Measurements of bromine oxide, iodine oxide and oxygenated hydrocarbons in the tropical free troposphere from research aircraft and mountaintops

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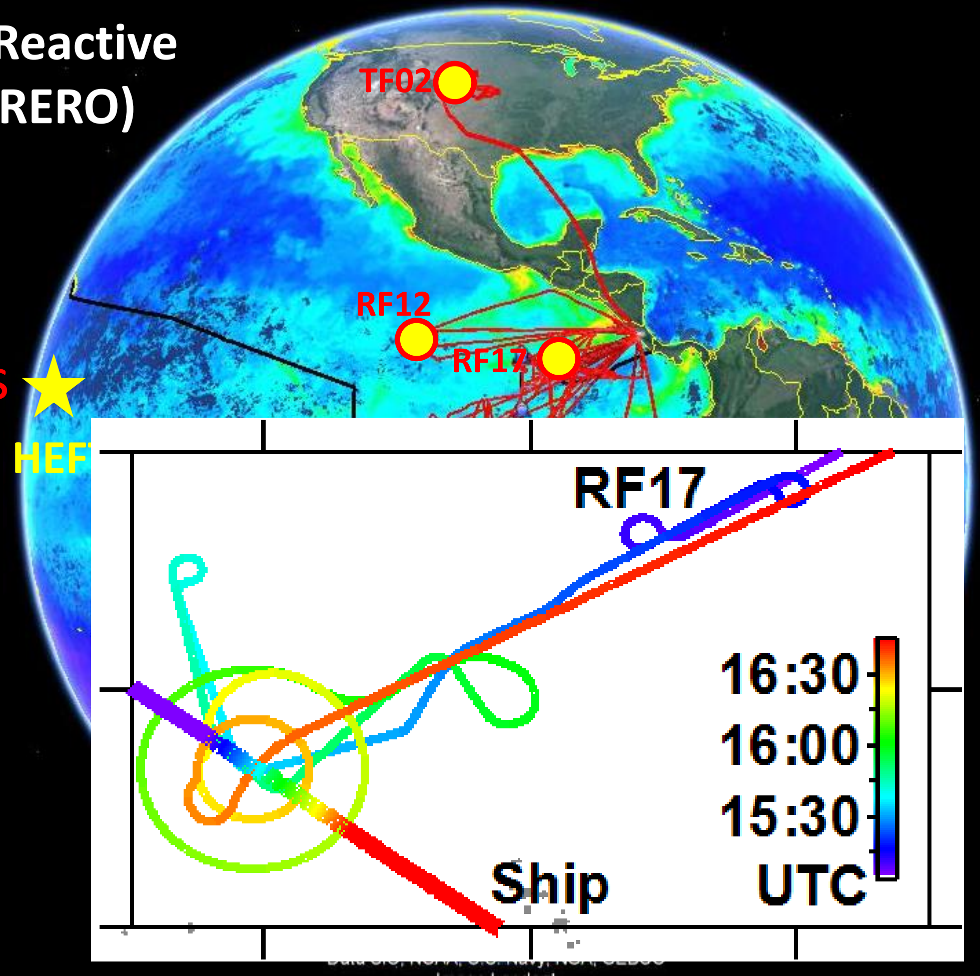
Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC (TORERO)

1. Instrumentation
2. Field measurements of short-lived oxygenated hydrocarbons
3. BrO vertical profiles in the tropical free troposphere
4. Comparisons of in-situ and remote-sensing



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

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}

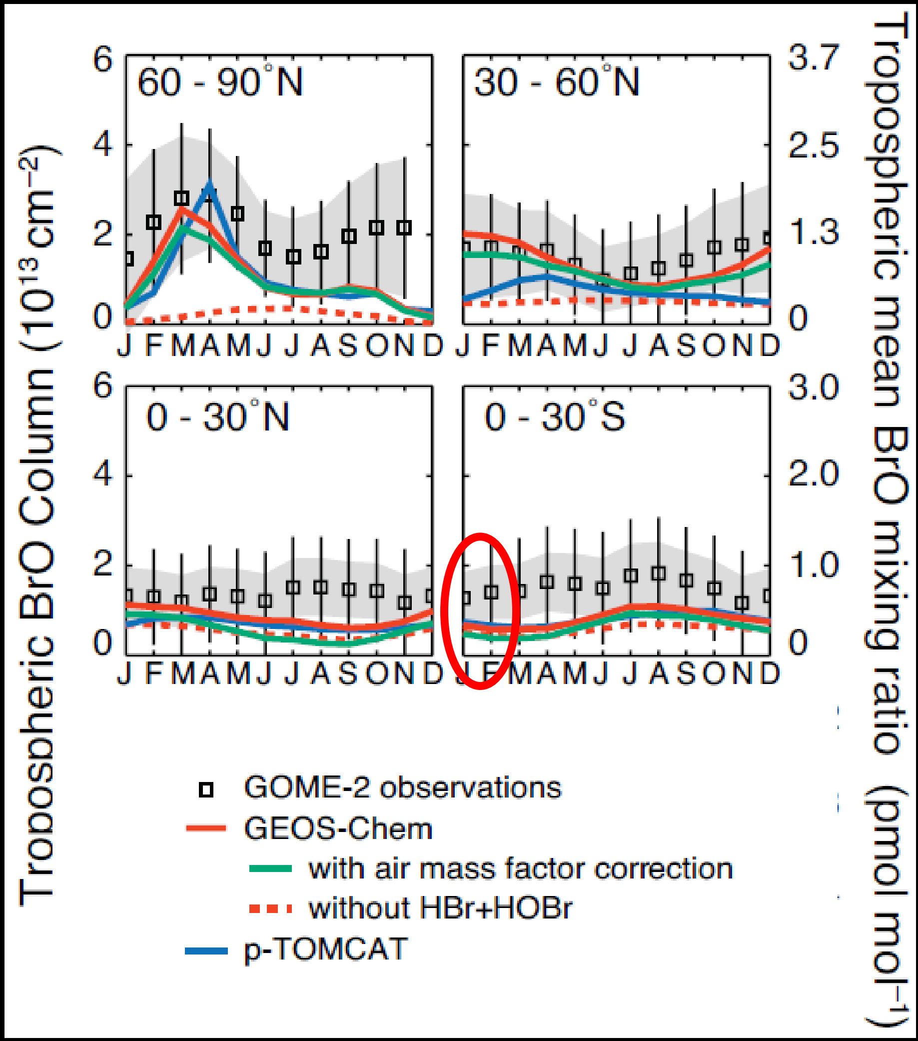
(Hendrick et al., 2007; Theys et al., 2007; Coburn et al., 2011; Coburn et al., 2014, in prep.)

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]

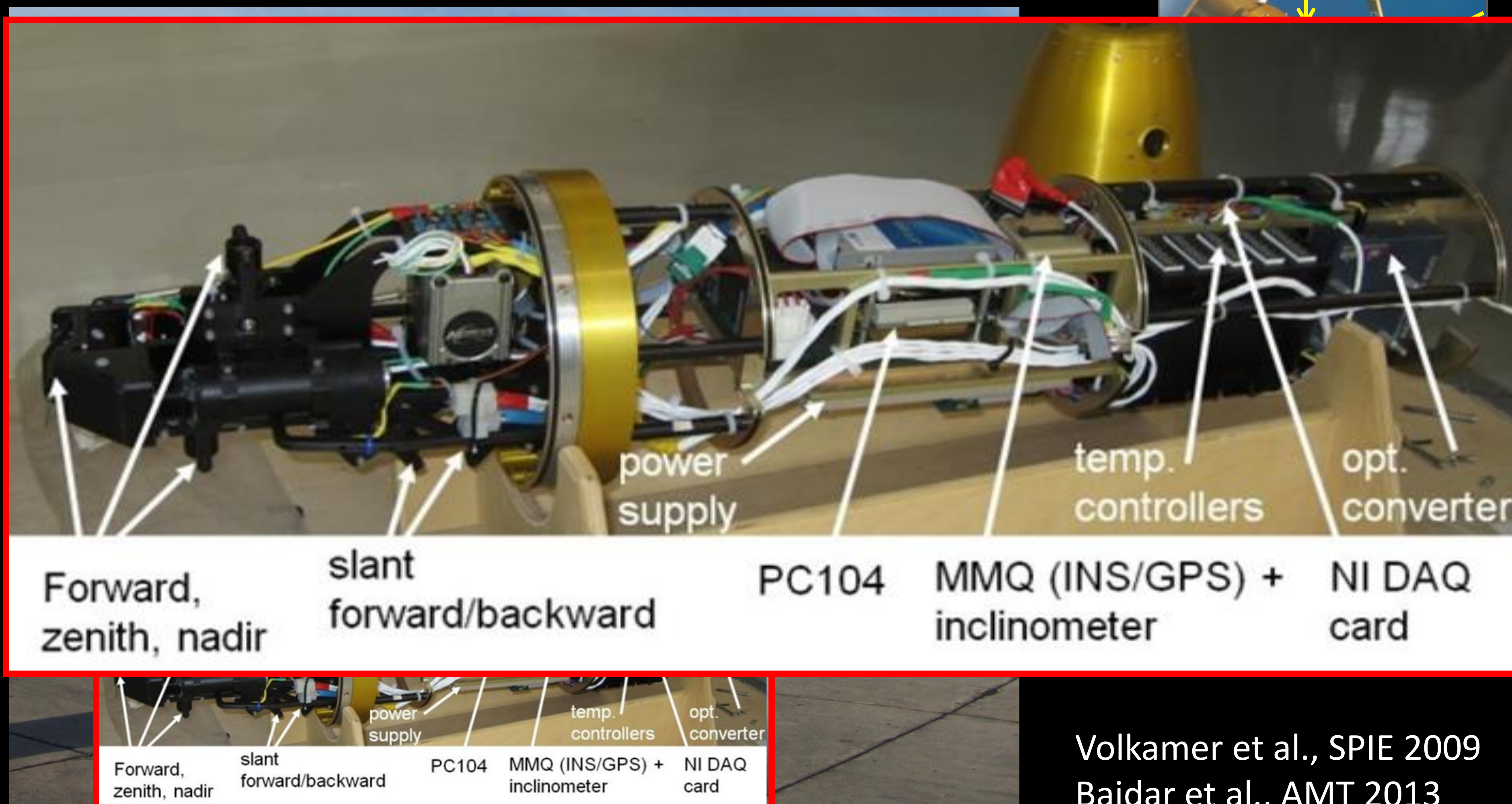
Halogens deplete the O_3 column by ~10% in the tropics (Saiz-Lopez et al., 2012)

