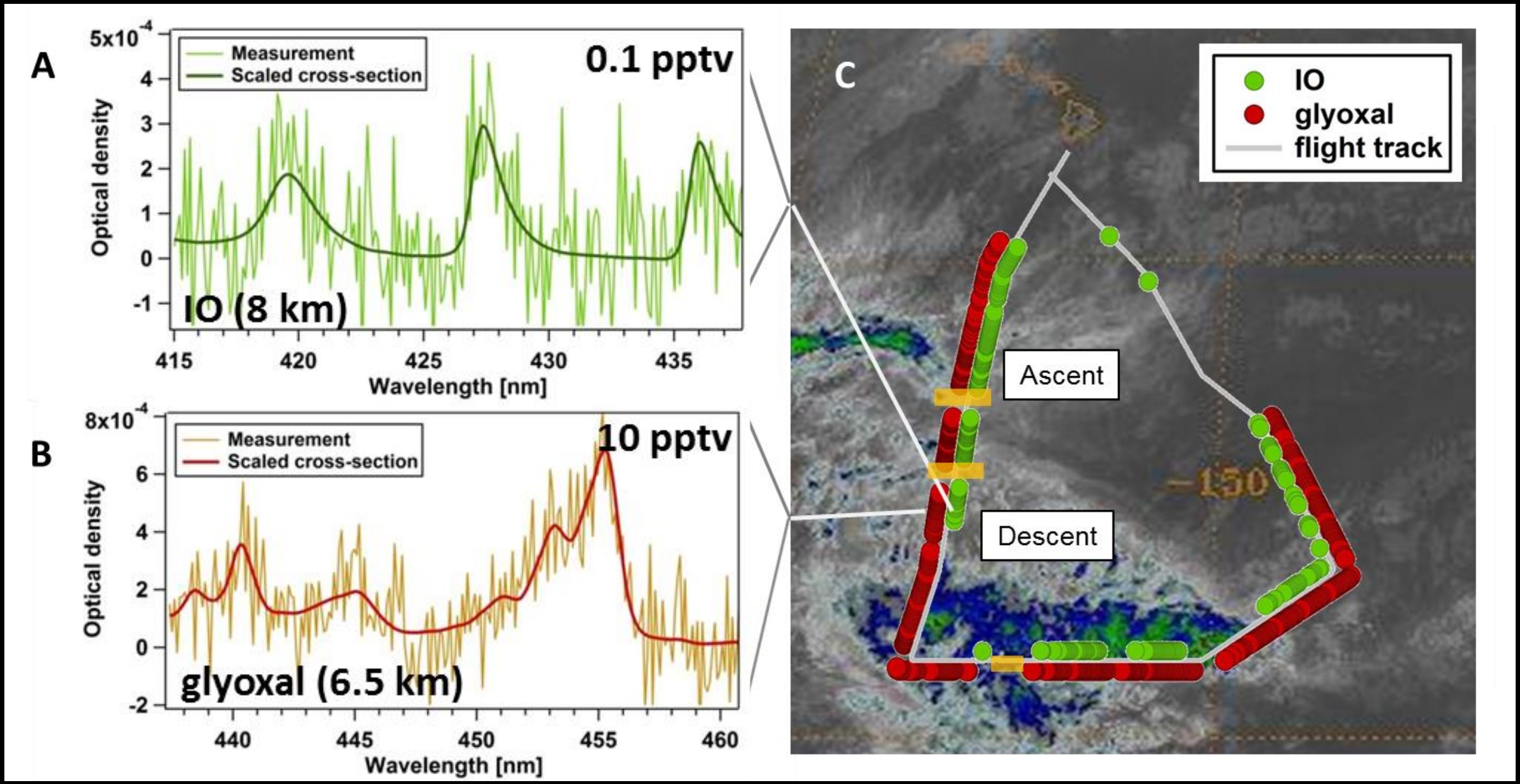
Volkamer et al., SPIE 2009
Baidar et al., AMT 2013

AMAX-DOAS updates prior to CONTRAST



- Telescope → tested upgrade (Baidar et al., 2013 AMT)
- Software → autonomous ground-control

CU AMAX-DOAS on NSF/NCAR GV (HEFT-10)



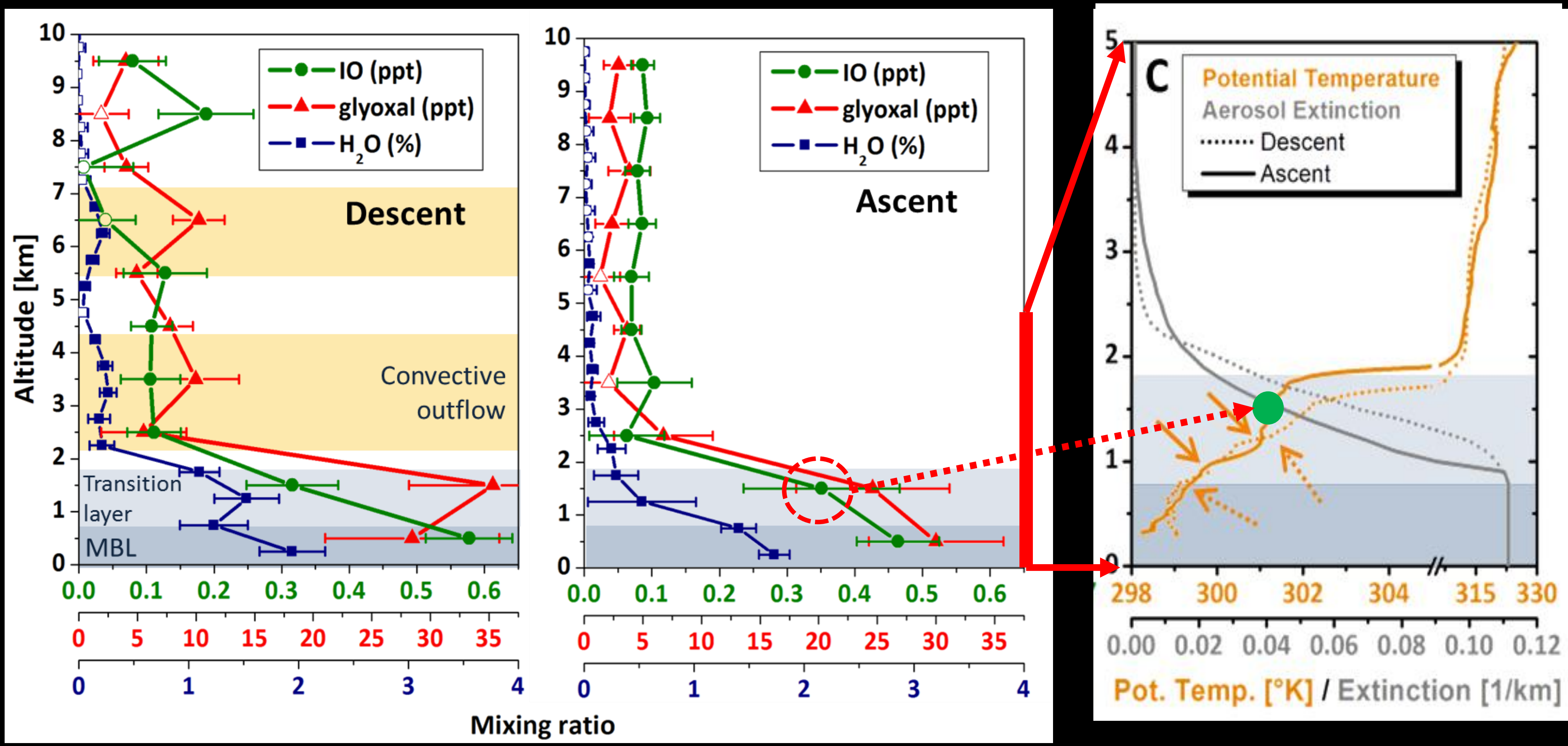
➔ Heterogeneous recycling of iodine is needed to explain vertical profile

