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

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MLO (since Jan 2014)

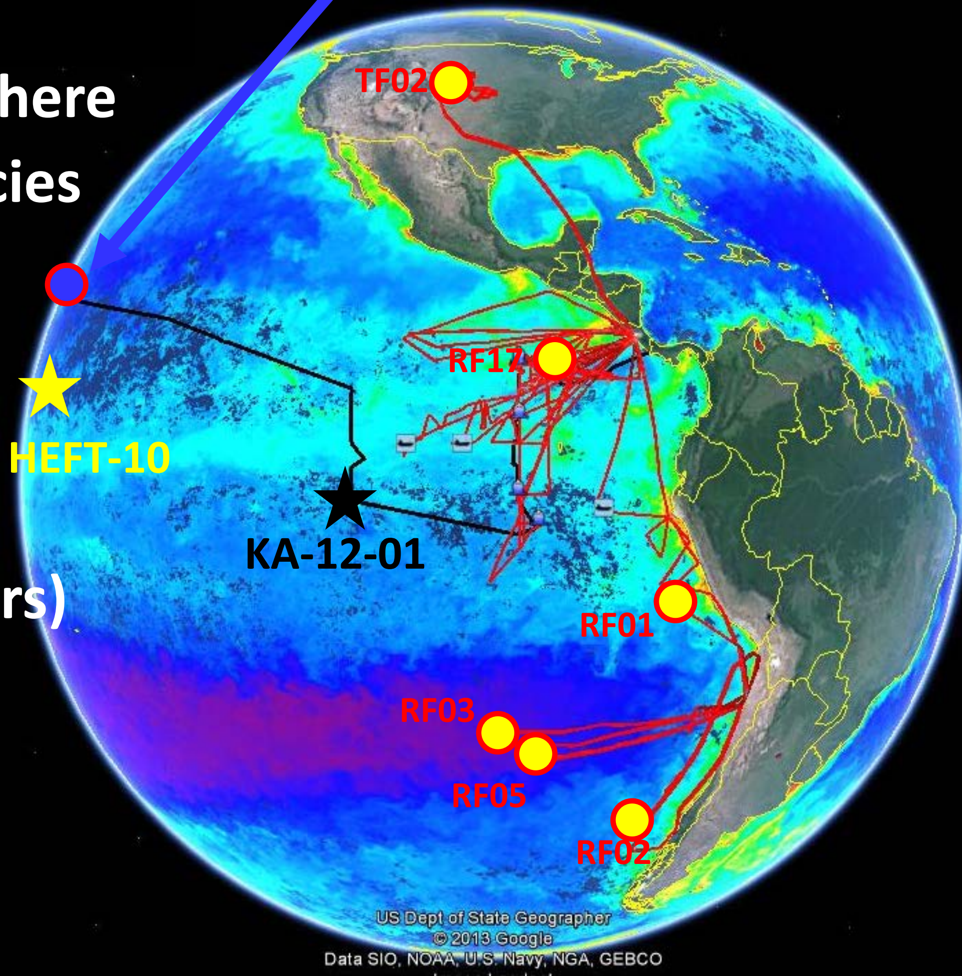
TORERO – Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated voc

NSF/NCAR GV (17 flights)

RV Ka (cruise KA-12-01)

- BrO and IO vertical profiles
- Very short lived OVOC (few hours)

