Sources of Br_y and I_y in the TTL & LS: Constraints from recent DOAS aircraft observations of BrO and IO

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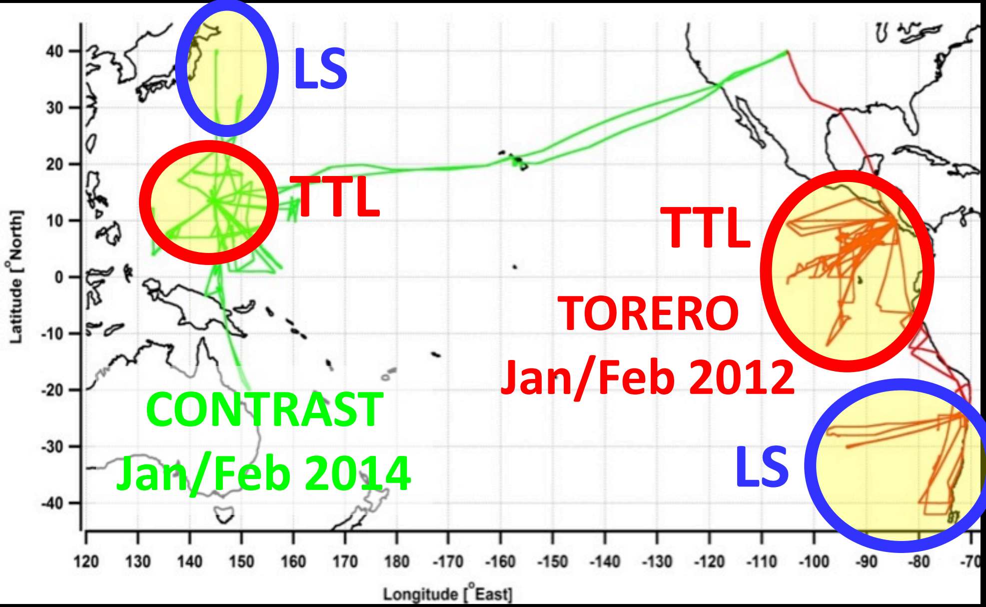
1. Instrumentation
2. TORERO & CONTRAST measurements of BrO and IO
3. Relevance: Tropospheric halogens impact O_3 lifetime, oxidize mercury and HO_x over the full tropical air column.
4. Br_y sources: Sea-salt, VSL, aerosol chemistry/dynamics?



Funding: NSF-CAREER, NSF-AGS, NASA, EPRI

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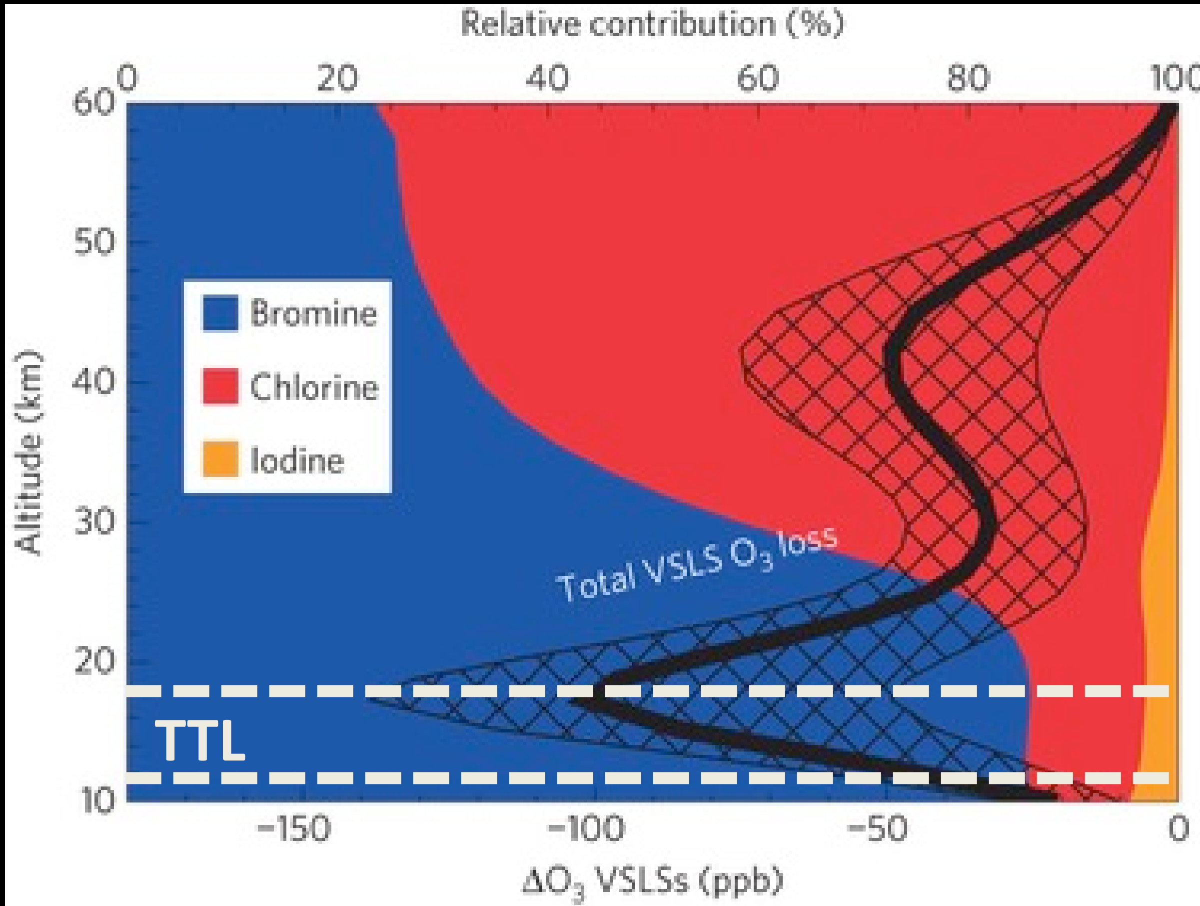
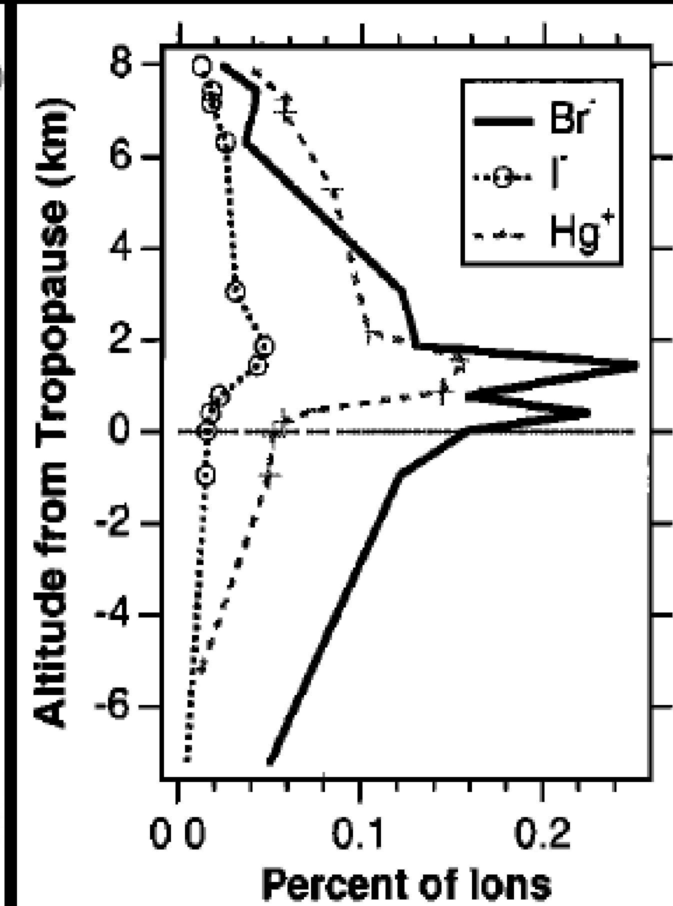
Relevance of Chlorine, Bromine, Iodine