Elevated IO in a decoupled MBL is incompatible with iodine lifetime

➔ Iodine is responsible for ~10% of ozone loss rate in the FT

<u>B. Dix, S. Baidar</u>, J.F. Bresch, S.R. Hall, K.S. Schmidt, <u>S. Wang, and R. Volkamer</u>: *Detection of Iodine Monoxide in the Tropical Free Troposphere*, PNAS, 2013

IO, glyoxal and H_2O profiles during HEFT-10



Chemical model simulations reveal:

- Elevated IO in a decoupled MBL are incompatible with iodine lifetime
- Fraction of the ozone loss rate is a strong function of ozone (up to 20%)

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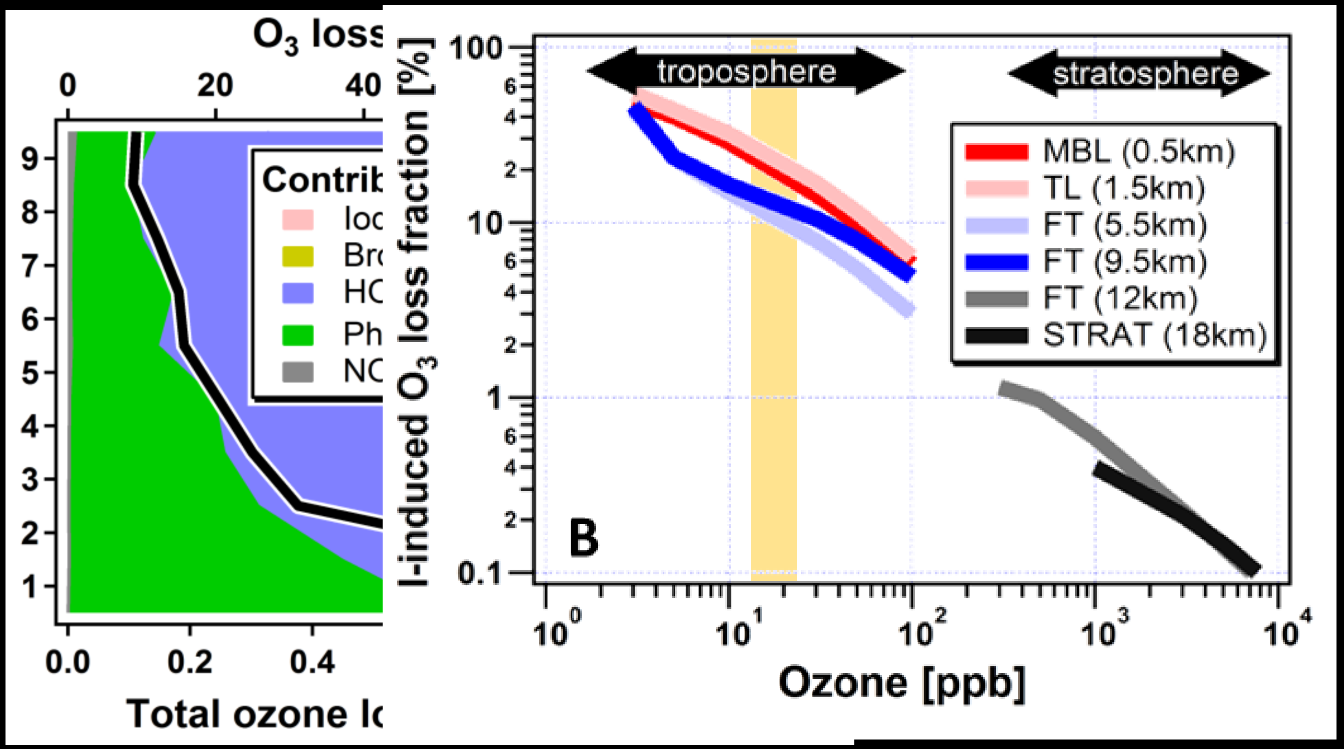
Relevance for ozone loss rates, satellite retrievals, and our perception of iodine sources