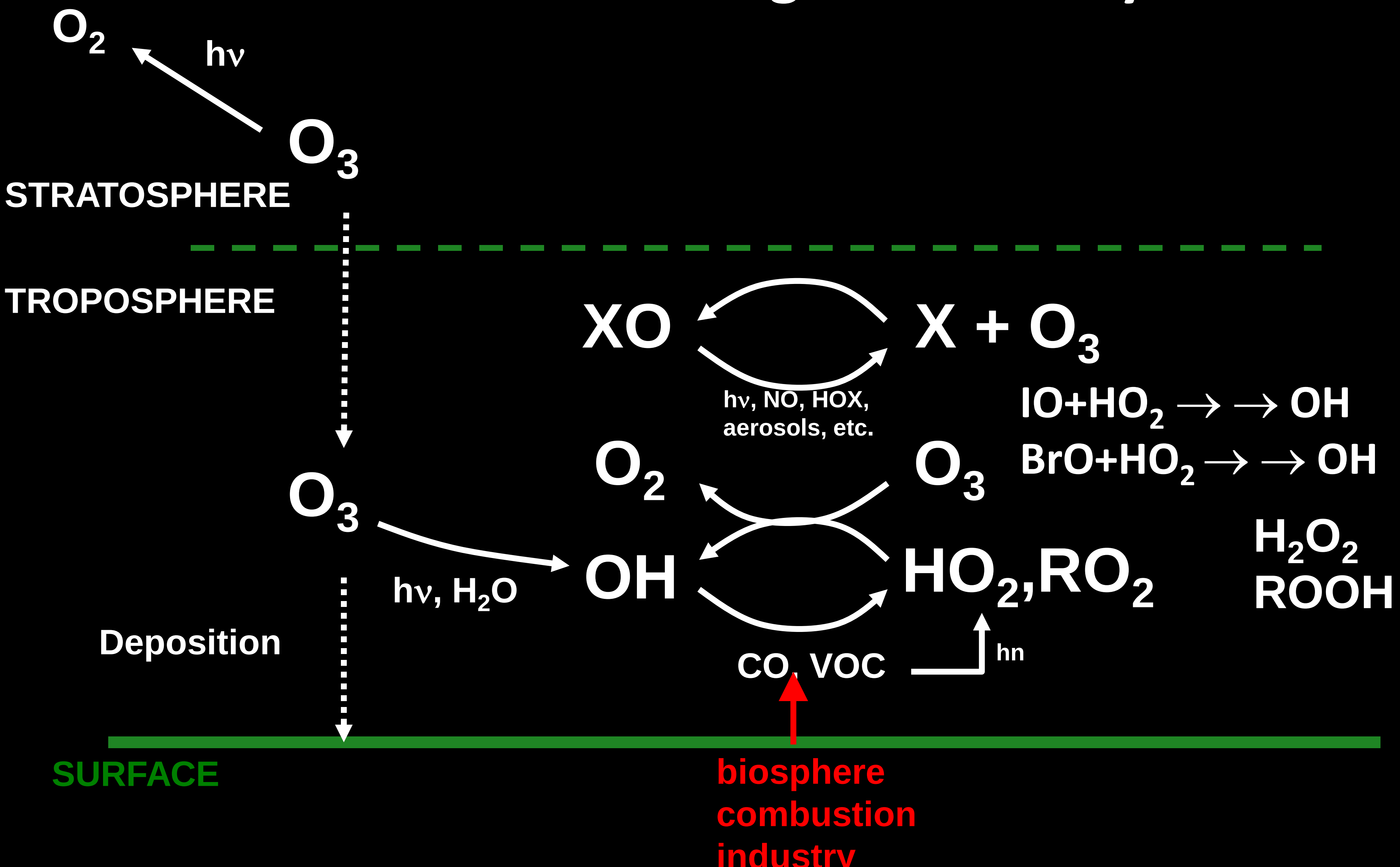
Glyoxal, MEK, Butanal



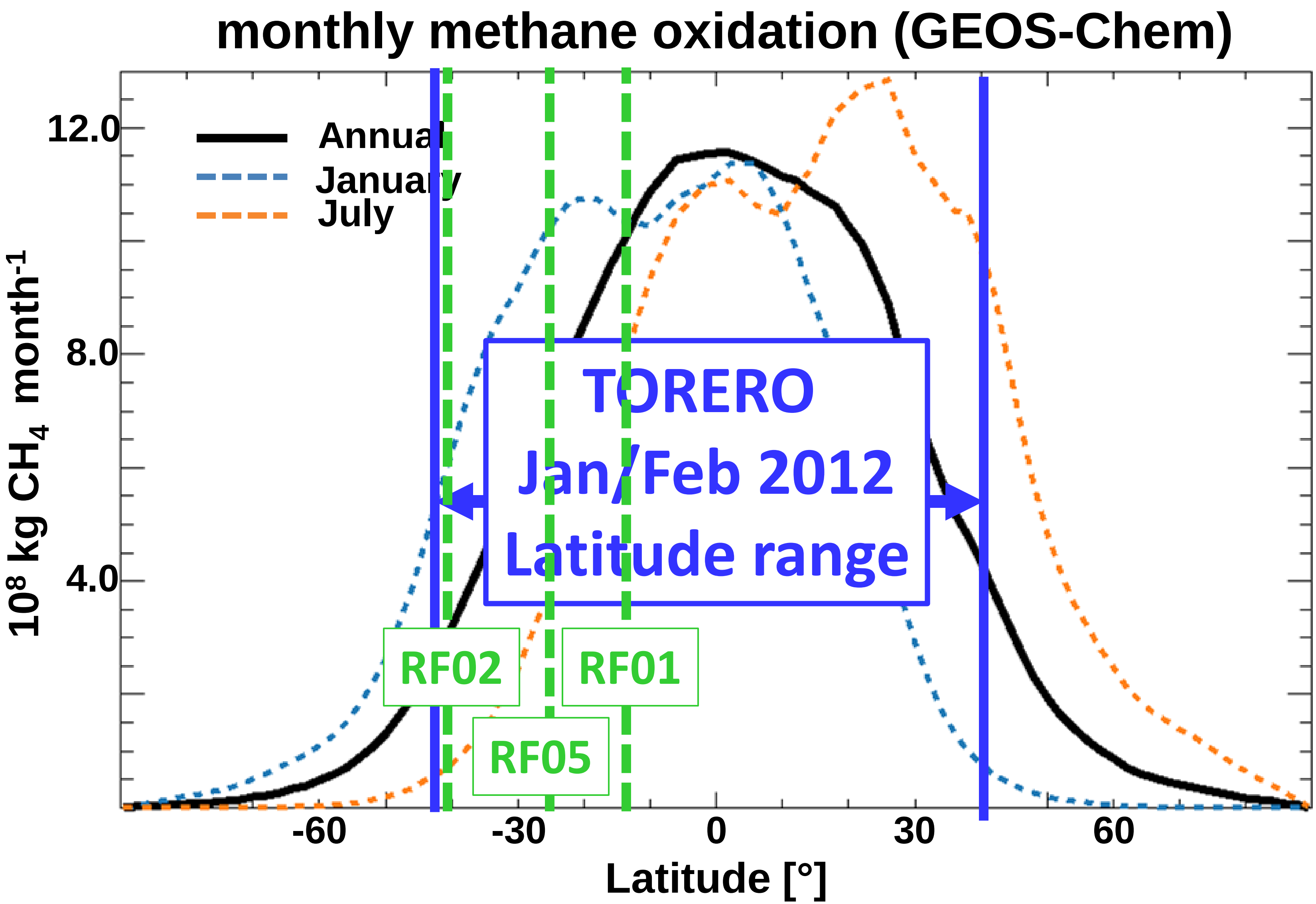
CIRES
Cooperative Institute for Research in Environmental Sciences