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

CU-AMAX-DOAS instrument aboard NSF/NCAR GV

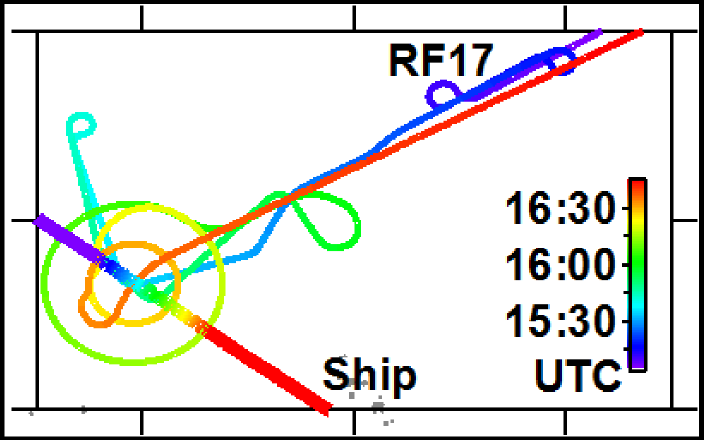
University of Colorado Airborne Multi-AXis Differential Optical Absorption Spectroscopy

Telescope pylon

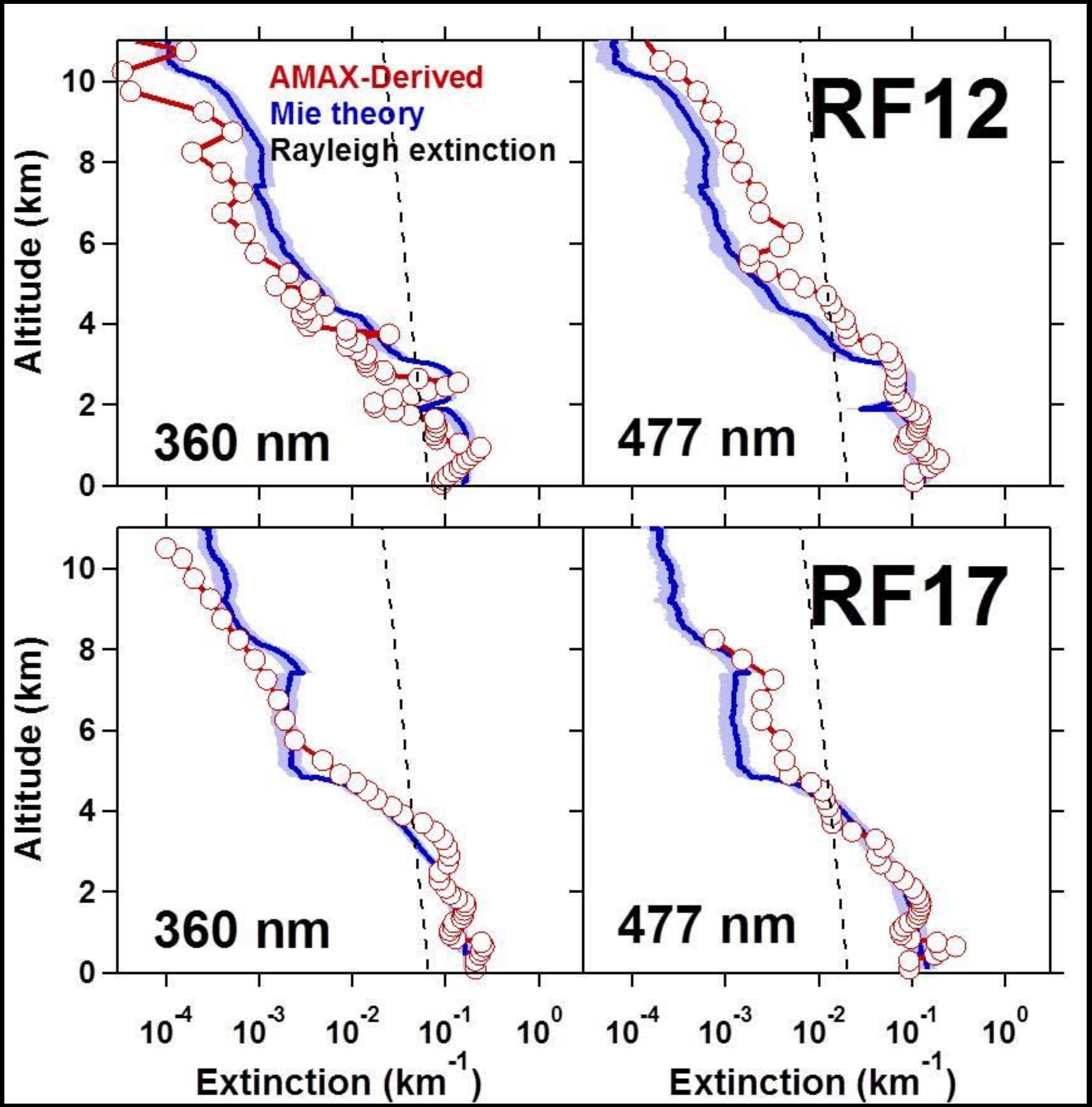


Volkamer et al., SPIE 2009
Baidar et al., AMT 2013

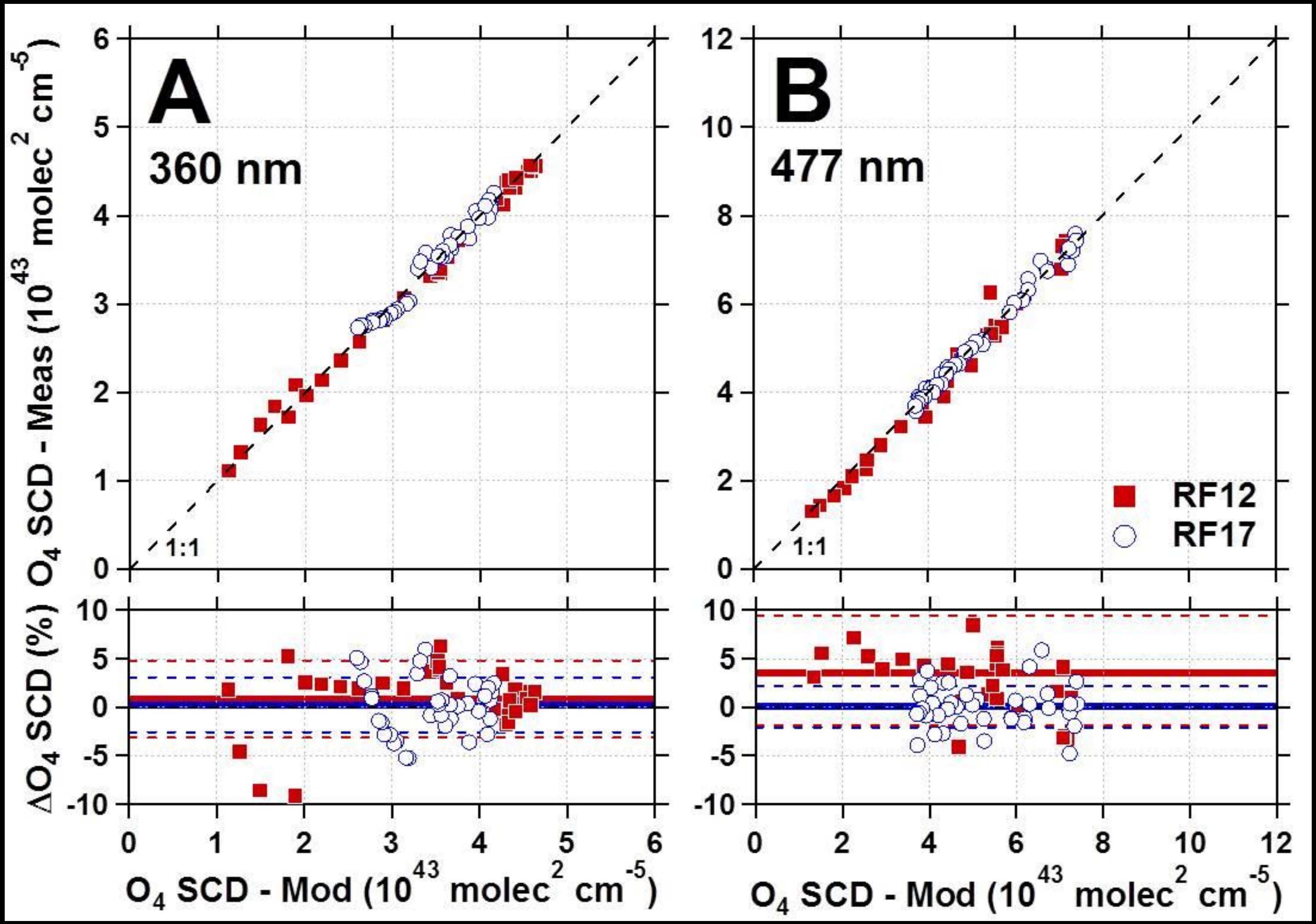
Comparison extinction profiles from Mie & AMAX



- Mie calculations of extinction (UHSAS size-distributions) agree well with the O_4 inferred extinction

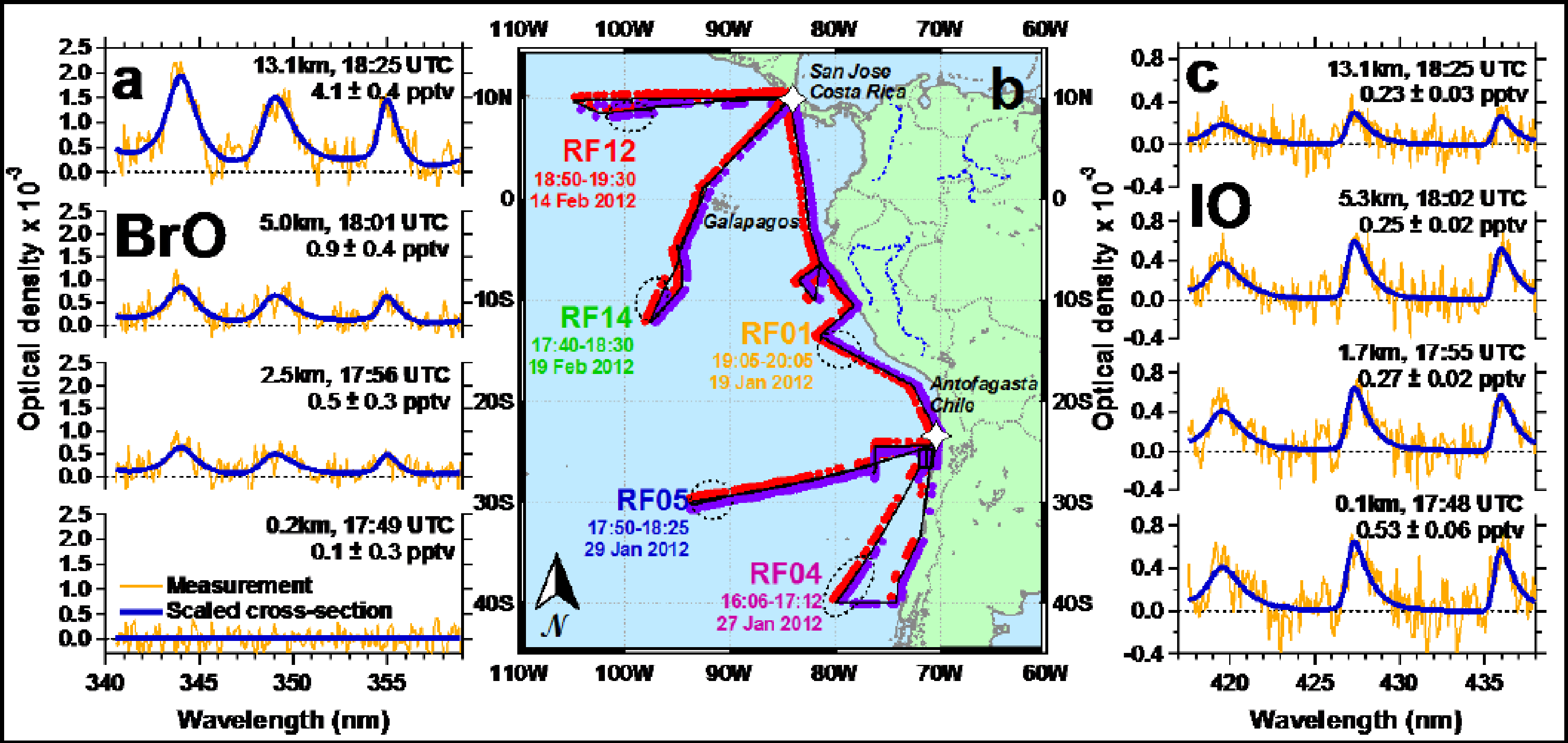


Comparison O_4 SCDs: AMAX & McArtim RTM



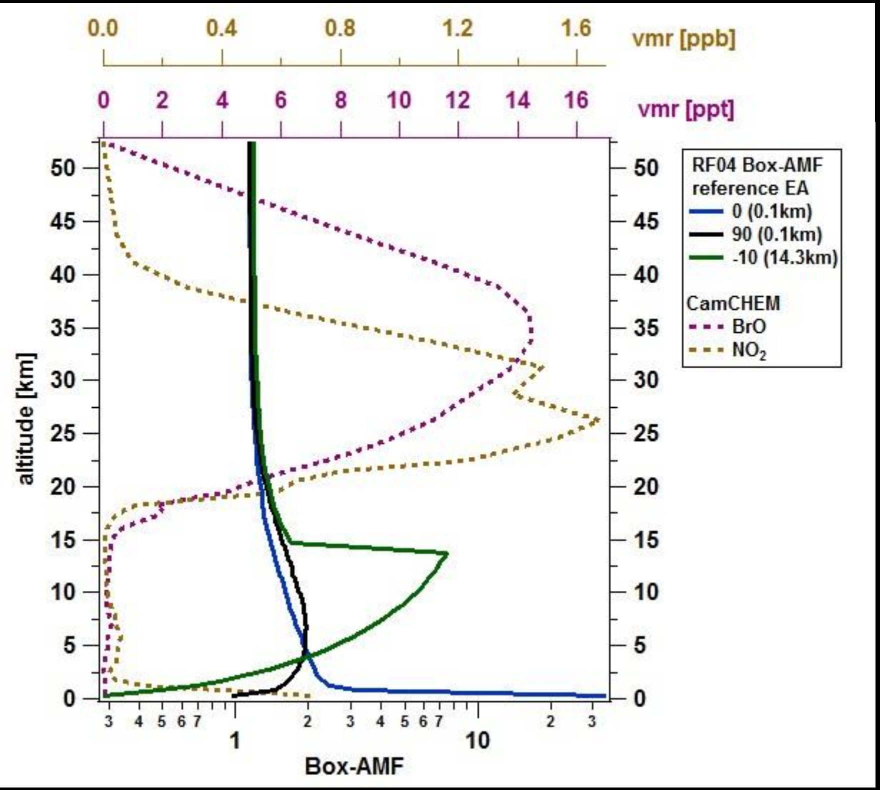
- Agreement generally better 5%
- No need for a correction factor