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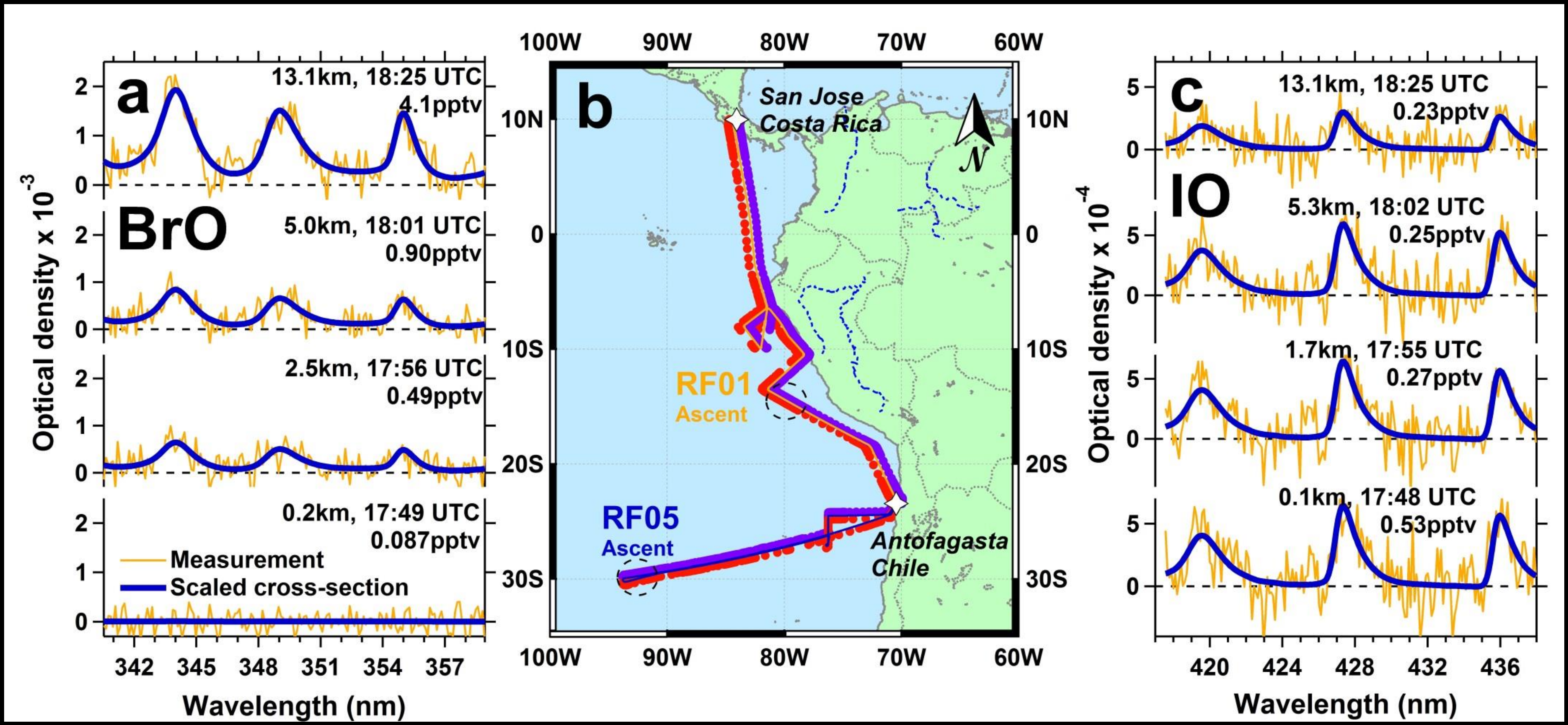
Relevance to CONTRAST

Importance of Aerosol Size Distributions
CH_3I instrument cross-calibrations

Central Pacific: ~0.1±0.04 pptv FT-IO @ <10 km (HEFT-10)
Eastern Pacific: ~0.2±0.04 pptv IO @ 14 km (TORERO)

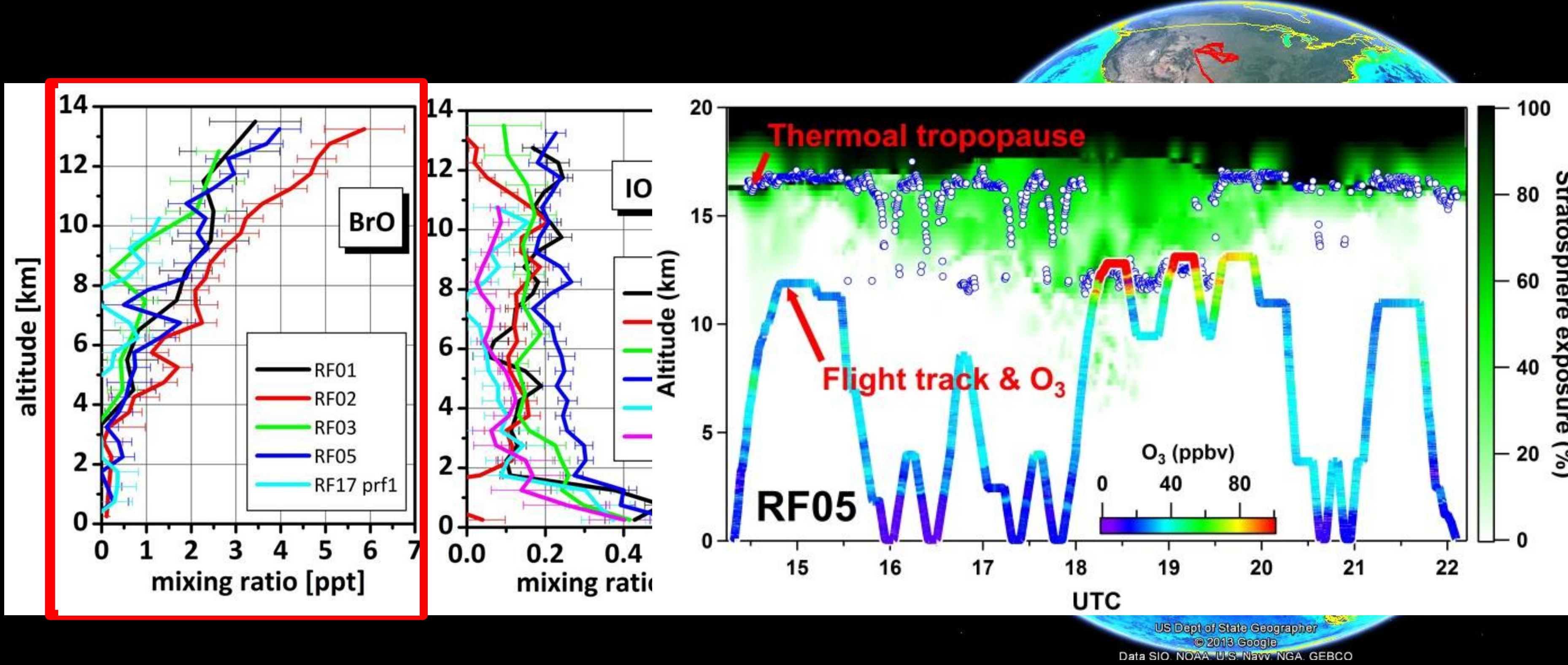
We can not explain the high IO in terms of CH_3I
Relevance of aerosol multiphase recycling reactions!
(Dix et al., 2013 PNAS; Carpenter et al., 2013 Nat-Geo)

