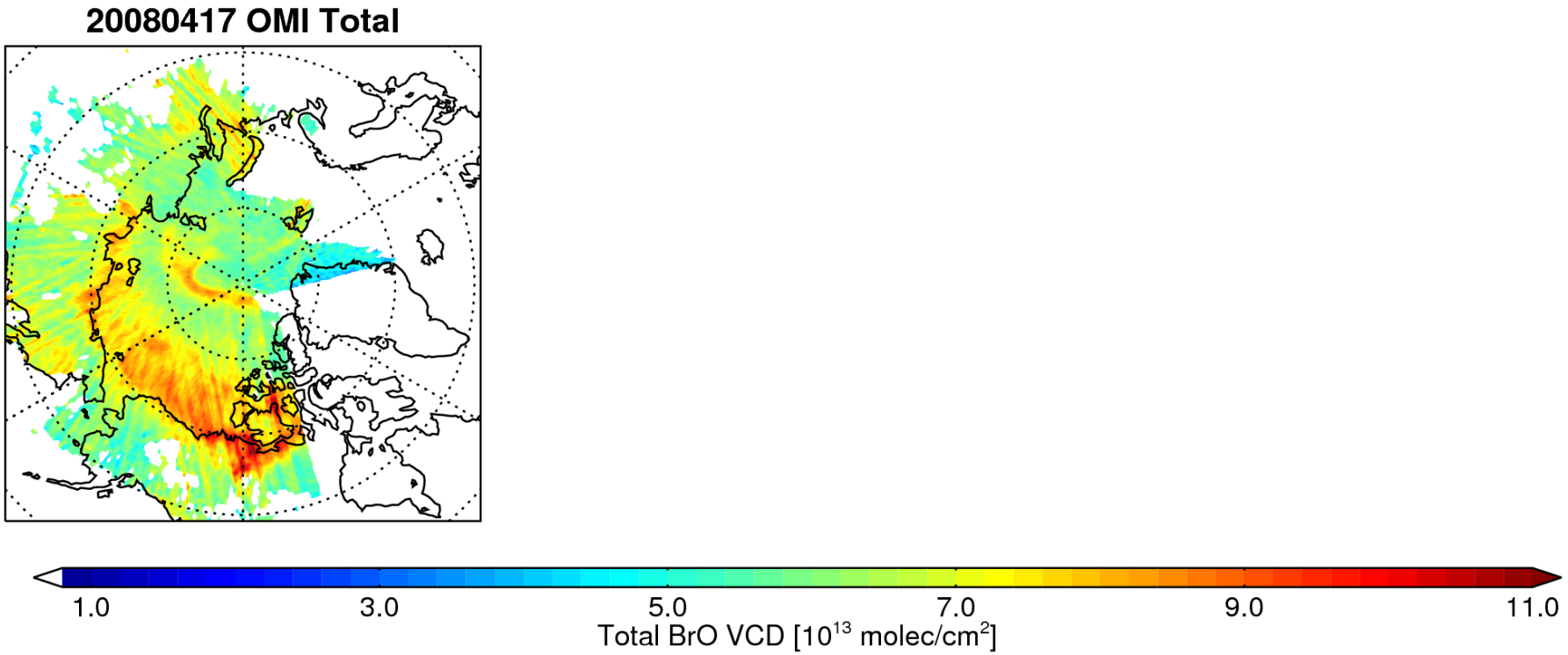
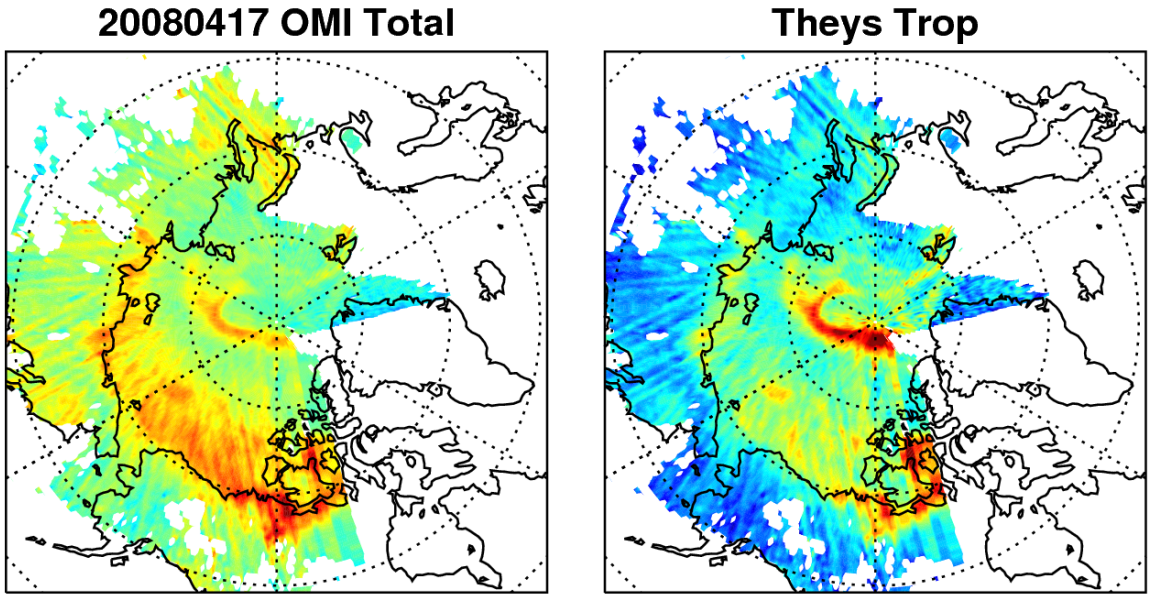
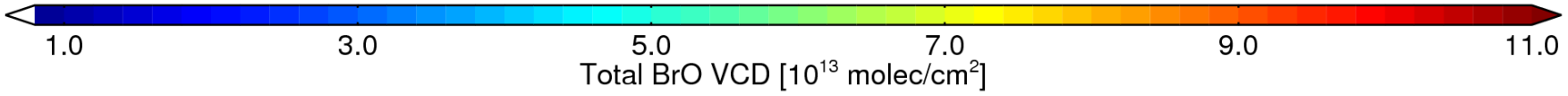
Tropical tropospheric bromine and stratospheric injection of Br_y from VSL compounds inferred from CONTRAST & ATTREX