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

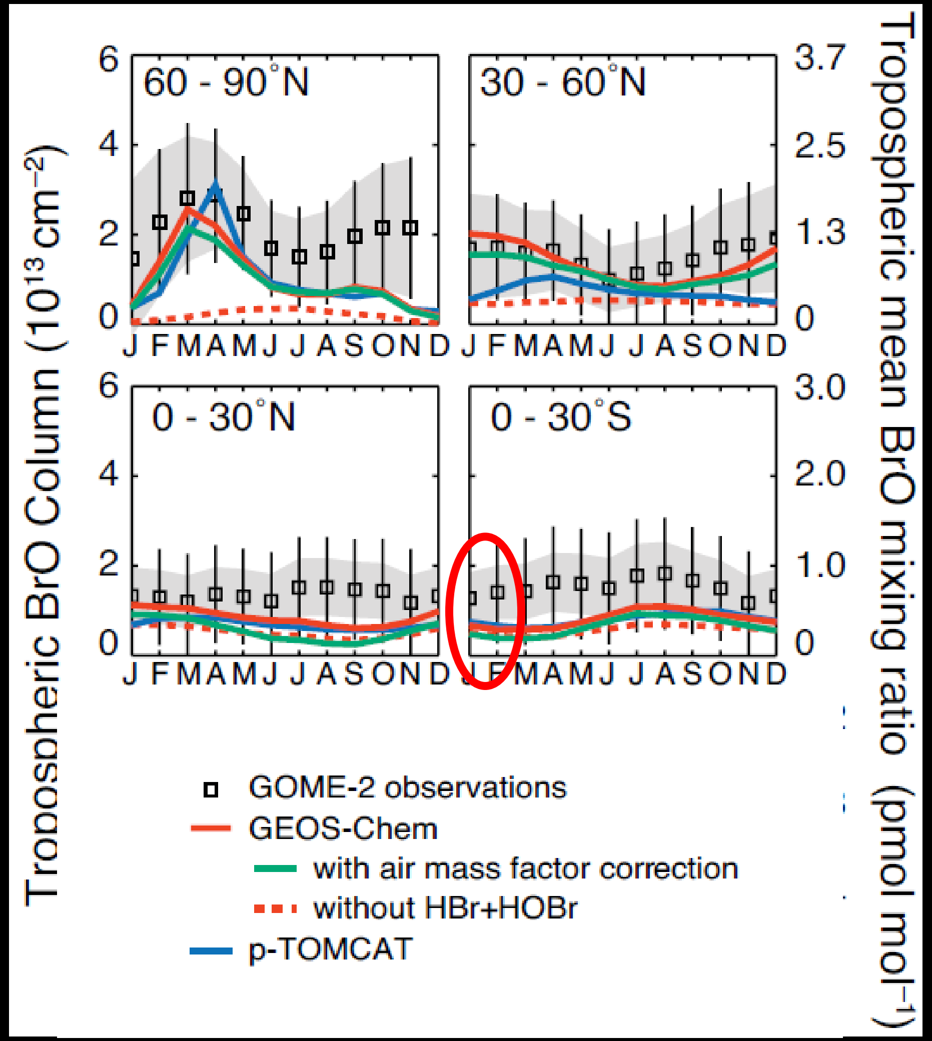
BrO comparison: GOME-2 with GEOS-Chem, p-TOMCAT

Satellite: 1-3 $\times 10^{13}$ 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 $\times 10^{13}$ 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 $\times 10^{13}$ molec cm^{-2}
(Pundt et al., 2002; Schofield et al., 2004, 2006; Dorf et al., 2008)

Models: 0.2-1.0 $\times 10^{13}$ molec cm^{-2}
(Saiz Lopez et al., 2012; Parrella et al., 2012)
– in the tropics



Theys et al. [2011]

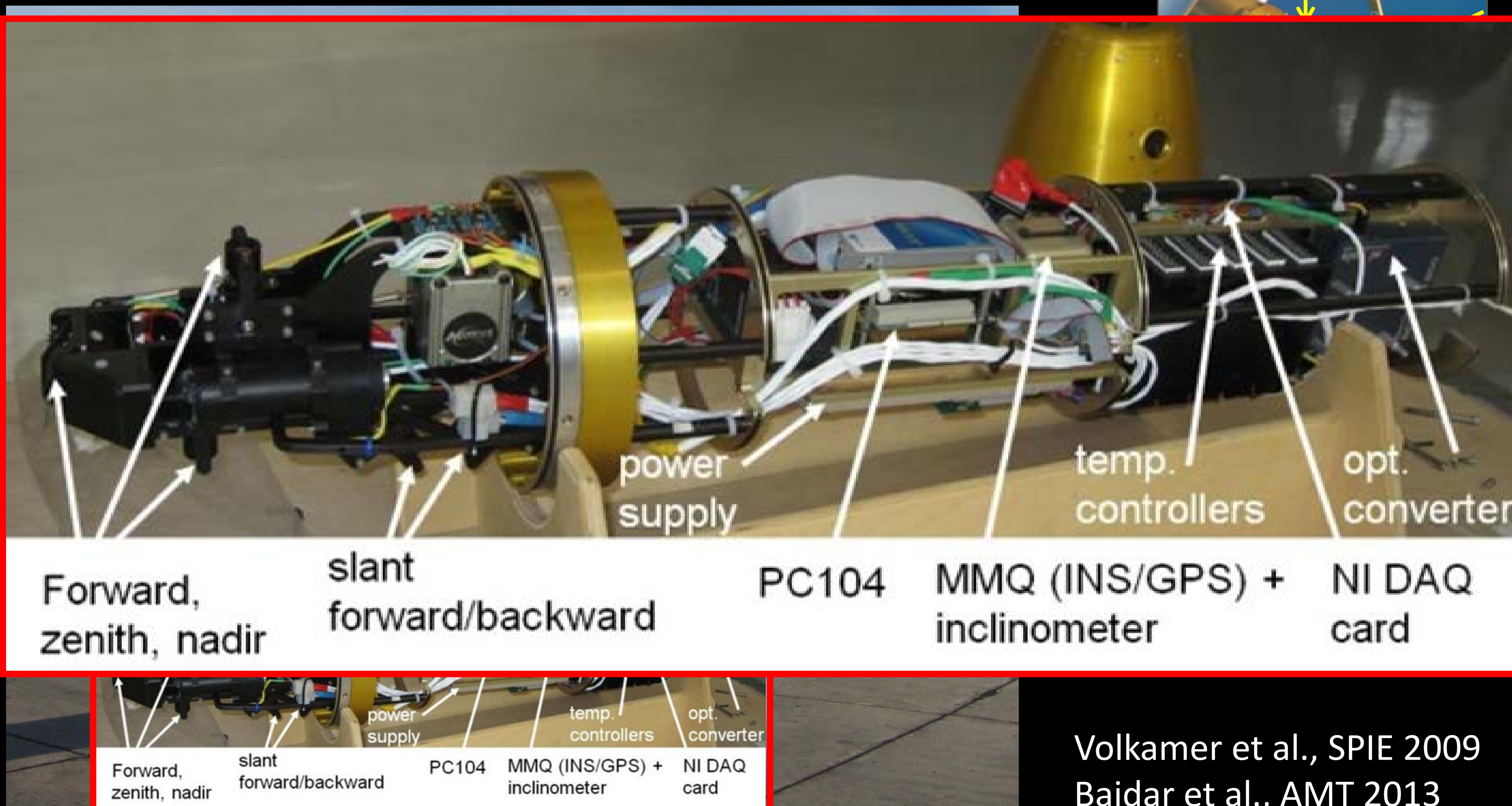
Halogens deplete the O_3 column by ~10% in the tropics (Saiz-Lopez et al., 2012)