3D distributions of BrO and IO



- BrO and IO are widespread in the tropical FT
- Very different vertical distributions! → **different sources**

Widespread BrO, IO, glyoxal, and NO_2 in the FT



- In-situ H_2O, column H_2O, and RAQMS agree well
- IO consistent with HEFT-10, and observed up to 14km
- BrO detected above 4km → strong increase with altitude

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)

TORERO – Maiden Science Mission

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

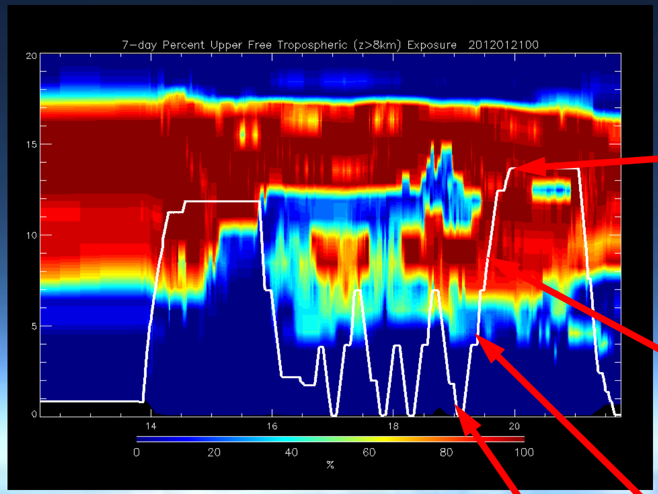
CU AMAX - DOAS

Volkamer group

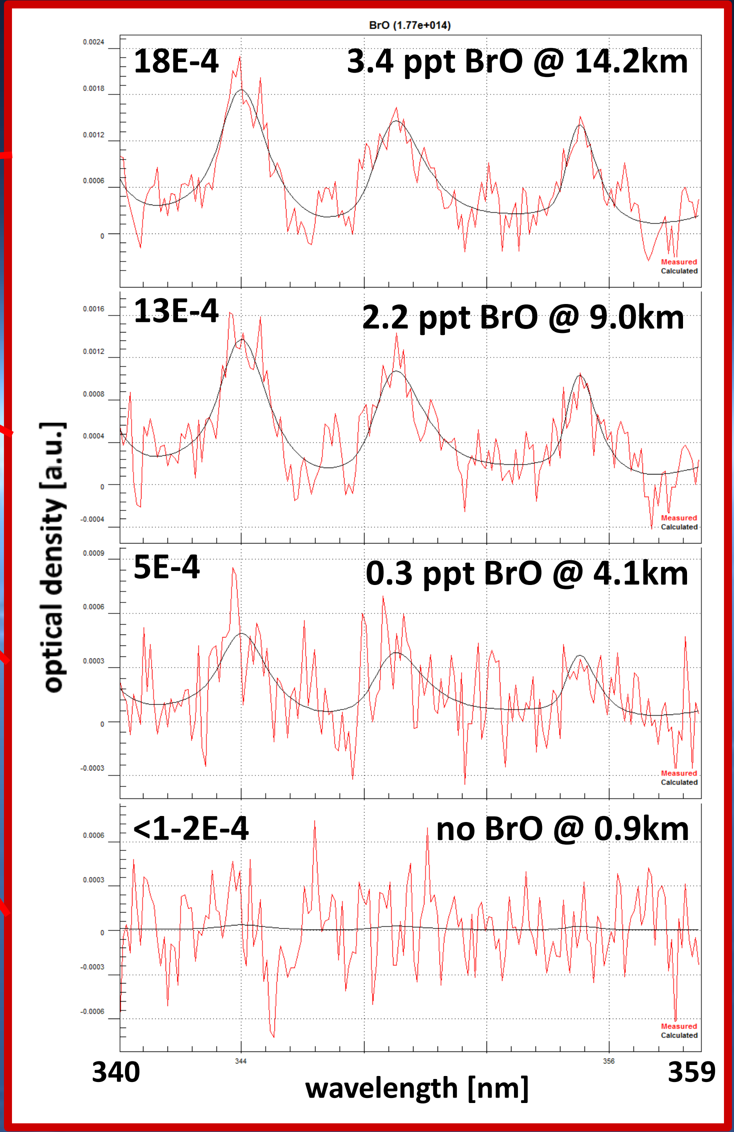
Parameters measured by CU AMAX-DOAS	Detection limit* / Accuracy
BrO	0.3 ppt **
IO	0.05 ppt
HCHO	100 ppt
CHOCHO	3 ppt
H_2O	5 ppm (590nm)
NO_2	10 ppt
OClO	0.7 ppt
HONO	12 ppt
Aerosol extinction from O_4 at 360, 477, and 577nm	0.01 - 0.03 km^{-1}