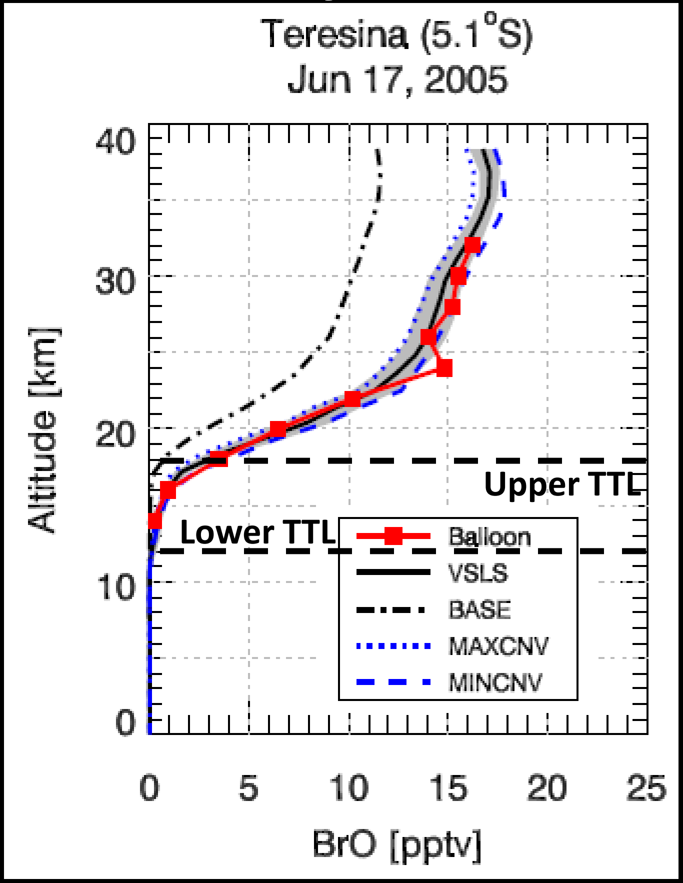


Hossaini et al., 2015 **Murphy et al., 2000 GRL**

- Bromine dominates over Chlorine and Iodine in UTLS
- Aerosols in LS are enhanced in bromide and iodide

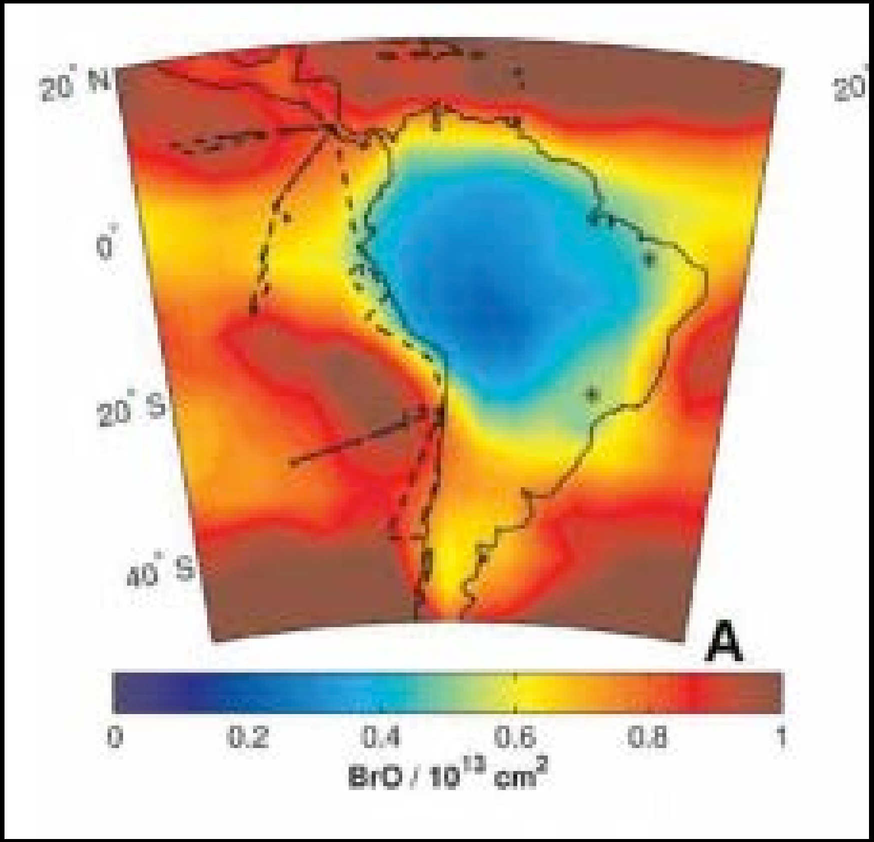
Previous measurements of bromine in the TTL and LS

GEOSCCM
Includes Bry from VSL



Dorf et al., 2008; Liang et al., 2014

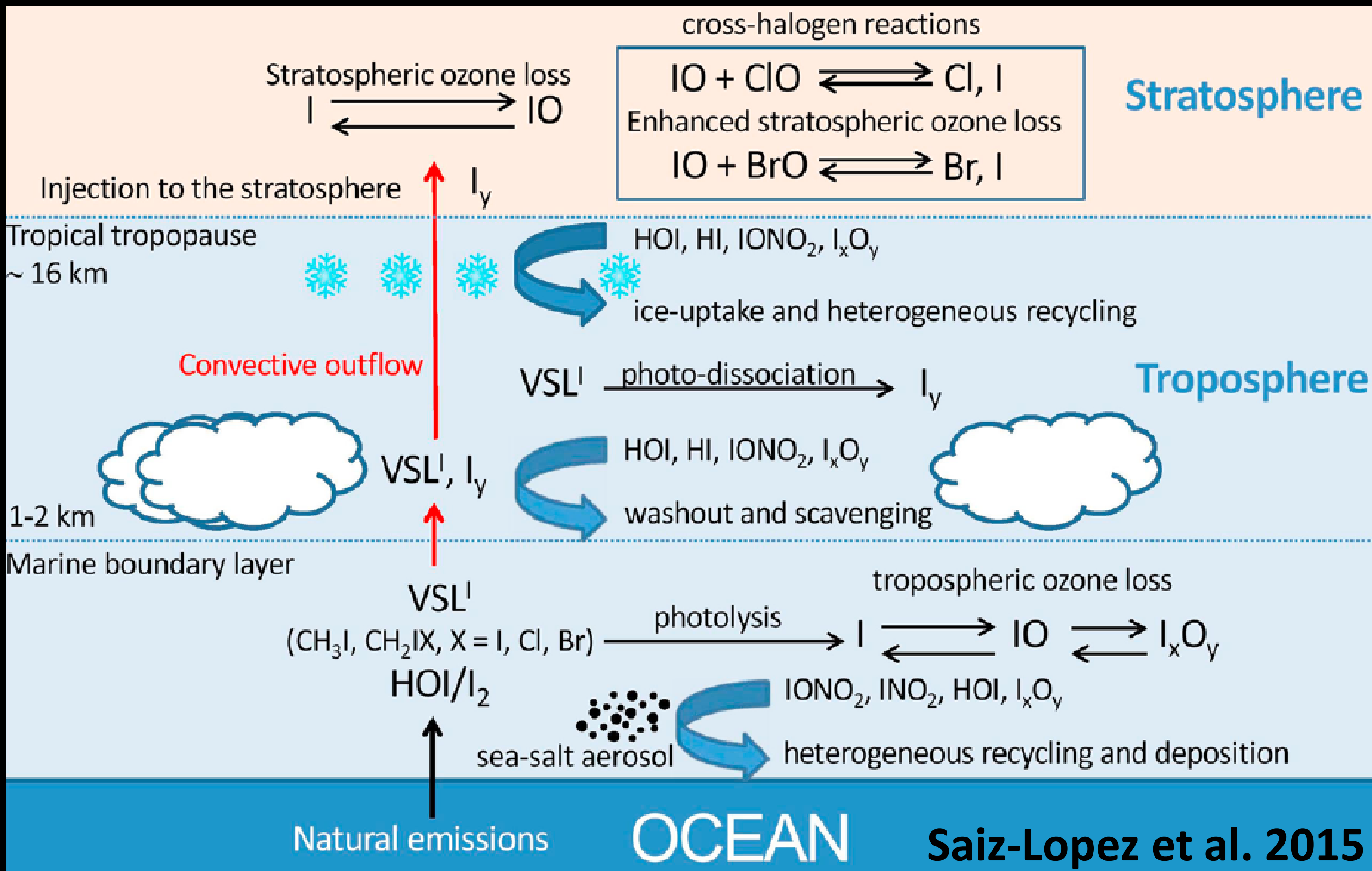
GEOS-Chem - TORERO
Includes Bry from VSL