BrO and IO detection SH tropical troposphere

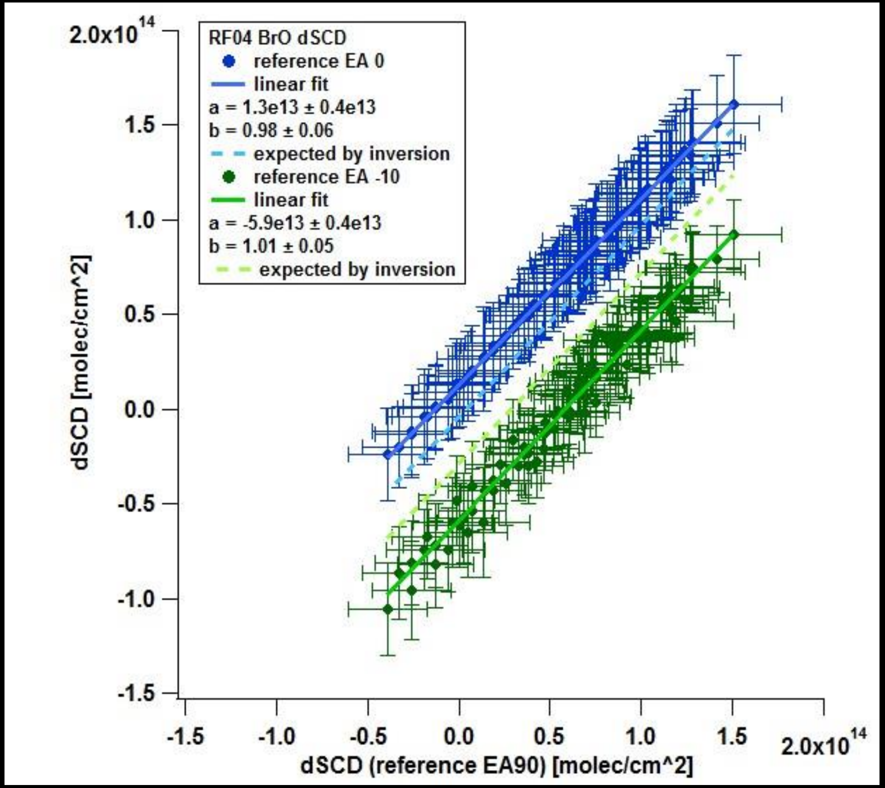


- NH/SH tropics: (1.5 ± 0.3) x10^{13} molec cm^{-2}
- SH sub-tropics: (1.7 ± 0.3) x10^{13} molec cm^{-2}
- SH mid-latitudes: (1.0 ± 0.3) x10^{13} molec cm^{-2}