Profile Scan: 0.5 - 2 min, Vertical Resolution ~ few 100 m

Spectral proof of BrO in the tropical FT



BrO measured by CU AMAX-DOAS



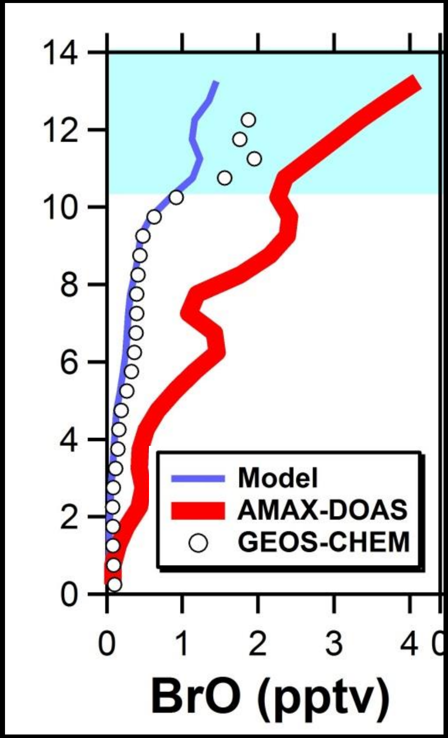
BrO is detectable over most of the tropospheric air column

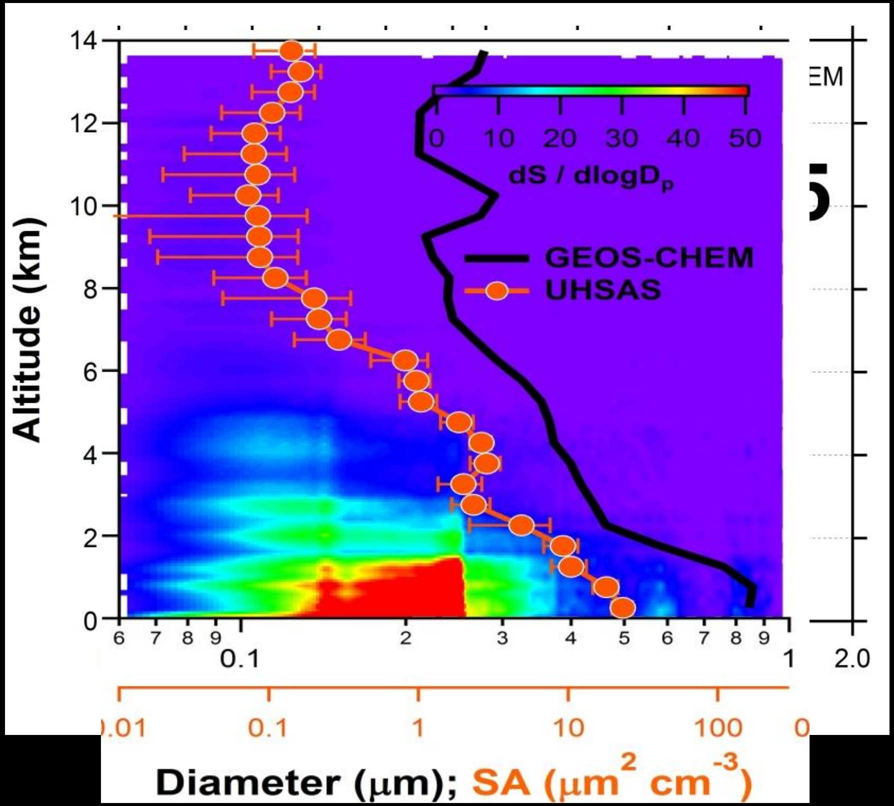
- ~ 0.3 ppt BrO in lower FT (4.1km)
- ~ 3.4 ppt BrO above 14km

DOAS detection limit:

~ 0.3 ppt BrO @ 1min data

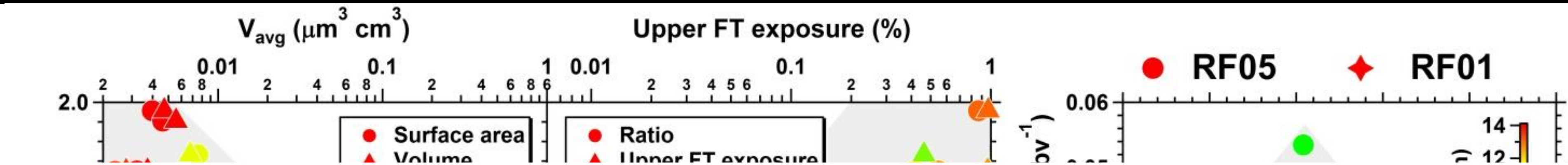
Case study RF05: GEOS-Chem & 1D box-model
What is the most likely source?



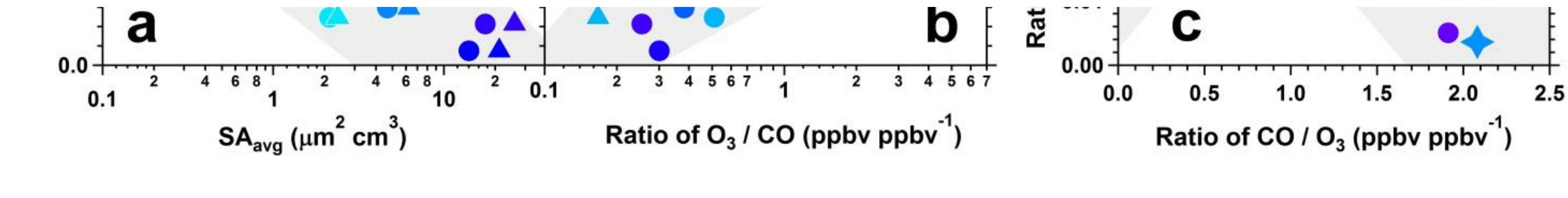


- GEOS-Chem predicts $CHBr_3$ and CH_2Br_2 well (within 30%)
- Aerosol surface area overpredicted (factor 2-10)
- **Organohalogens + sea salt aerosol debromination explain the minor share (~30%) of the observed tropospheric BrO!**

BrO and IO comparison RF01 and RF05



BrO in the upper tropical FT (10S lat) is connected to the stratosphere –
the mechanism does NOT involve lower tropical FT