Wang et al., 2015

Much of our understanding about Br_y in the UTLS is based on measurements downwind of terrestrial convection

Tropospheric Chemistry of Halogens

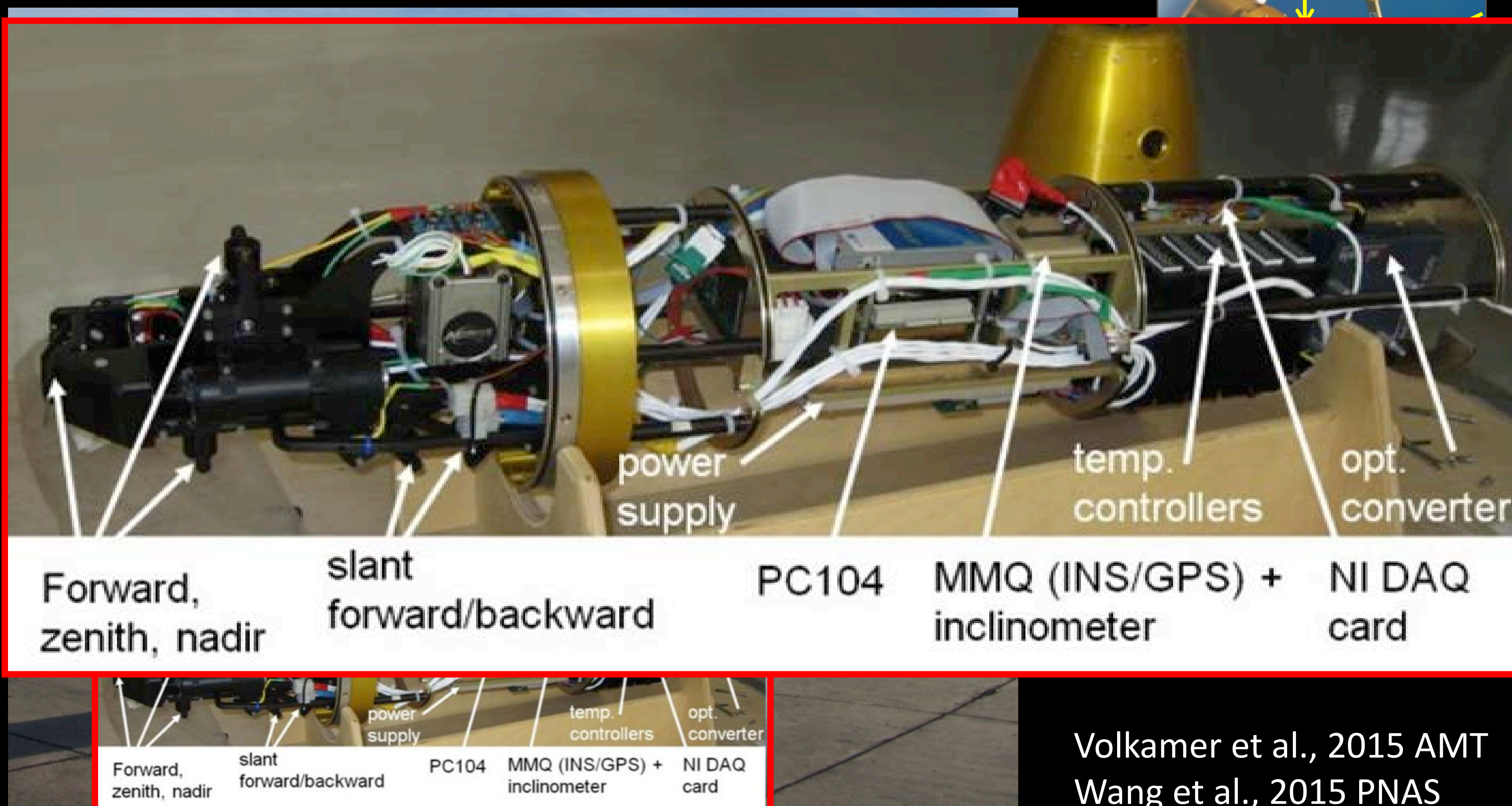


VSL – organic	Br_y	550 Gg Br/yr	I_y	600 Gg I/yr
Inorganic		1620 Gg Br/yr		1600-3230* Gg I/yr
Strat-Trop Exchange		49 Gg Br/yr		NN
		Schmidt et al., 2016		Sherwen et al. 2016

CU-AMAX-DOAS instrument aboard NSF/NCAR GV

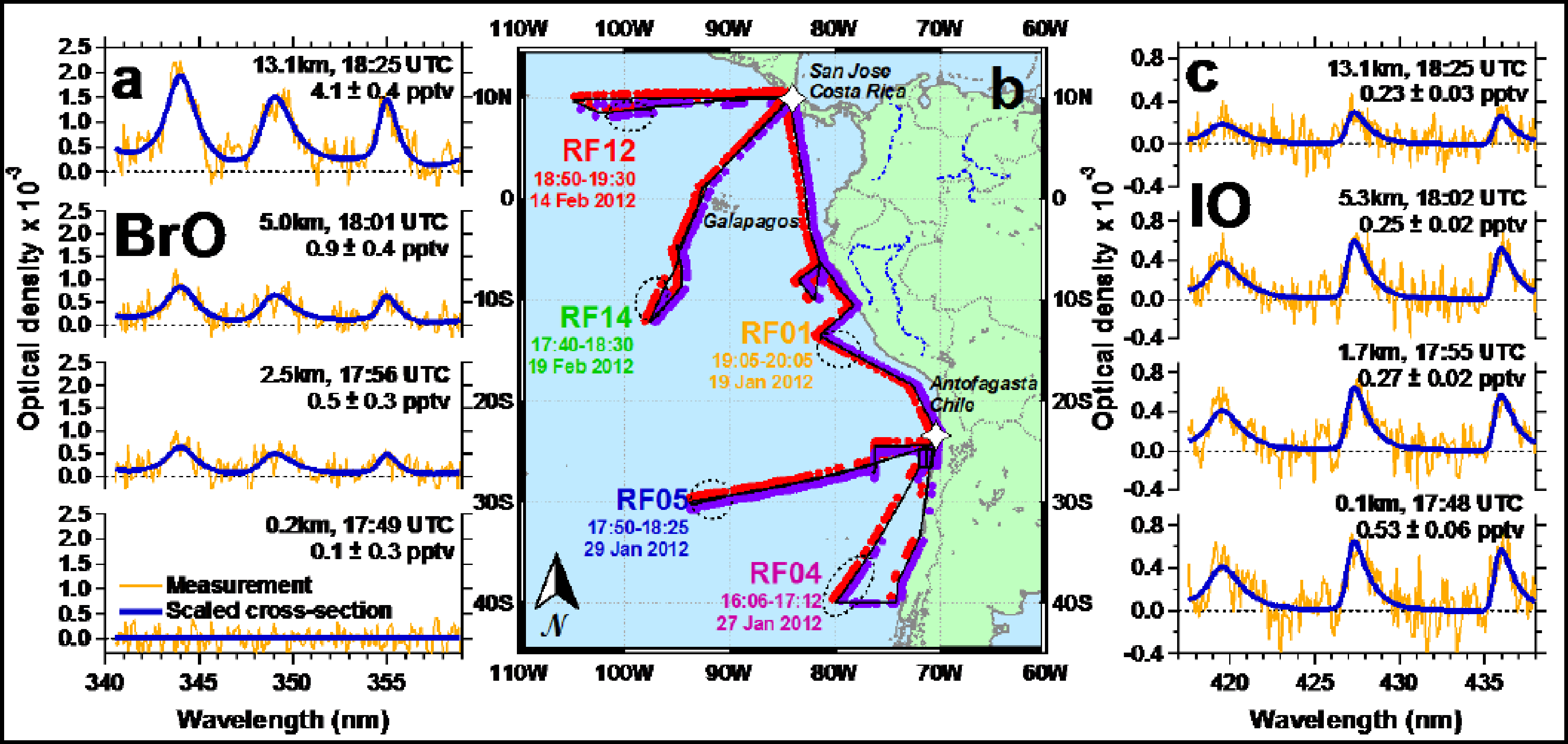
University of Colorado Airborne Multi-AXis
Differential Optical Absorption Spectroscopy