BrO retrieval - robustness



stratospheric correction

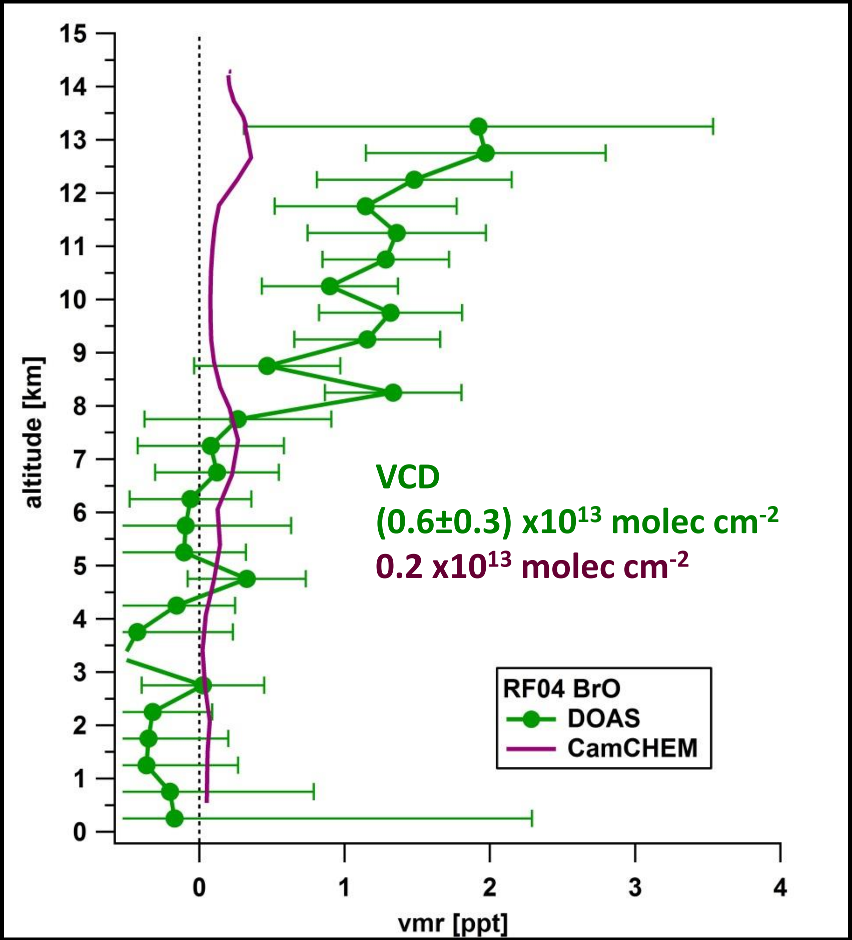


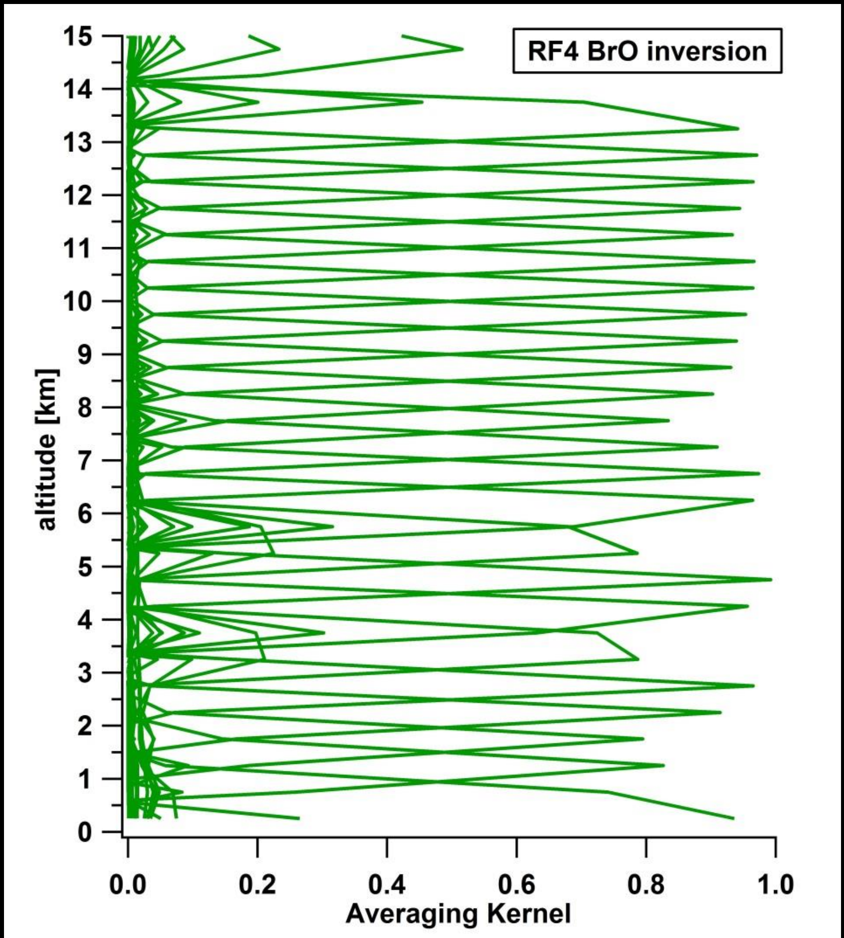
consistency between references

→ stratospheric contributions are reliably cancelled out

→ consistent dSCD offset between different reference geometries

RF04 BrO vertical profile

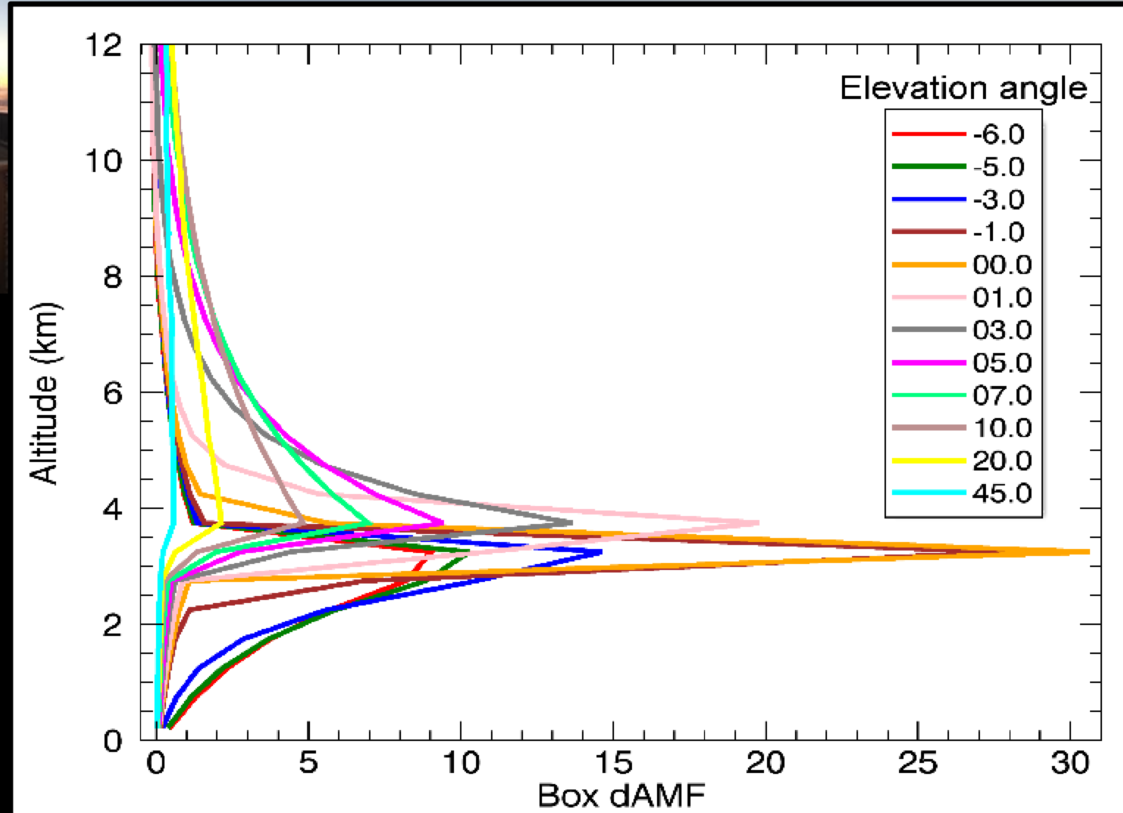


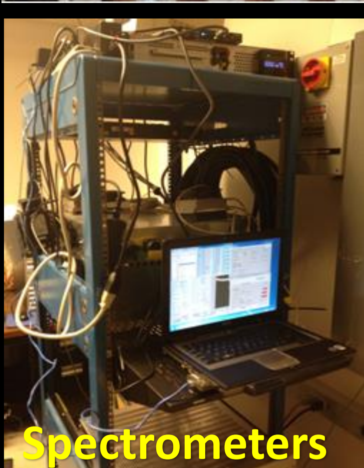


→ high DoFs; inversion is fully constrained by measurements

→ observed BrO underestimated in upper FT by model

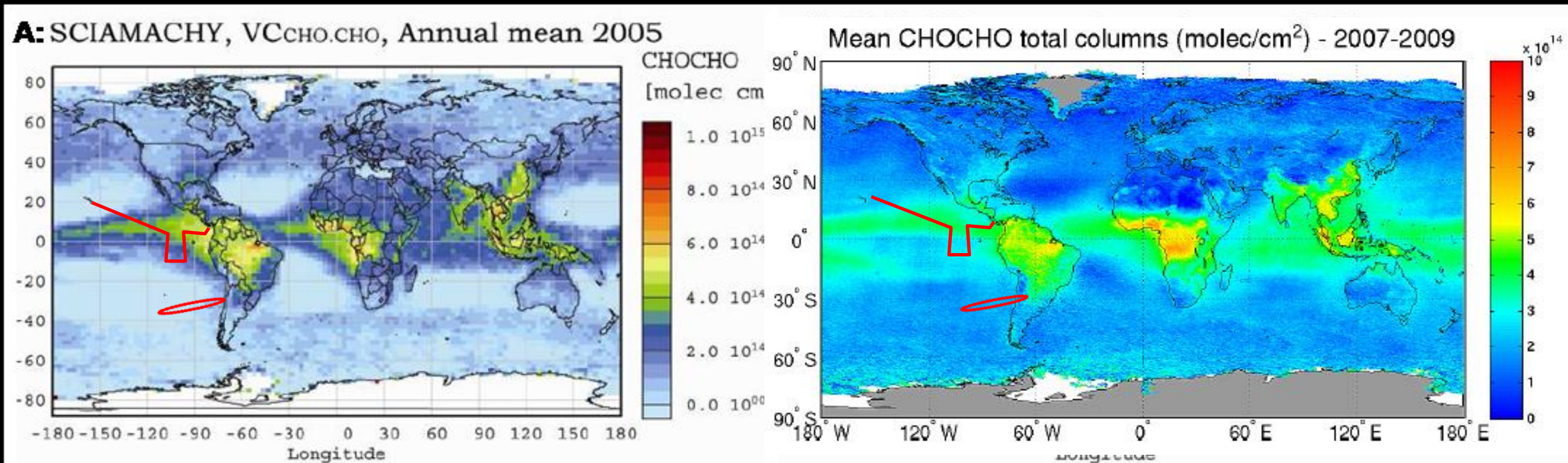
Mauna Loa Observatory, Hawaii





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

Satellites show widespread glyoxal over oceans, but disagree over the remote ocean



Wittrock et al., 2006; Myriokefalitakis et al., 2008; Sinreich et al., 2010; Lerot et al., 2010