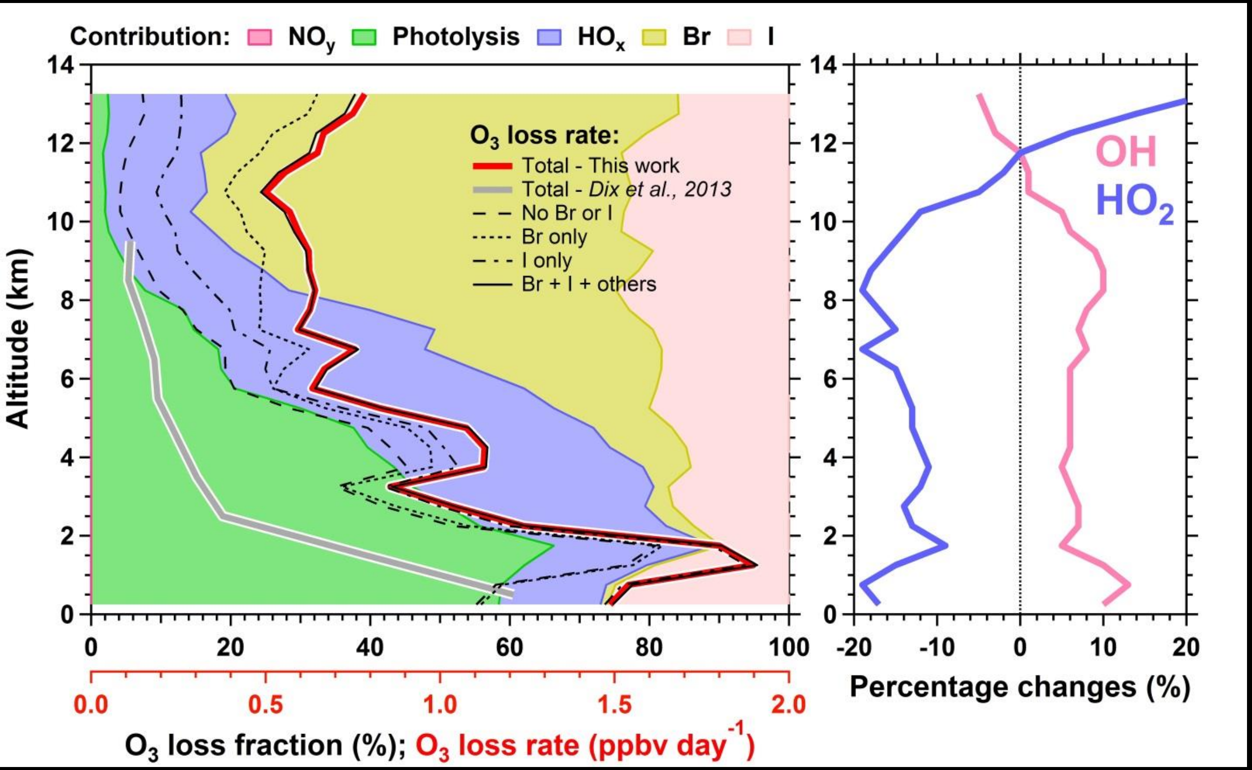


BrO shows little variability, and is observed above 2-4km

IO is slightly more variable, similar to Central Pacific

Unexplained BrO correlates with TTL/stratospheric tracers

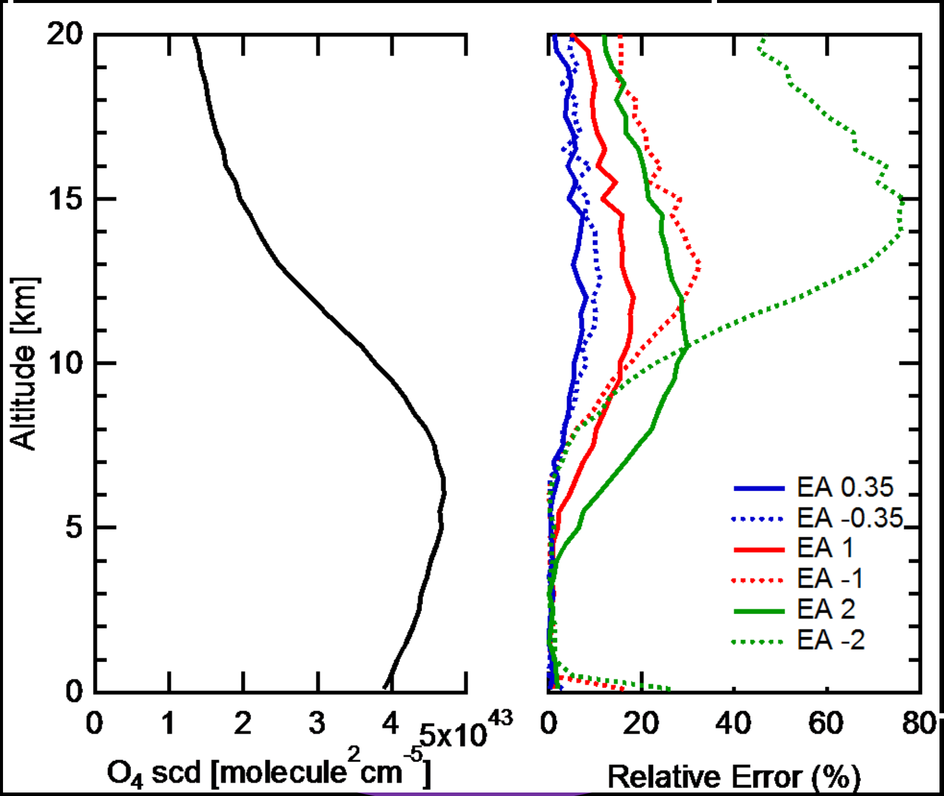
Ozone loss rates in the tropical FT

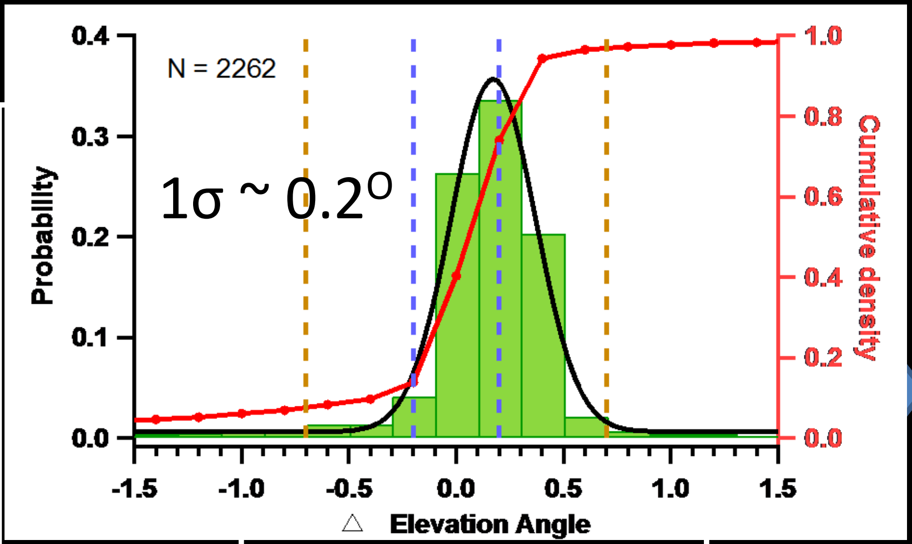


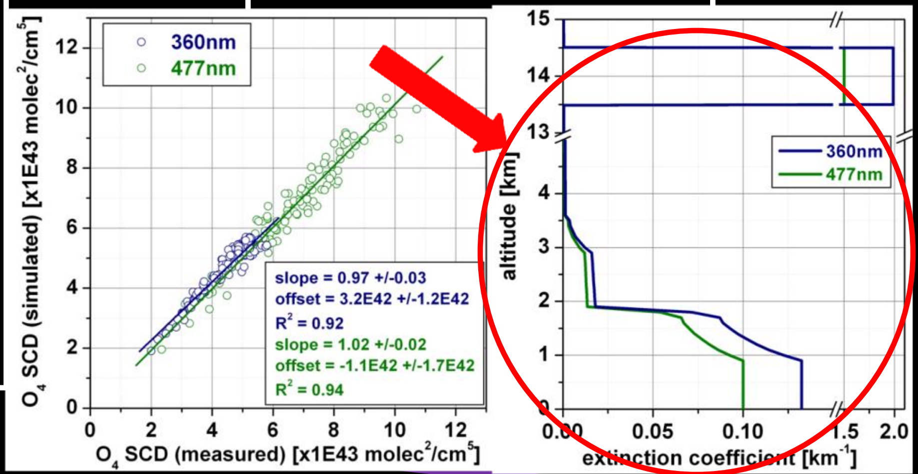