Telescope pylon



Volkamer et al., 2015 AMT
Wang et al., 2015 PNAS

BrO and IO detection SH tropical troposphere



tWPO – BrO VCD

NH tropics: (1.6 ± 0.6) x10^{13}

(CONTRAST RF03, 04, 07, 15)

tEPO – BrO VCD (molec cm^{-2})

NH/SH tropics: (1.5 ± 0.3) x10^{13}

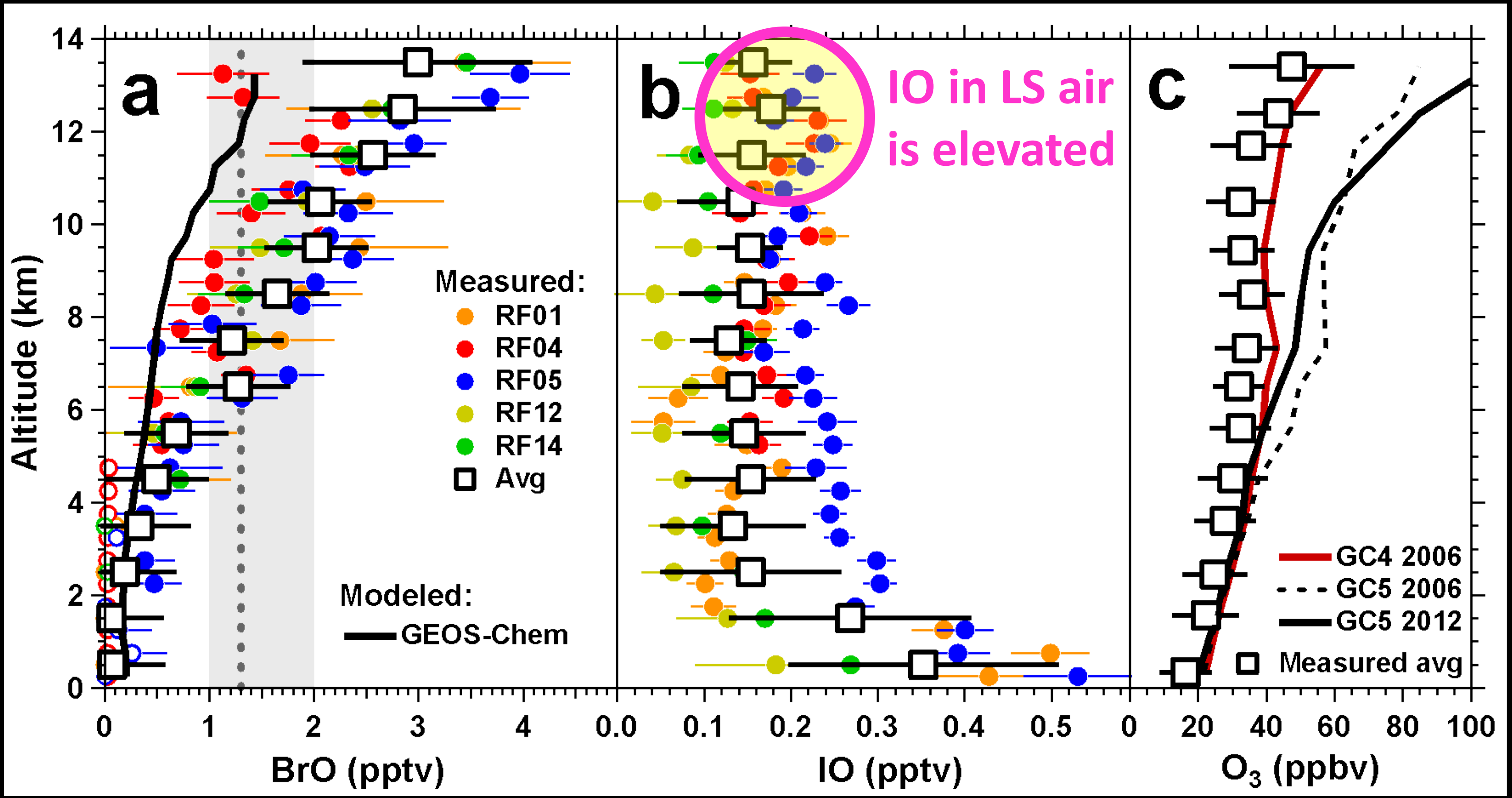
(TORERO RF01, 04, 05, 12, 14, 17)

Volkamer et al., 2015 AMT

Wang et al., 2015 PNAS

Koenig et al., 2016, in prep.

BrO and IO profiles in the tropics & subtropics



- Downwind of maritime convection tropospheric BrO is elevated, and 2-4 times higher than predicted.
- Sea-salt sources influence Br_y, and inorganic ocean sources influence I_y in the TTL (and LS?)

Wang et al., 2015 PNAS

BrO comparison with previous studies in the tropics

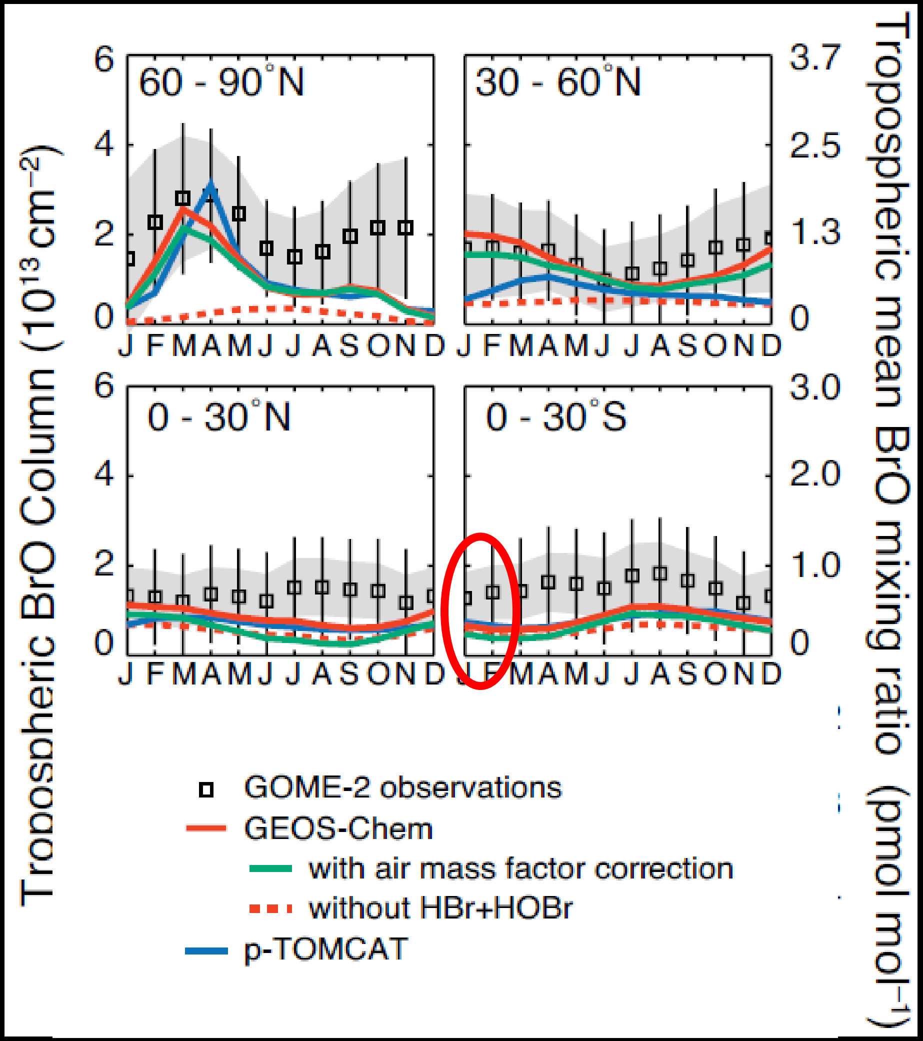
Aircraft: 1-2 x10^{13} molec cm^{-2}
(Volkamer et al., 2015; Wang et al., 2015)