Atmospheric models do not predict any glyoxal over oceans

Continental source: ~45 TgC/yr

- **50% unaccounted**
- **30% biogenic (i.e. isoprene)**
- **14% anthropogenic**
- **6% biomass burning**

Atmospheric lifetime: ~ 2.5hrs

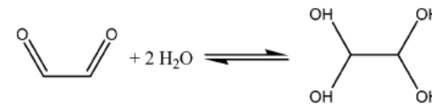
- **52% photolysis**
- **18% OH**
- **22% SOA in clouds/aerosols?**
- **8% Dry/wet deposition**

Stavrakou et al., 2009

Atmos. Meas. Tech., 7, 1–17, 2014
www.atmos-meas-tech.net/7/1/2014/
doi:10.5194/amt-7-1-2014

Atmospheric Measurement Techniques
Open Access

Measurements of diurnal variations and eddy covariance (EC) fluxes of glyoxal in the tropical marine boundary layer: description of the Fast LED-CE-DOAS instrument



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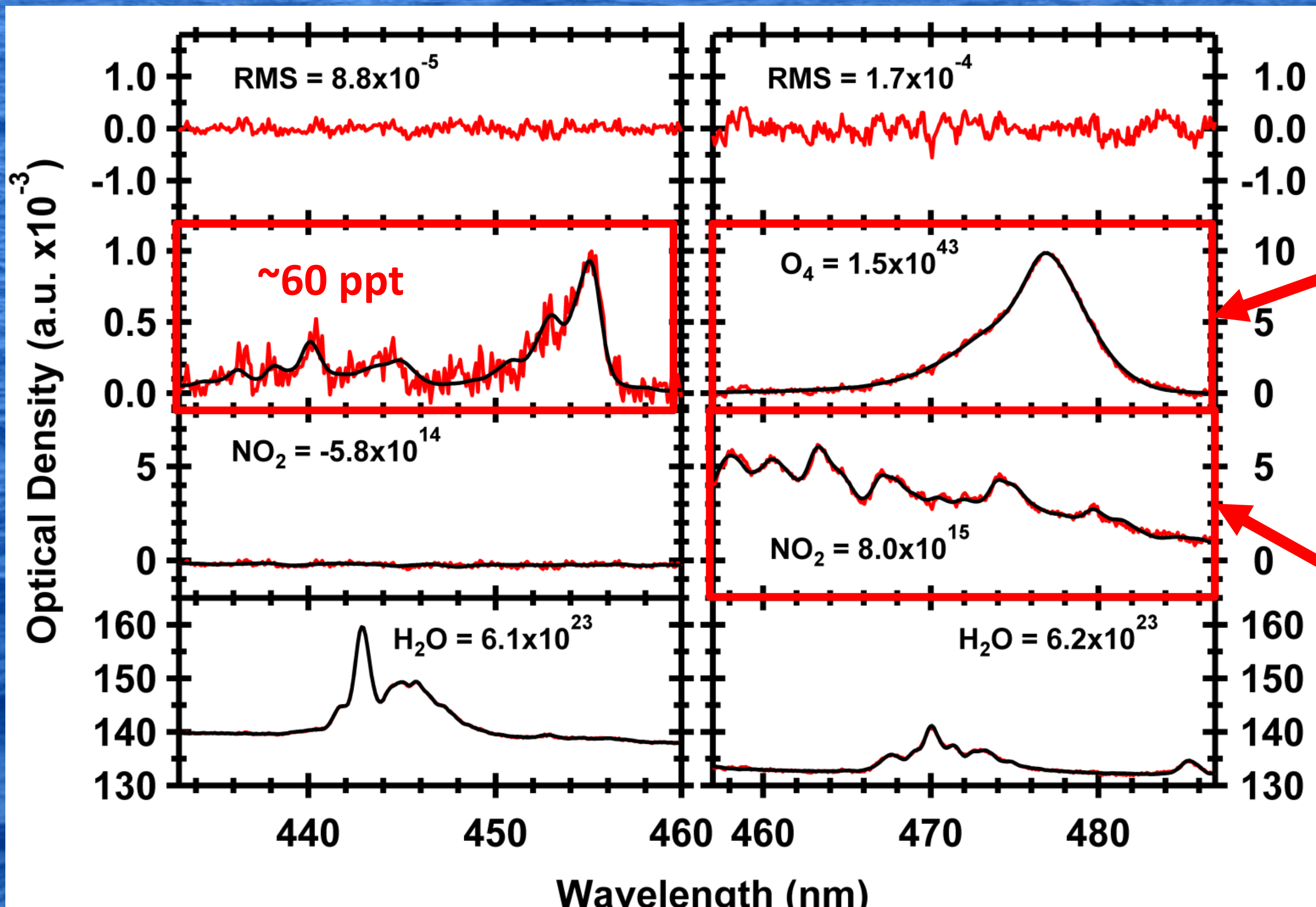
Unique information about marine organic carbon sources