- Halogens are responsible for 33% of the column integral O_3 loss
- Bromine and iodine chemistry are decoupled in the FT
- Halogens account for 5-10% increase in OH radical concentrations (implications for methane lifetime)

Vertical profiles: Non-linear Optimal Estimation

Technological innovation:
Motion stabilization & low RMS







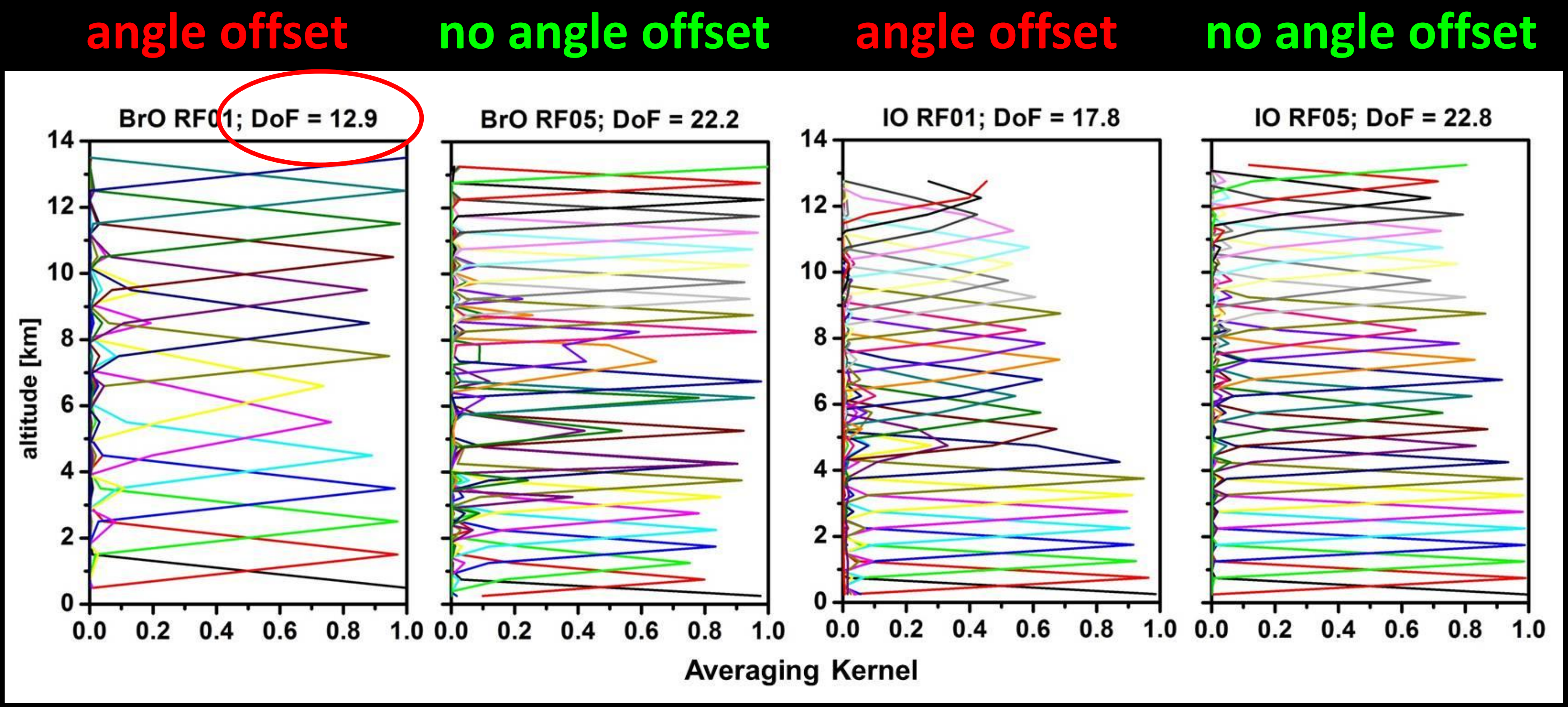
⇒ O_4 observations in a Rayleigh atmosphere & GV C-migit sensor