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 : <0.4-3 x10^{13} molec cm^{-2}
(Leser et al., 2003; Hendrick et al., 2007; Theys et al., 2007; Coburn et al., 2011; 2016)

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

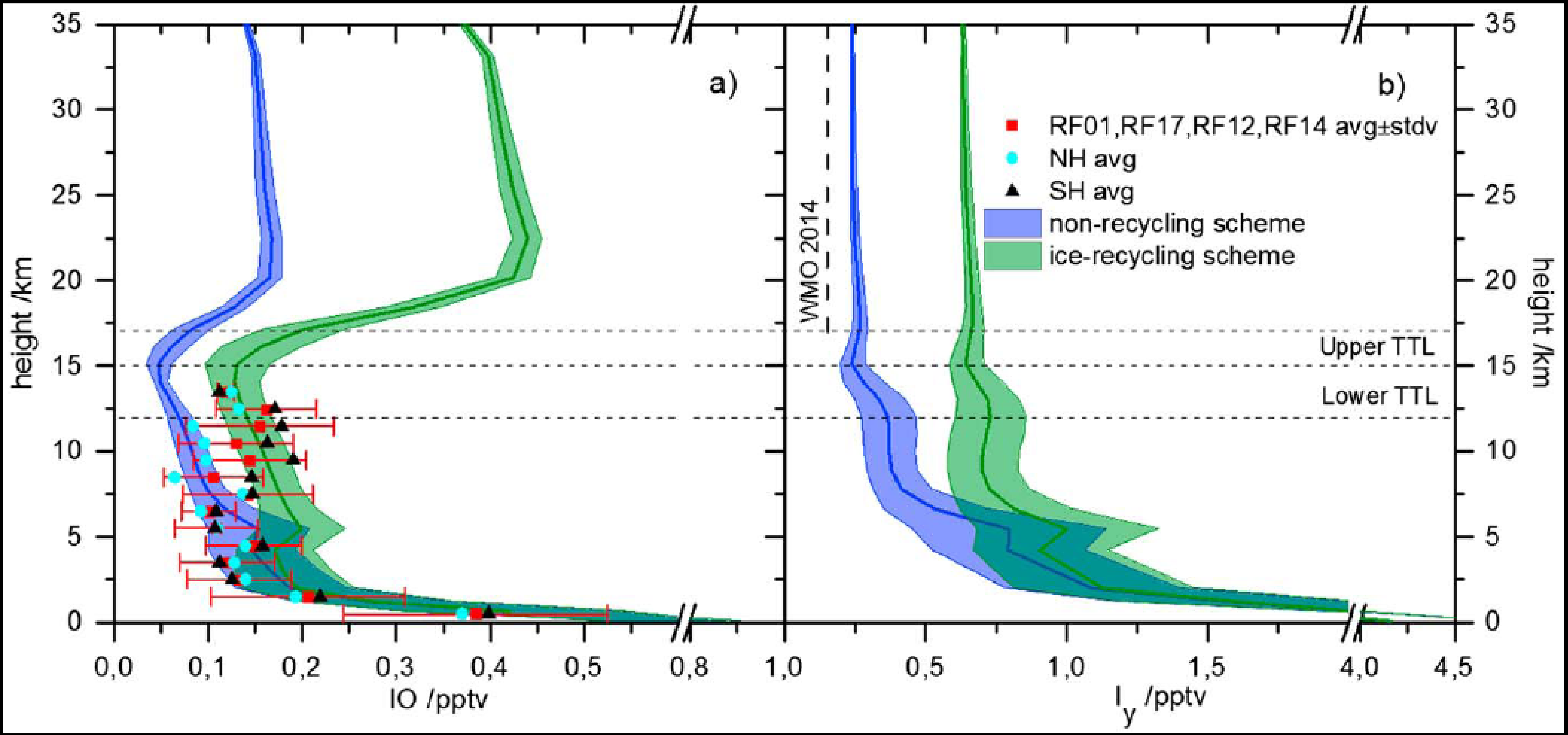
Models: 0.2-1.0 x10^{13} molec cm^{-2}
(von Glasow et al., 2004; Yang et al., 2010; Theys et al., 2011; Saiz-Lopez et al., 2012; Parrella et al., 2012; Long et al., 2014) – in the tropics



"A reassessment of Br_y and I_y in the UTLS is needed"