~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

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)

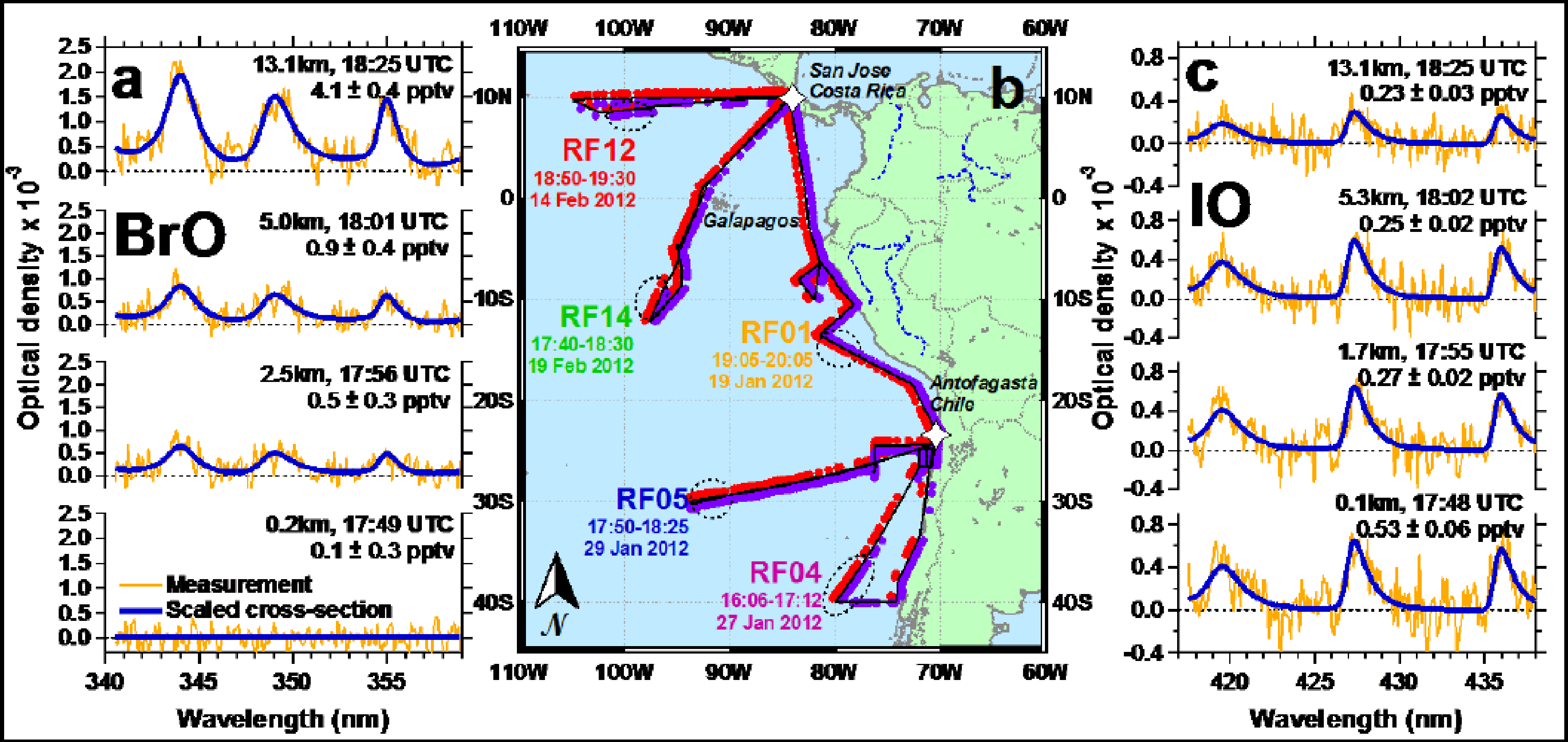
CU AMAX - DOAS

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}

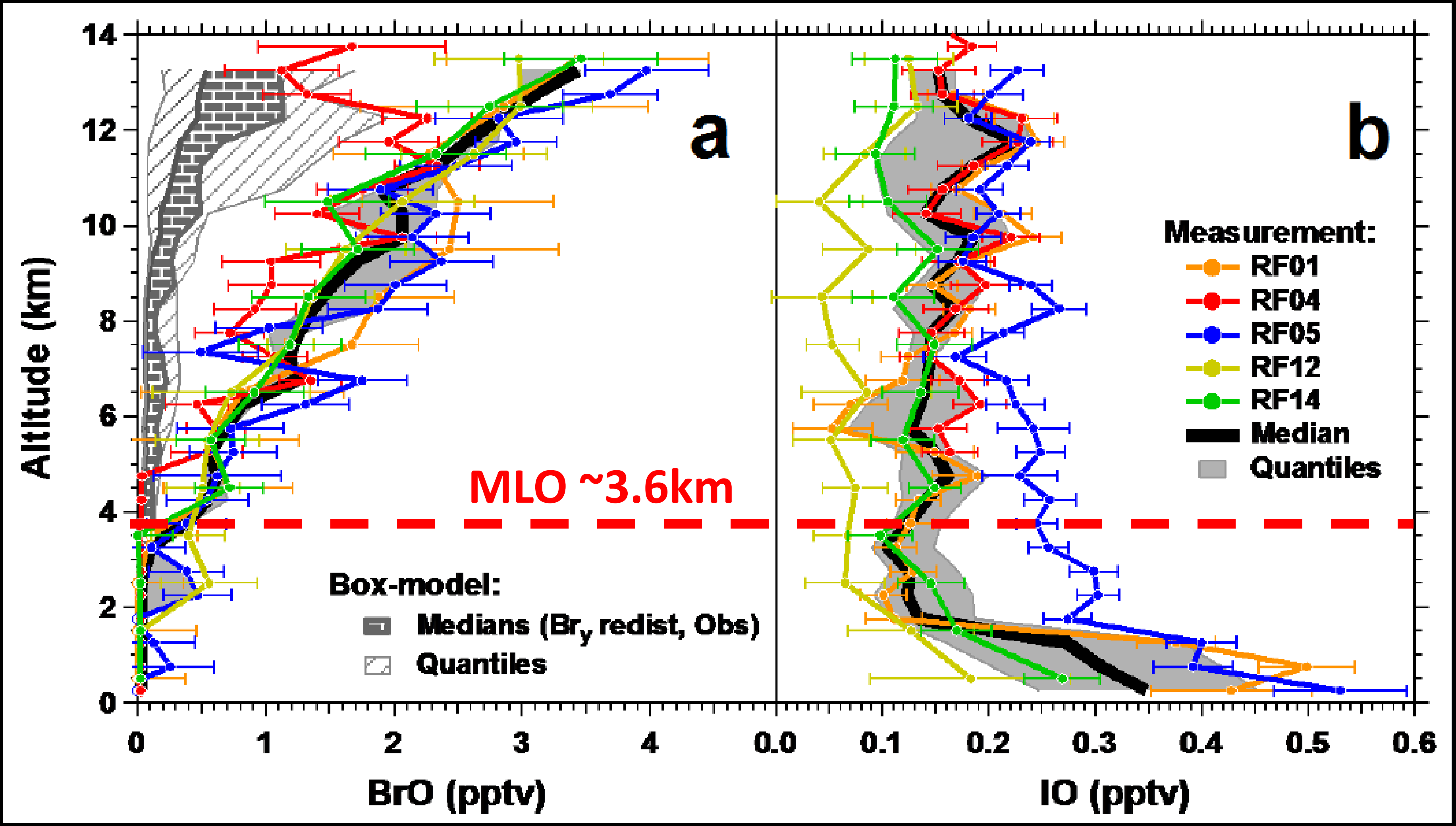
* 30 sec; ** 60 sec integration time

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}