⇒ Trace gases and aerosol extinction profiles

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

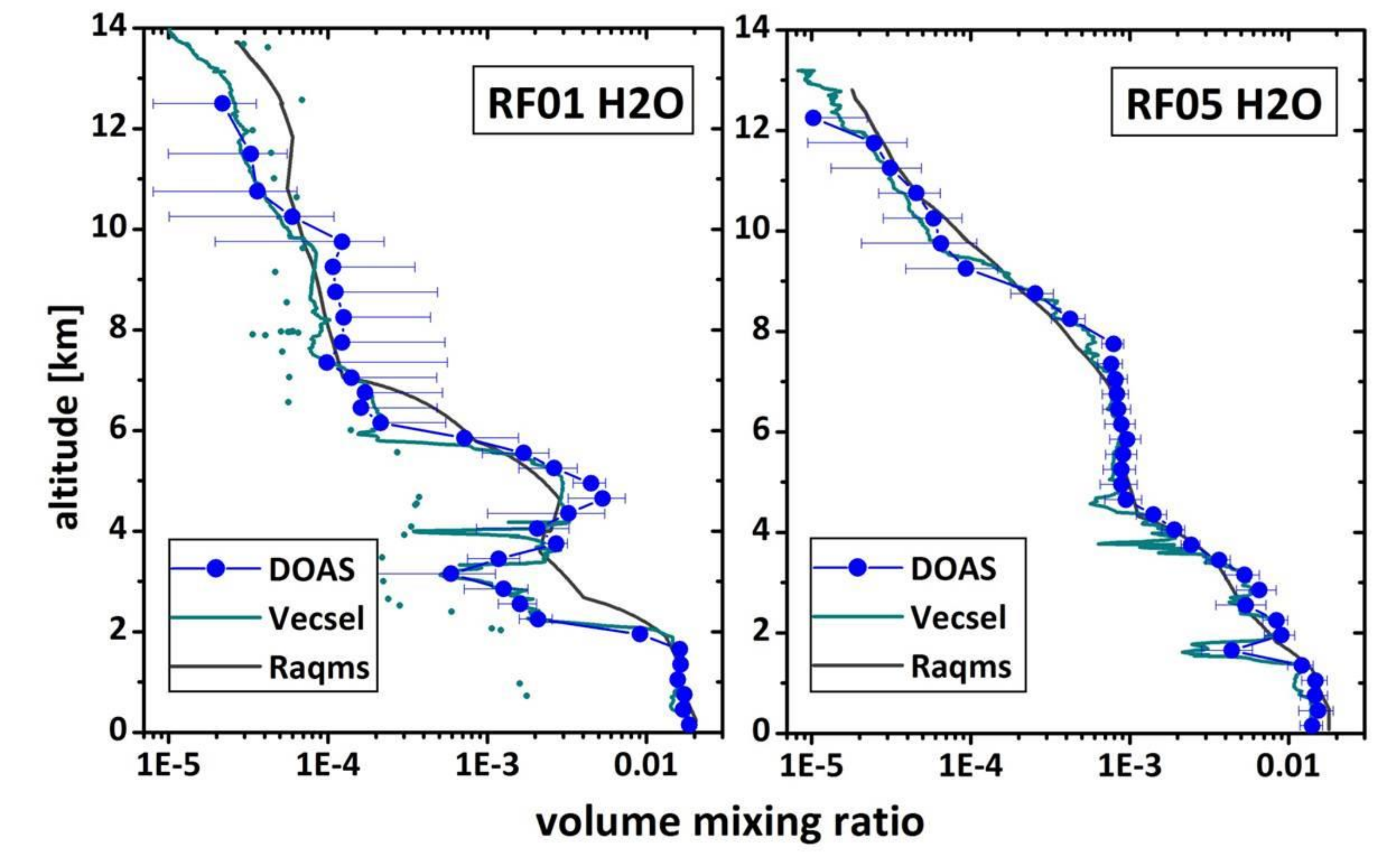
[1] http://rtm.iup.uni-heidelberg.de/McArtim
[2] Rodgers (2000)

Effect of motion sensor performance



- We can compensate by modified inversion grid
- For optimal performance: we need post flight model atmosphere early to assess the sensor performance

H_2O as transport tracer & RTM control



- Remote sensing & *in-situ* are complementary (also for other species)
- Bridge spatial scales → measurement: ~40-200 km → benefit!
- Develop an 'instrument mask' for best measurement & model integration

Reality/Constraints from NSF funding

- NSF cut all PI budgets (3yr -> 2yr project or >40% analysis time)
- SoW impact:
  - "The data analysis is limited to flights with more than 1hr daylight."
  - "Final data will be available ~1.5 years after the field campaign."
  - We plan to provide dSCD data for BrO and IO with AMAX-DOAS participation (24-48 hr), and are making progress towards NRT-RTM

→ TORERO algorithms accelerate our analysis substantially

→ Note to PIs:

- → We need quick turn-around WACCM model output for NRT-RTM
  - → NetCDF flight track through 6/12 hr forecast → when available?
- → Budget limitations will require us to compromise
  - → Which flights should we focus on?
  - → Does AMAX-DOAS participate in night time/twilight flights?

TORERO findings relevant to CONTRAST

- Bromine sources & heterogeneous reaction rates:
  - UHSAS → rates of multiphase recycling reactions
  - MTP ? → Tropopause structure → bromine sources from stat. ?
  - Instrument mask → integrate remote sensing & *in-situ* & model
  - CCl_4, and other stratospheric tracers ?
  - Stratospheric tracer release during forcast ?
- Relevance of OVOC for bromine chemistry?
  - No inlet with AMAX-DOAS – benefit to measure OVOC
  - Synergies with TOGA
- AMAX needs (relevant to flight planning):
  - Reference spectrum above cloud deck
  - Vertical profiles:
    - No need for level legs during ascent/descent
    - continuous climb preferred (constant heading en-route)
  - Model output for NRT-RTM

TORERO RF17

GEOS-Chem

WACCM