Volkamer et al., 2015

Potential implications of iodine injections into the LS

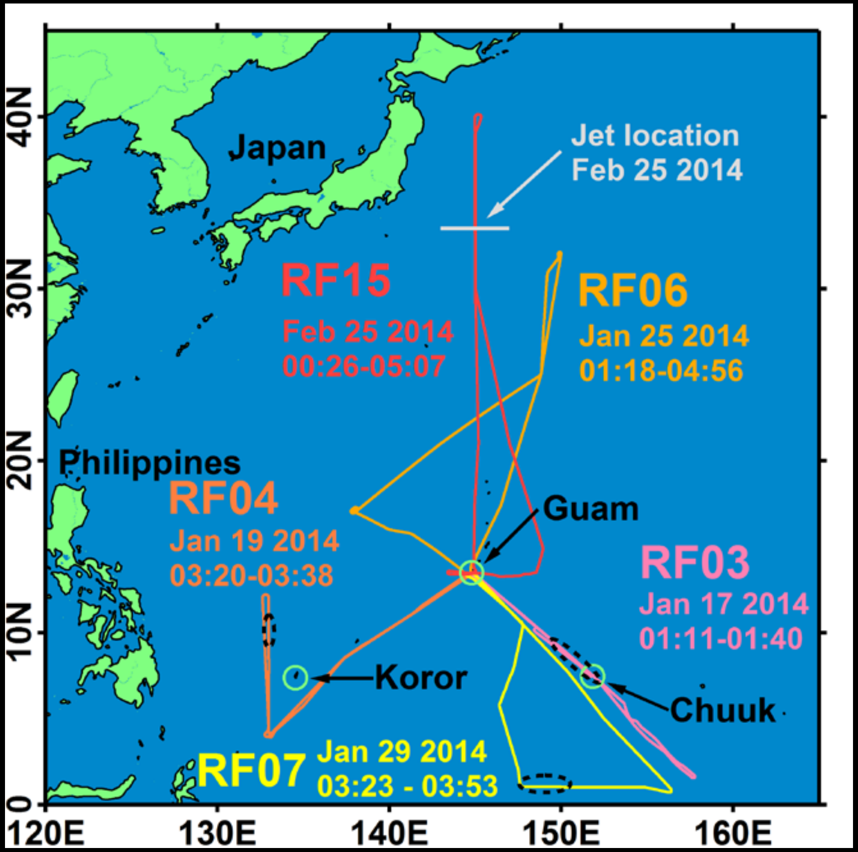


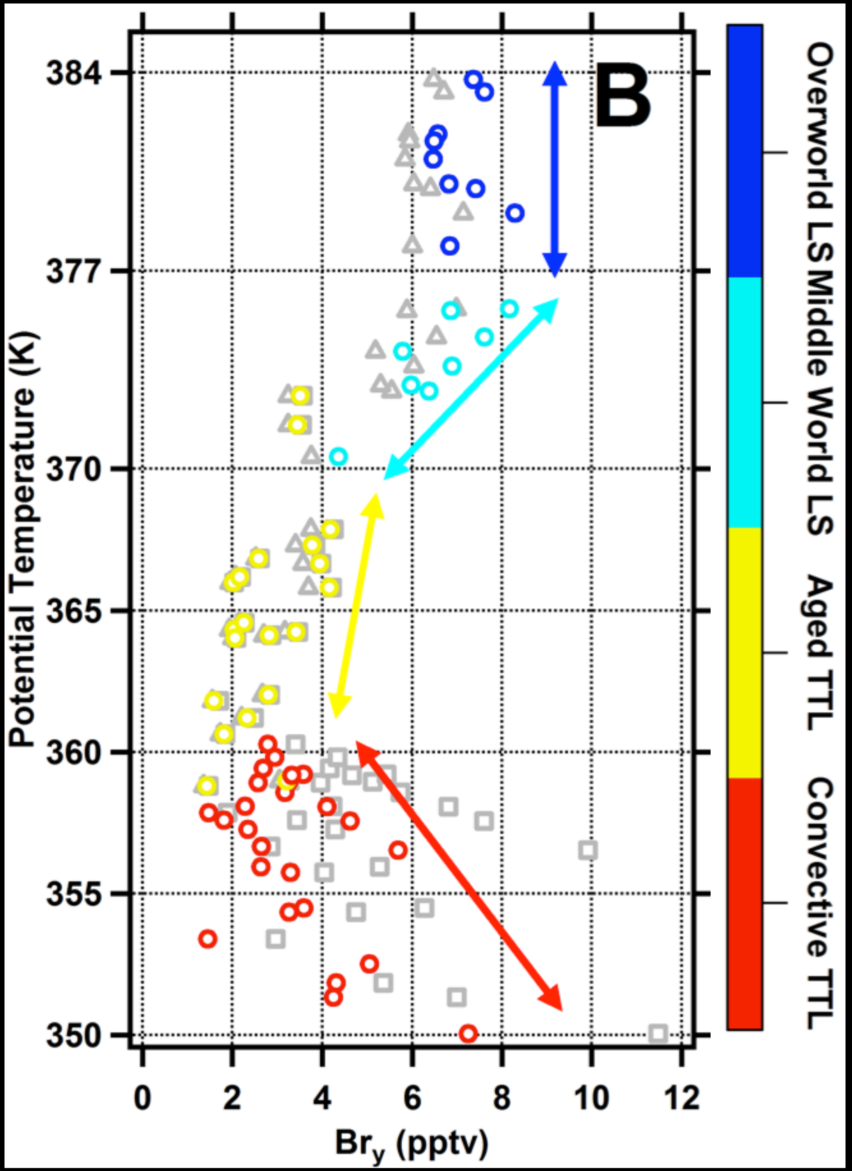
Saiz-Lopez et al., 2015; Volkamer et al., 2015

0.15 pptv IO in the lower TTL suggest that 0.25–0.7 pptv I_y can be injected into the stratosphere via tropical convective outflow.

The accepted WMO upper limit suggests <0.15 pptv I_y

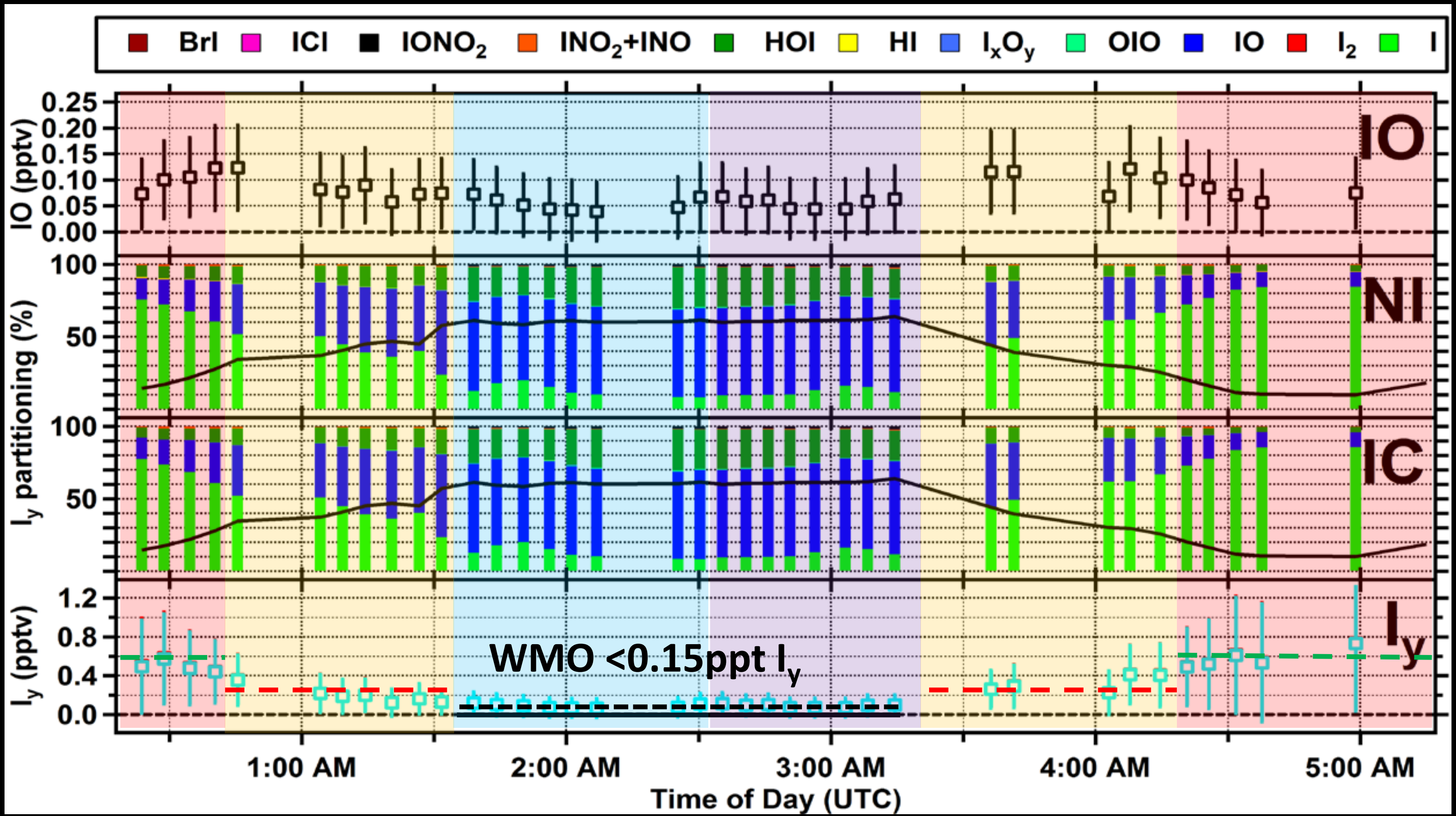
CONTRASTRF15: TTL into mid-latitude LS - Western Pacific
Br_y in the UTLS exhibits a minimum in the aged TTL (360 K)





- Overworld 7.1 ± 0.6 pptv Br_y
- Middle World 6.5 ± 1.2 pptv Br_y
- Aged TTL 2.8 ± 0.9 pptv Br_y
- Convective TTL 2-7 pptv Br_y