Molecule	MBL concentration (pptv)	K_H (M atm^{-1})	Lifetime* (days)	reference flux Measurement in MBL
CO_2	380–400 ($\times 10^6$)	0.035	$> 3 \times 10^5$	Fairall et al. (2000)
CO	60–150 ($\times 10^3$)	1×10^{-3}	16	Blomquist et al. (2012)
Acetone	700–900	30.3	10	Marandino et al. (2005)
O_3	10–30 ($\times 10^3$)	0.011	6	Bariteau et al. (2010)
Methanol	300–900	222	4	Yang et al. (2013)
DMS	20–1500	0.485	0.8	Hubert et al. (2004)
Acetaldehyde	200–300	14.1	0.2	Yang et al. (2014)
Glyoxal	25–80	4.2×10^5	9×10^{-2}	This work

Coburn et al., 2014, AMT

Fast LED-Cavity Enhanced DOAS instrument



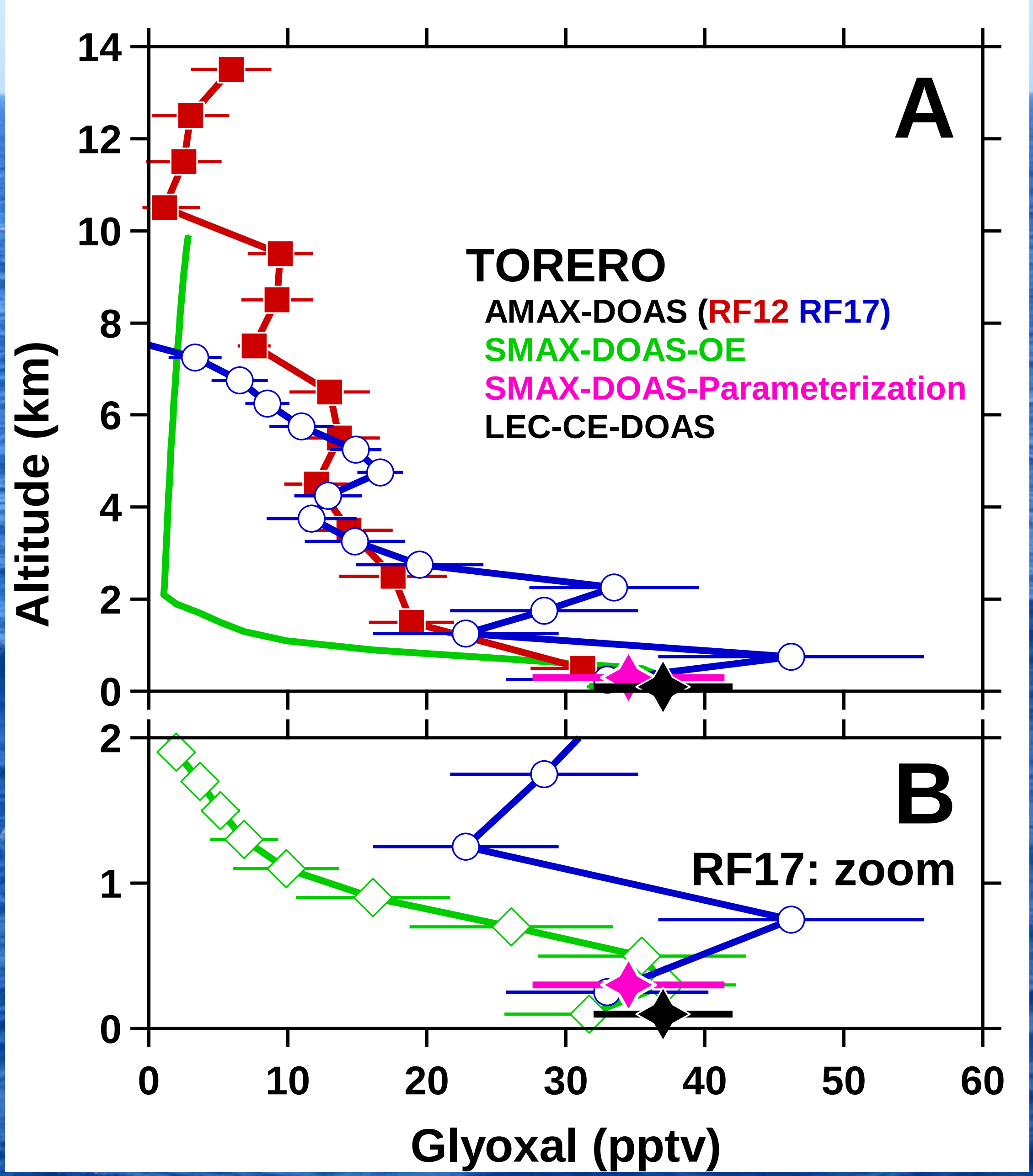
O_4 measurements for instrument characterization