Vertical profiles & comparison with models

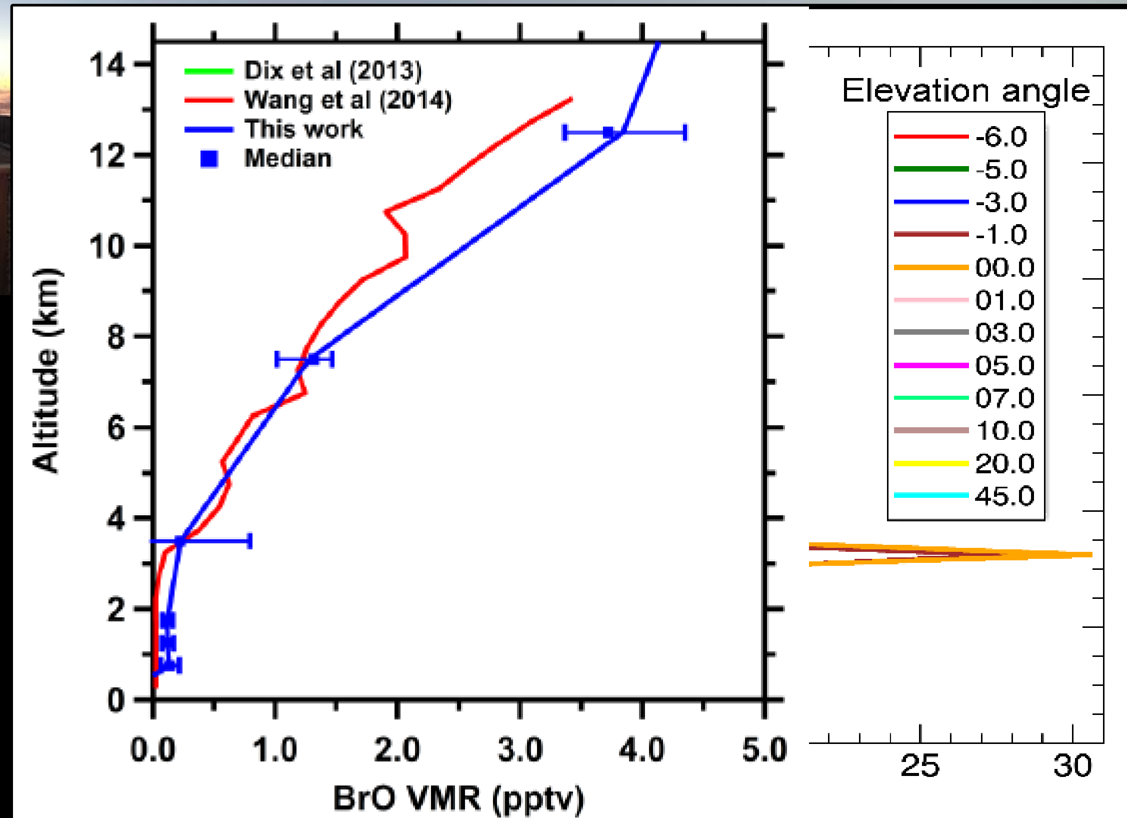


- GEOS-Chem: underestimates BrO by a factor 2-4
- Box-model (organohalogens, aerosol SA) -> even less BrO

Interim Conclusions

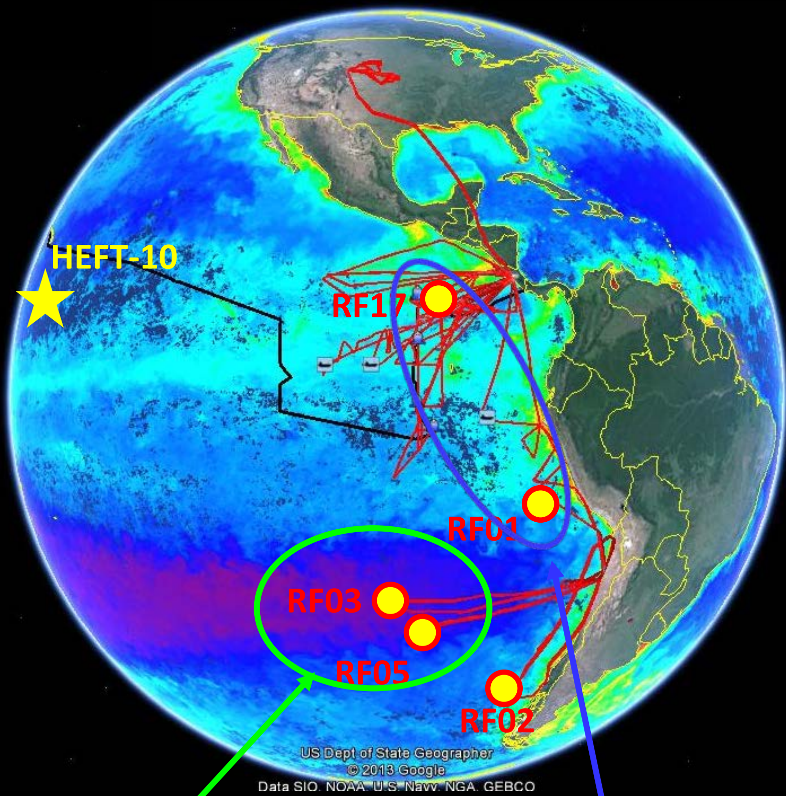
- *Ours are the first limb-observations of BrO and IO in the tropics*
- *BrO is detected regularly above 2-4 km; BrO and IO are abundant throughout the air column*
  - *Consistent with the GOME-2 satellite, ground-based MAX-DOAS data (Theys et al., 2011)*
  - *~8 times higher than direct-sun profiles (Dorf et al.)*
  - *~2-4 times more than predicted by models*
- *Measurements support ~10-15 pptv Br_y in the tropical UTLS (~5-6 pptv Br_y unaccounted ?)*