CONTRAST RF15: TTL into mid-latitude LS - Western Pacific
IO detected in the LS –I_y decreases from TTL into LS



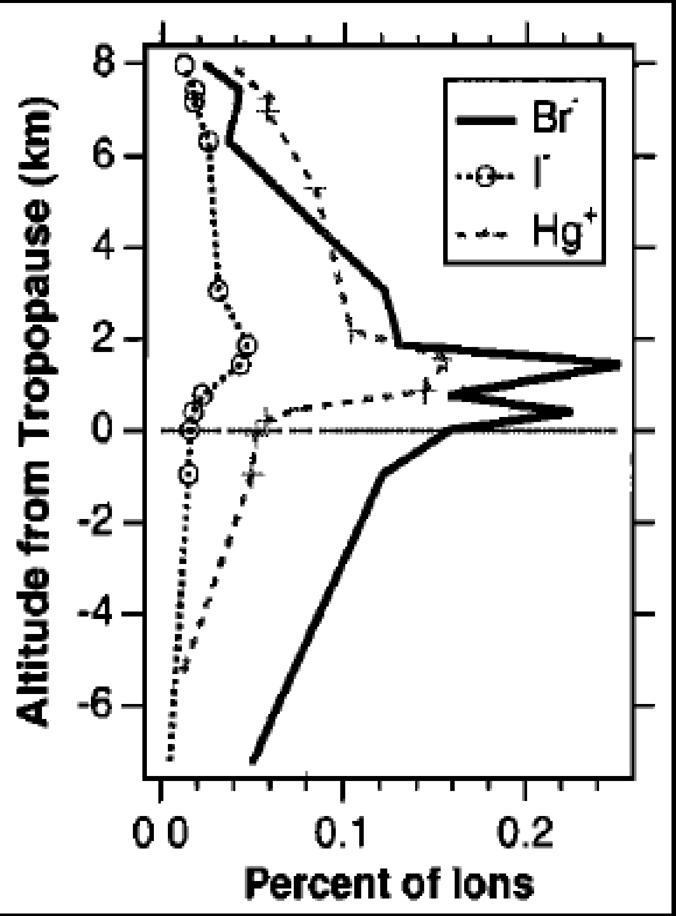
0.26 ppt I_y in aged TTL **0.26 ppt I_y in aged TTL** **0.54 ppt I_y in convective TTL**

At least 0.26 pptv I_y are injected into the stratosphere (~2 times WMO)

Previous low IO upper limits are probably due to I_y partitioning to aerosols

Summary & Conclusions

- We have detected BrO and IO in the TTL and n
first time over the tEPO and tWPO.
- Inorganic Br_y and I_y are abundant throughout
  - Unaccounted Br_y (probably from sea salt) adds up
  - Influences of inorganic halogen sources are under
  - IO over the Western Pacific is consistent with ou
Pacific (Volkamer et al., 2015; Wang et al., 2015;
- Iodine was detected in the lower stratosphere
  - The amount of inorganic I_y injected into the strat
higher than WMO estimate ~0.26 pptv I_y.
- tWPO: complex structure of Br_y and I_y from TT
  - How much iodine and bromine is partitioning to a
  - The halogen budget in the LS is not closed – due t
from LS



Murphy et al., 2000 GRL

- tEPO: Tropospheric halogens are responsible for 34% tropospheric O
loss rate. Relevance for HO_x and atmospheric mercury oxidatio
et al., 2015, PNAS)

Acknowledgement: NCAR/EOL, TORERO & CONTRAST science teams

Acknowledgements

Instrument/Model	Parameters used to constrain box model	PI and Co-I
AMAX	BrO	T. Koenig, R. Volkamer, S. Baidar, B. Dix
HARP	Photolysis Rates	S. Hall, K. Ullmann
TOGA	Propane, Isobutane, n-Butane, HCHO, CFC-11, Benzene	E. Apel, N. Blake, A. Hill, R. Hornbrook
AWAS	Ethane, Propane, Isobutane, n-Butane, CFC-11, Benzene	E. Atlas, S. Schauffler, V. Donets, R. Lueb, M. Navarro
ISAF	HCHO	T. Honisco, G. Wolfe, D. Anderson
Chemiluminescence	NO, NO_2, O_3	A. Weinheimer
VUV	CO	D. Reimer
PICARRO	Methane	D. Reimer
UHSAS	Aitken mode aerosol surface area	M. Reeves
GV	Pressure, temperature, water, location	T. Campos, P. Romashkin
Project/General		L. Pan, R. Salawitch, S-Y. Wang, S. Honomichl, P.

Pavel Romashkin

NSF

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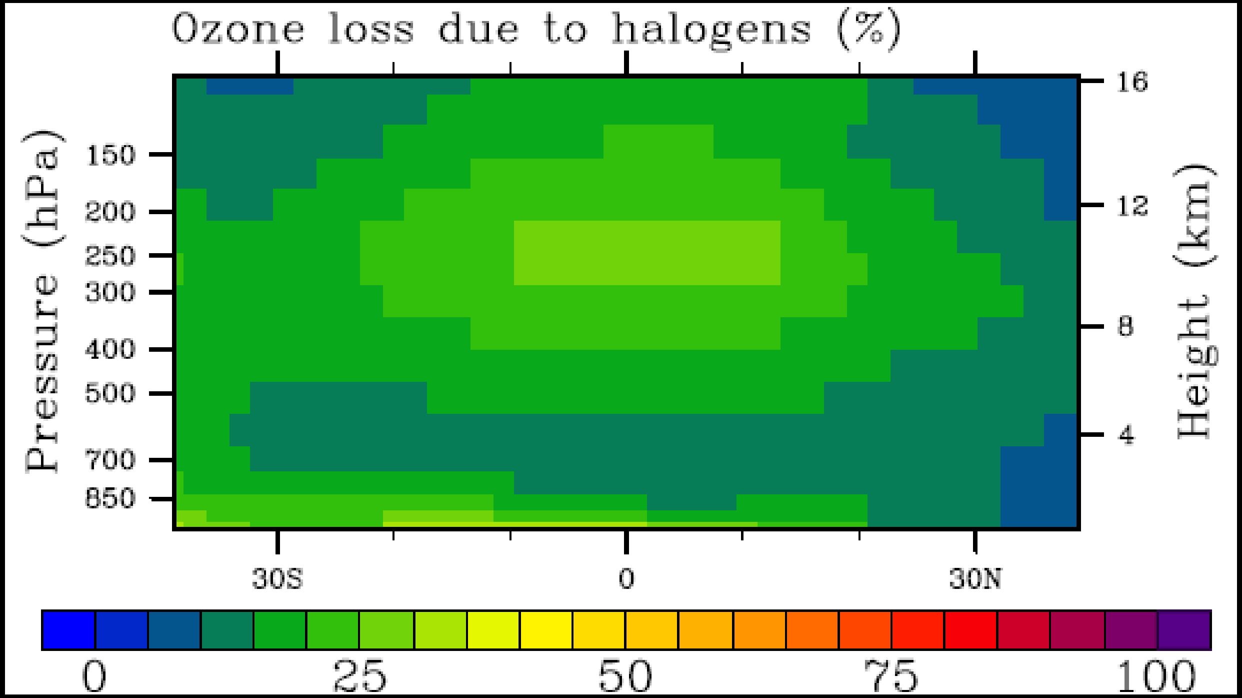
Relevance of bromine and iodine ?