NO_2 measurements for data filtering

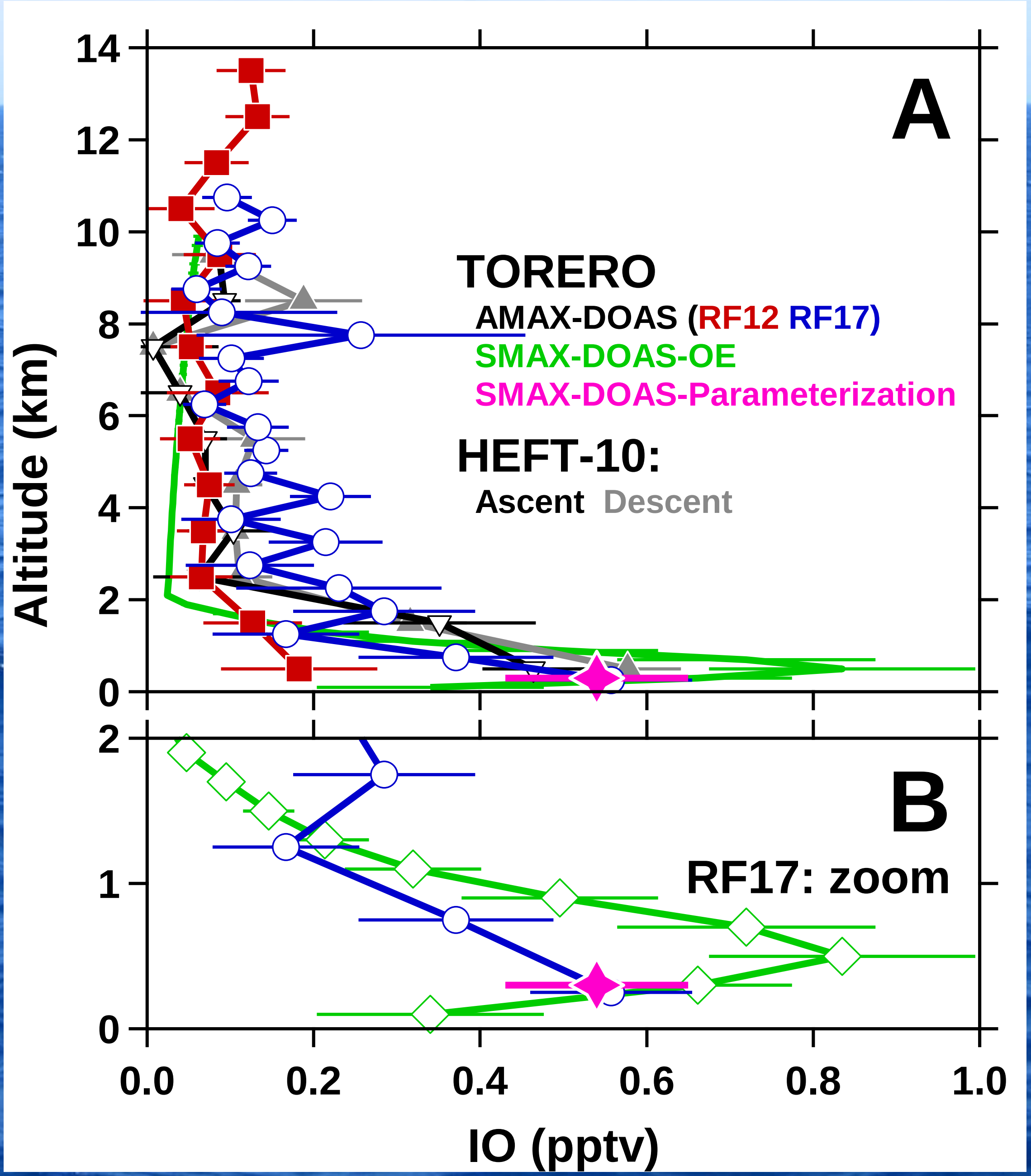
Sensitivity glyoxal: 40 ppt $s^{-1/2}$

Coburn et al., 2014, AMT

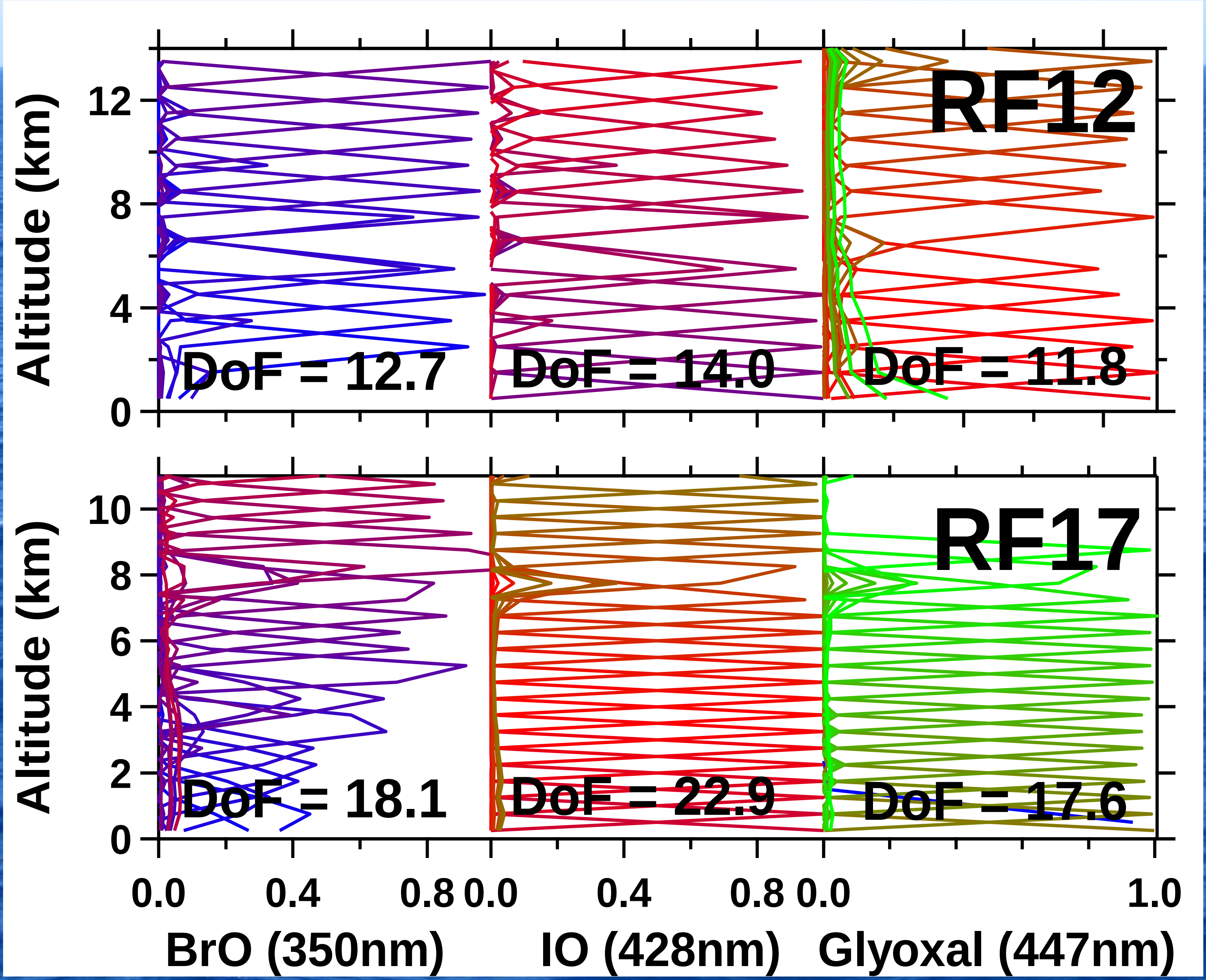
Comparison in-situ and remote sensing (CHOCHO)



Comparison Ship and AMAX remote sensing (IO)



AVKs: BrO, IO, CHOCHO



Conclusions

- *First BrO vertical profiles by limb-sounding in the tropical FT show elevated BrO in higher than expected amounts that support the ubiquitous presence of bromine in the uFT*
  - *BrO dSCDs are robust*
  - *RTM is well constrained*
  - *Profiles are well constrained -- BrO: 13-18 DoF*

- *IO and CHOCHO are widespread in the tropical FT*
  - *Most of the IO and CHOCHO reside in the FT*
  - *3 instruments (in-situ and remote sensing) agree well in remote MBL for CHOCHO (and not so well for IO)*
  - *Significant differences between ship- and airborne profile retrievals*
  - *Profiles are very well constrained from airborne limb measurements*

    CHOCHO: 14-23 DoF

    IO: 12-18 DoF

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Acknowledgements: NCAR/EOL and RAF, TORERO team

Selected recent publications

O_4 and radiative transfer:

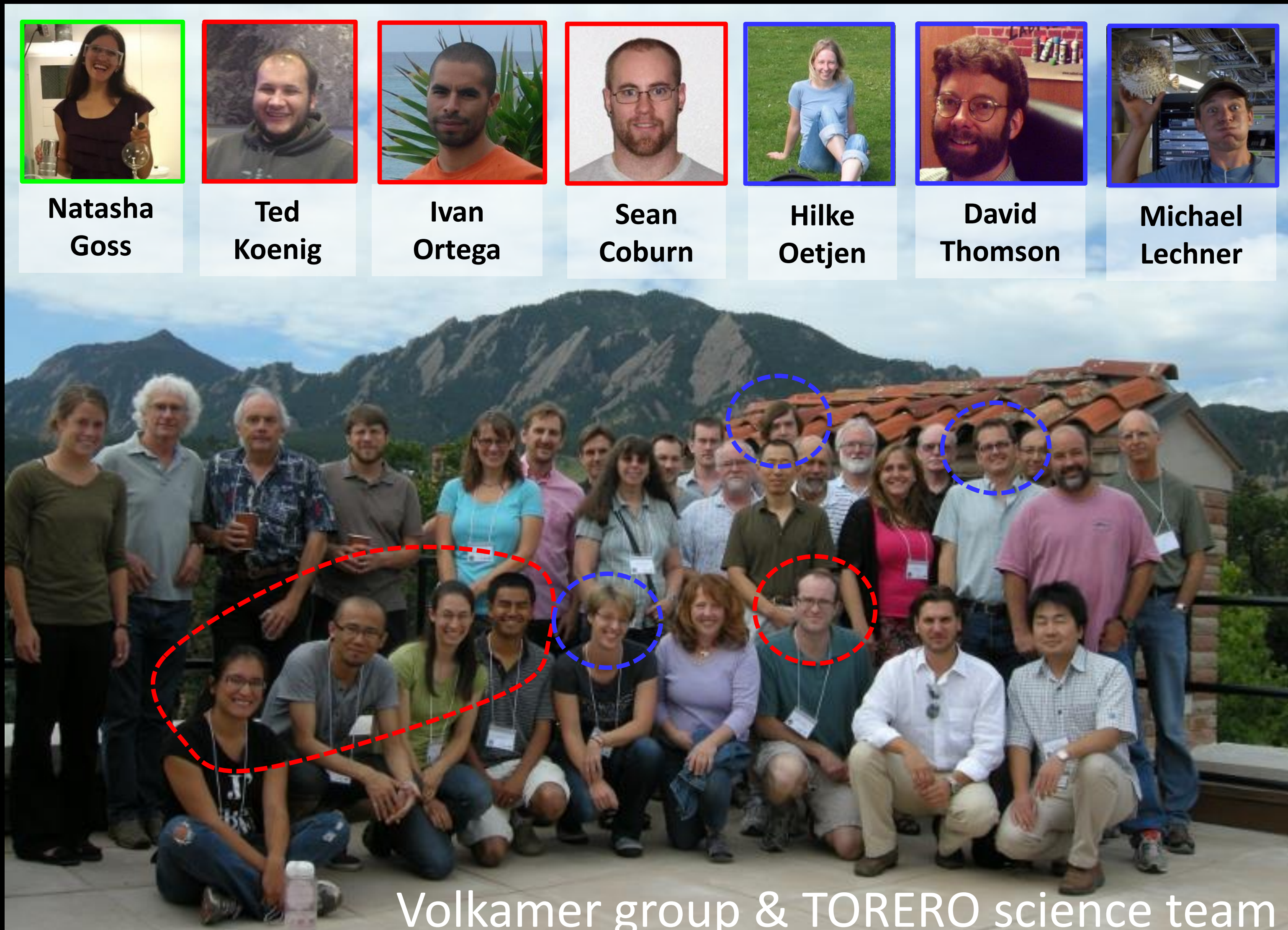
- Spinei et al., Direct sun and airborne MAX-DOAS measurements of the collision induced oxygen complex, O2O2, absorption with significant pressure and temperature differences. 2014, Atmos. Meas. Tech. Discuss., 7, 10015-10057, 2014.
- Thalman, R., K. Zarzana, M.A. Tolbert and R. Volkamer, Rayleigh scattering cross-section measurements of nitrogen, argon, oxygen and air. 2014, JQSRT, 147, 171-178.
- Thalman, R. and R. Volkamer. Temperature Dependant Absorption Cross-Sections of O2-O2 Collision Pairs between 340 and 630 nm at Atmospherically Relevant Pressure, 2013, PCCP, 15(37), 15371-15381.