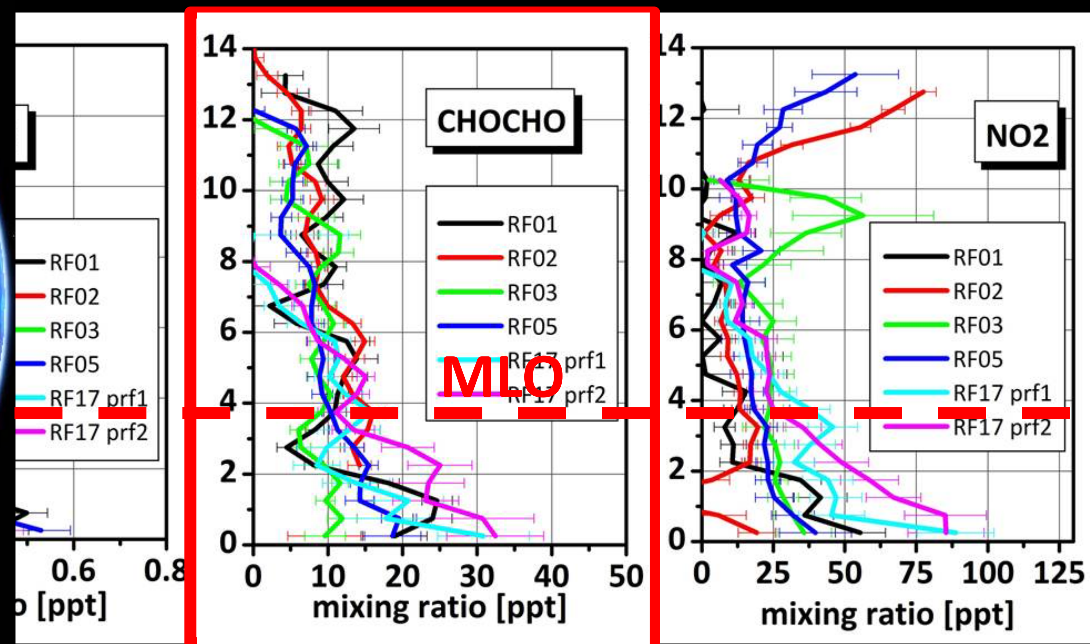
Mauna Loa Observatory, Hawaii



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

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



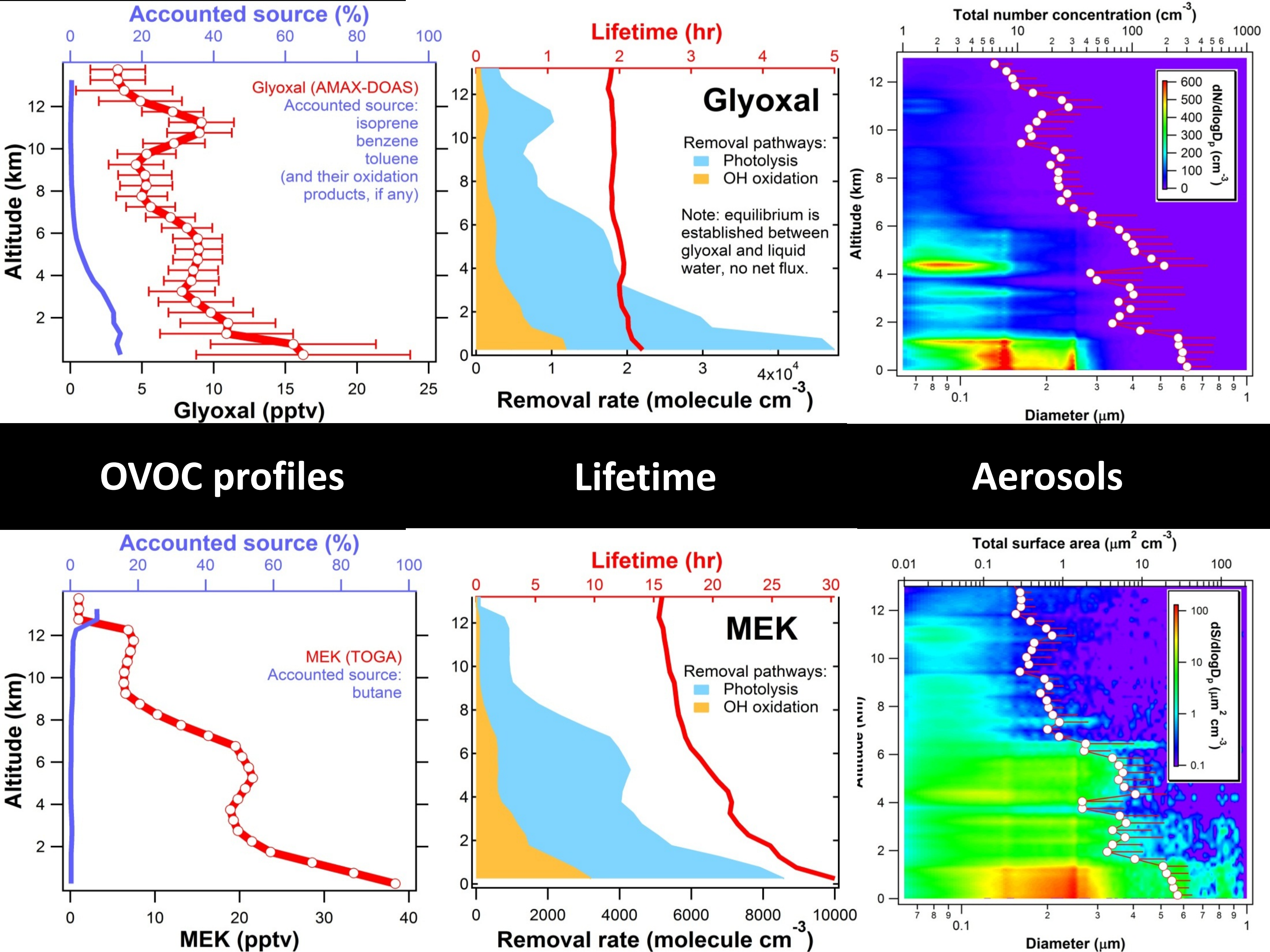


Chl-a < 0.02 mg/m³   Chl-a ~ 0.2-0.5 mg/m³

- Oligotrophic ocean: ~ 15 pptv (10-20 pptv)
- Mesotropic ocean: ~ 28 pptv (20-35 pptv)

} **Ocean biology signature ?**

- FT: 5-15 ppt (Eastern) and 3-10 ppt (Central Pacific – HEFT-10)
- Stratosphere: < 3 pptv – no signal is detectable
- Glyoxal is widespread, possibly ubiquitous → a biogeochemical cycle



Accounted source (%)
Glyoxal (AMAX-DOAS)
Accounted source:
isoprene
benzene
toluene
(and their oxidation
products, if any)
Altitude (km)
Glyoxal (pptv)
Lifetime (hr)
Glyoxal
Removal pathways:
Photolysis
OH oxidation
Note: equilibrium is
established between
glyoxal and liquid
water, no net flux.
Removal rate (molecule cm-3)
Total number concentration (cm-3)
dN/dlogDp (cm-3)
Altitude (km)
Diameter (μm)
OVOC profiles
Lifetime
Aerosols
Accounted source (%)
MEK (TOGA)
Accounted source:
butane
Altitude (km)
MEK (pptv)
Lifetime (hr)
MEK
Removal pathways:
Photolysis
OH oxidation
Removal rate (molecule cm-3)
Total surface area (μm2 cm-3)
dS/dlogDp (μm2 cm-3)
Diameter (μm)