- MBL: up to 45% of ozone loss is due to halogens
- Mostly due to iodine → Br : I : (I+Br) = 0.3 : 1 : 1.7
  - BrO + IO -> Br + I + O_2 (Br atom recycling)
  - HO_2 + IO -> OH + I + O_2 (OH radical recycling)

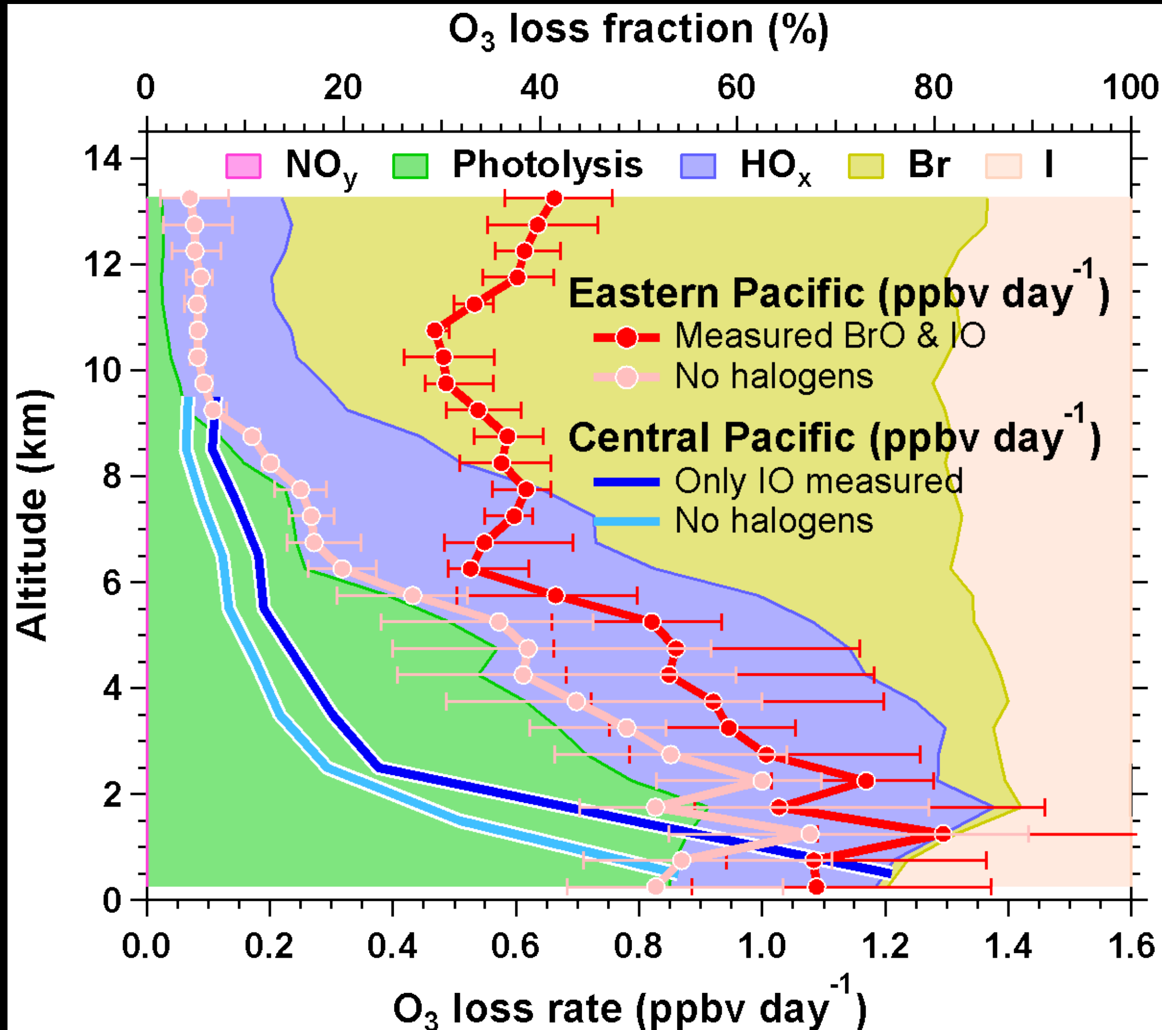


CAM-Chem model:
BrO ~ 0.2ppt
IO ~ 0.1 ppt

⇒ **Atmospheric models remain untested in FT**

Saiz Lopez et al., 2012
Parella et al., 2012

Relevance for O_3 loss rates



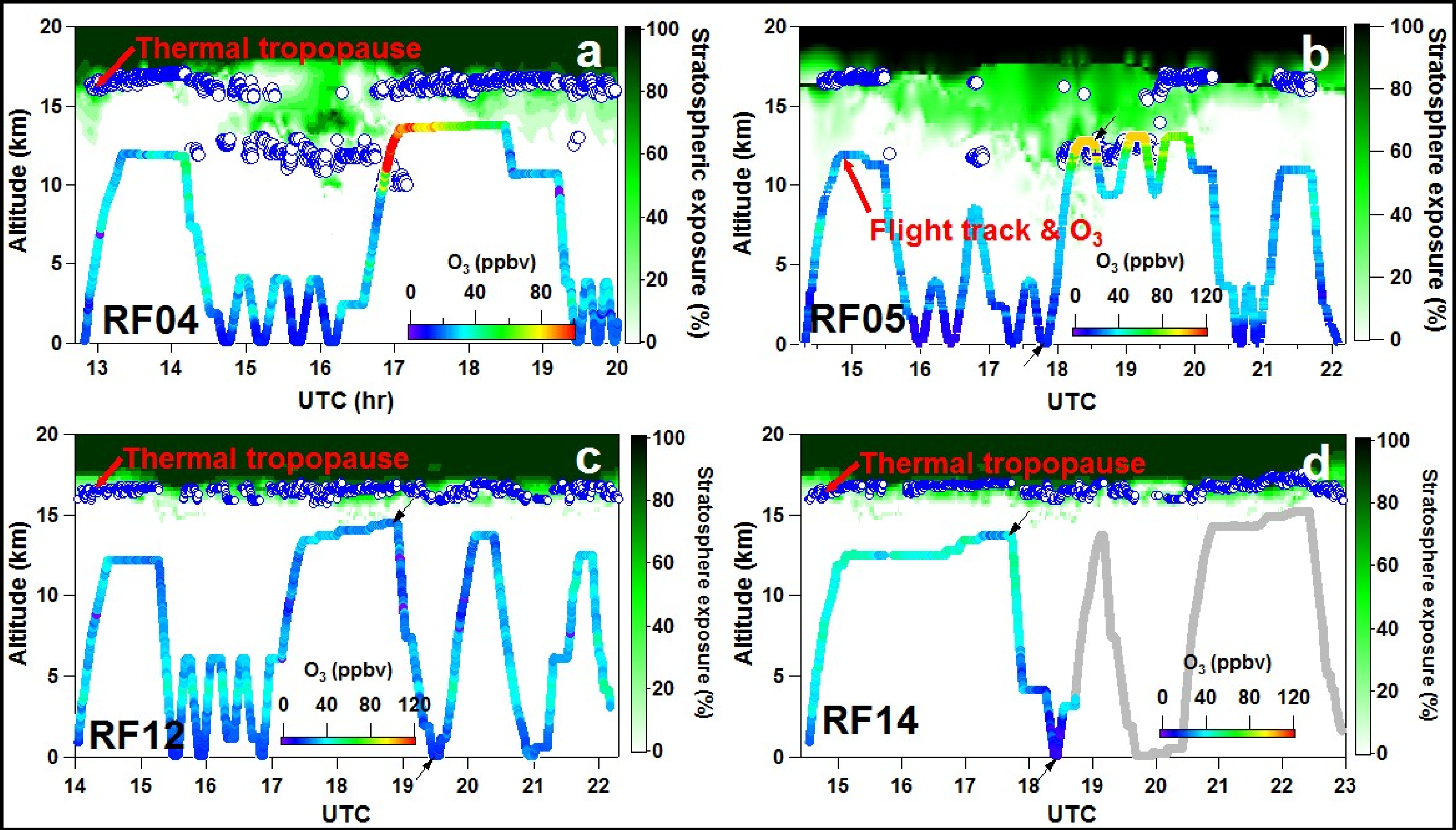
Bromine and Iodine account for 34% of the O_3 loss rate (tEPO)

Wang et al., 2015, PNAS

Double tropopause & tropical flights

SH mid-latitudes

SH subtropics



SH tropics

SH tropics