Instruments & intercomparisons:

- Coburn et al., Measurements of diurnal variations and Eddy Covariance (EC) fluxes of glyoxal in the tropical marine boundary layer: description of the Fast LED-CE-DOAS instrument. 2014, Atmos. Meas. Tech., 7, 3579-3595.
- Thalman et al., Instrument inter-comparison of glyoxal, methyl glyoxal and NO2 under simulated atmospheric conditions. 2014, *Atmos. Meas. Tech. Discuss.,*7, 8581-8642.
- Ortega et al., The CU Two Dimensional MAX-DOAS instrument - part 1: retrieval of NO2 in 3 dimensions and azimuth dependent OVOC ratios. 2014, Atmos. Meas. Tech. Disc., in press

Applications:

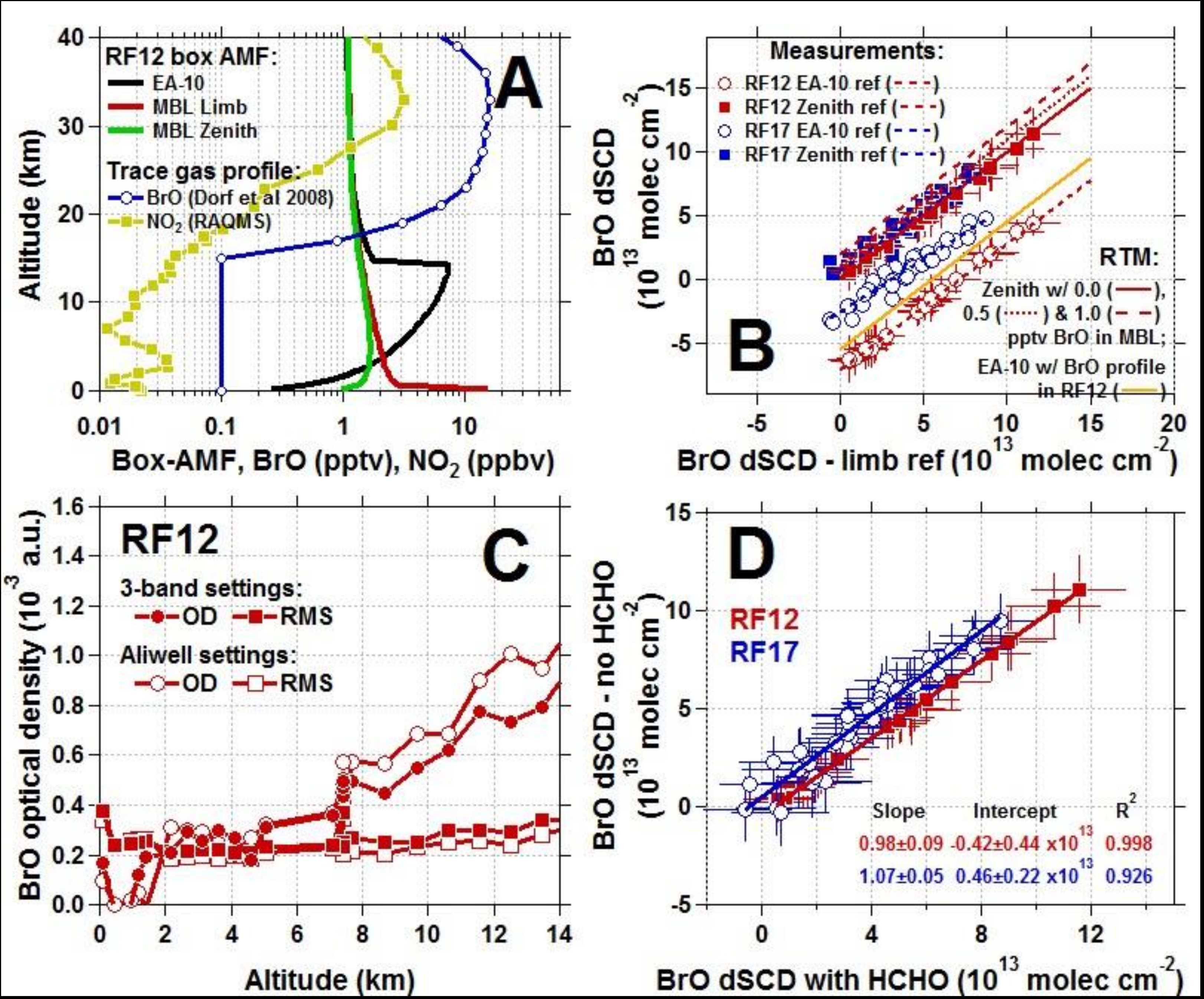
- Baidar et al., Combining Active and Passive Airborne Remote Sensing to Quantify NO2 and Ox Production near Bakersfield, CA, 2013. British J. for Environ. Climate Change, 3(4), 2013, 566-586.



Graduate students (left to right): Laura Gonzalez, Siyuan Wang, Eleanor Waxman, Sunil Baidar, Ryan Thalman; top row (left to right): Ted Koenig, Ivan Ortega, Sean Coburn

Postdocs & senior personnel: Barbara Dix, Christopher Kampf, Roman Sinreich, Hilke Oetjen, Doug Day (not shown), Michael Lechner, David Thomson

Undergraduates: Andrew Hadd, Andrew Hattel, Gregory Humphrey, LeShaun Jones, Natasha Goss (Honors thesis)



A
RF12 box AMF:
EA-10
MBL Limb
MBL Zenith
Trace gas profile:
BrO (Dorf et al 2008)
NO2 (RAQMS)
Altitude (km)
Box-AMF, BrO (pptv), NO2 (ppbv)
B
Measurements:
RF12 EA-10 ref
RF12 Zenith ref
RF17 EA-10 ref
RF17 Zenith ref
RTM:
Zenith w/ 0.0, 0.5 & 1.0 pptv BrO in MBL;
EA-10 w/ BrO profile in RF12
BrO dSCD (10^13 molec cm^-2)
BrO dSCD - limb ref (10^13 molec cm^-2)
C
RF12
3-band settings:
OD
RMS
Aliwell settings:
OD
RMS
BrO optical density (10^-3 a.u.)
Altitude (km)
D
RF12
RF17
Slope
Intercept
R^2
0.98±0.09
-0.42±0.44 x10^13
0.998
1.07±0.05
0.46±0.22 x10^13
0.926
BrO dSCD - no HCHO (10^13 molec cm^-2)
BrO dSCD with HCHO (10^13 molec cm^-2)