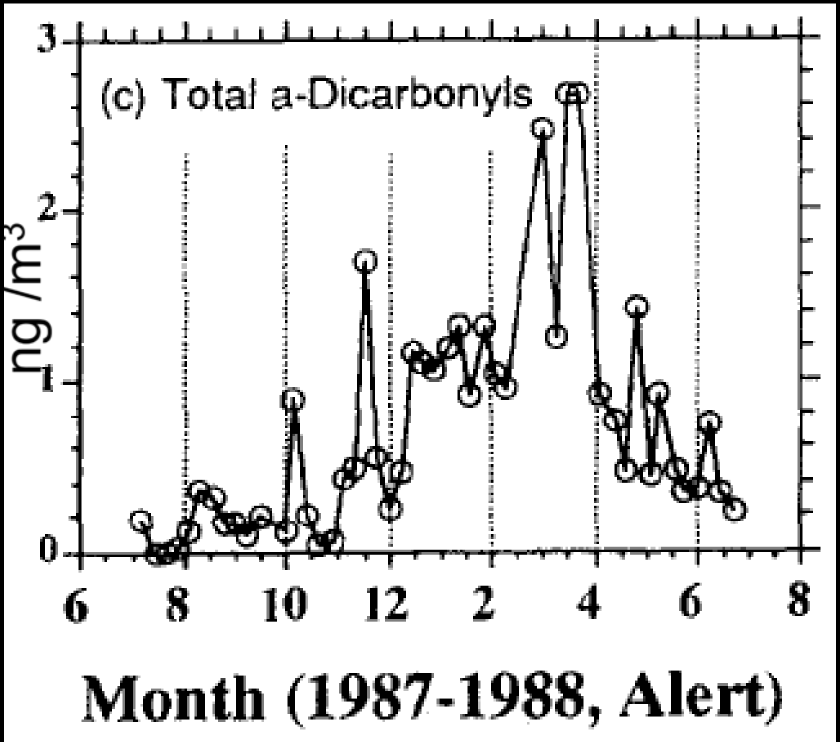
Conclusions

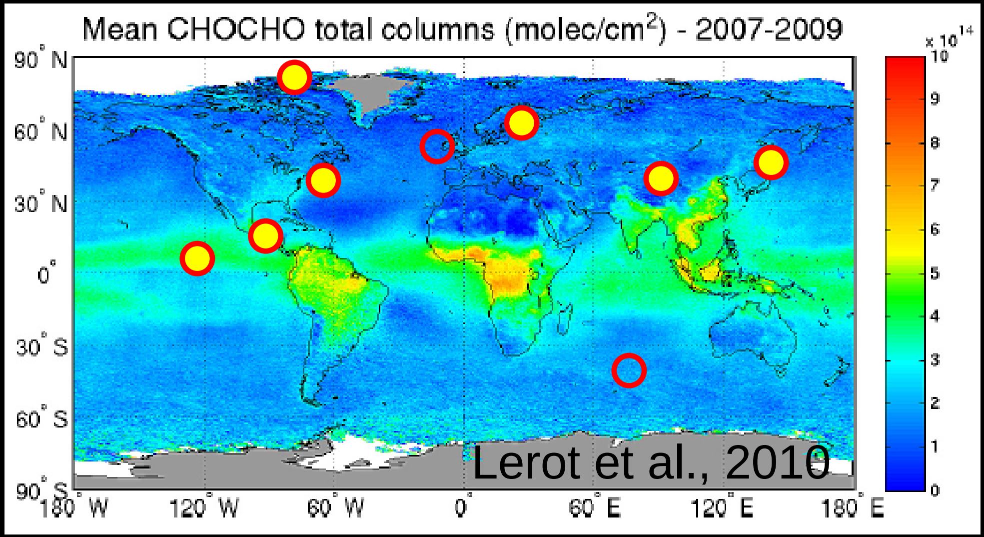
- *The TORERO mission was very successful – strong focus on technological innovation*
  - *first limb-observations of BrO and IO in the tropics*
  - *~10-15 pptv Br_y in the tropical UTLS*
  - *What is the Br_y content in the lower stratosphere, and how much stratospheric Br_y reaches the UTLS?*
- *OVOC are widespread over oceans in the FT*
  - *Detected by multiple techniques (DOAS, GC-MS)*
  - *Unaccounted ocean source of marine organic carbon (can NOT be explained from isoprene, monoterpenes)*
  - *Most of the OVOC column resides in the FT*
  - *implications for aerosols, oxidative capacity?*

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

Acknowledgements: NCAR/EOL and RAF, TORERO team

Glyoxal in particles: Field evidence





Glyoxal is a ubiquitous product of anthropogenic and biogenic/marine precursors, and found in aerosols

Arctic aerosol: Alert

Peak in early spring
Few weeks earlier than diacids
3-4 times more GLY than MGLY

Marine aerosol: Hokkaido Island

GLYg = 42 ng /m^3 (18 ppt)
P / (P + G) = 0.46

Alert: Kawamura et al., 1996
Mexico City: Volkamer et al., 2007
Continental (Tibet): Meng et al., 2013

Marine: Matsunaga and Kawamura, 2004
Biogenic (Hyytiälä): Kampf et al., 2012
Southern Hemisph.: Rinaldi et al., 2011