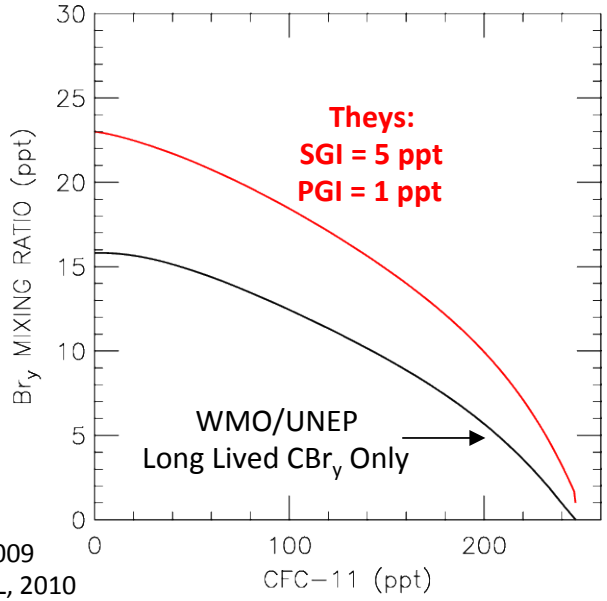
Ross Salawitch, Pam Wales, Julie Nicely, Dan Anderson, Tim Canty, Sungyeon Choi, Joanna Joiner, Elliot Atlas, Sue Schauffler, Valeria Donets, Richard Lueb, Maria Navarro, Eric Apel, Nicola Blake, Alan Hills, Rebecca Hornbrook, Daniel Riemer, Dexian Chen, Greg Huey, David Tanner, Rainer Volkamer, Theodore Koenig, Sunil Baidar, Barbara Dix, Andrew Weinheimer, Glenn Wolfe, Tom Hanisco, Sam Hall, Kirk Ullmann, Rafael Fernandez, Alfonso Saiz-Lopez, Doug Kinnison, Jean-Francois Lamarque, Shawn Honomichl, and Laura Pan

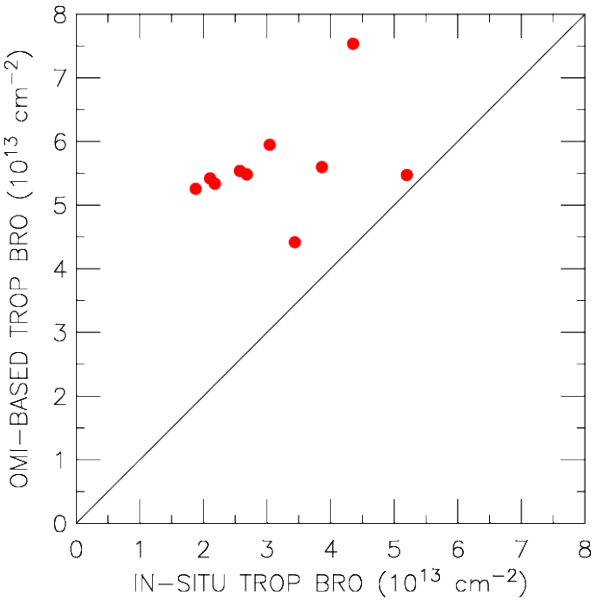


Theys et al., ACP, 2009
Salawitch et al., GRL, 2010
Choi et al.,ACP, 2014
Liao et al., ACP, 2014









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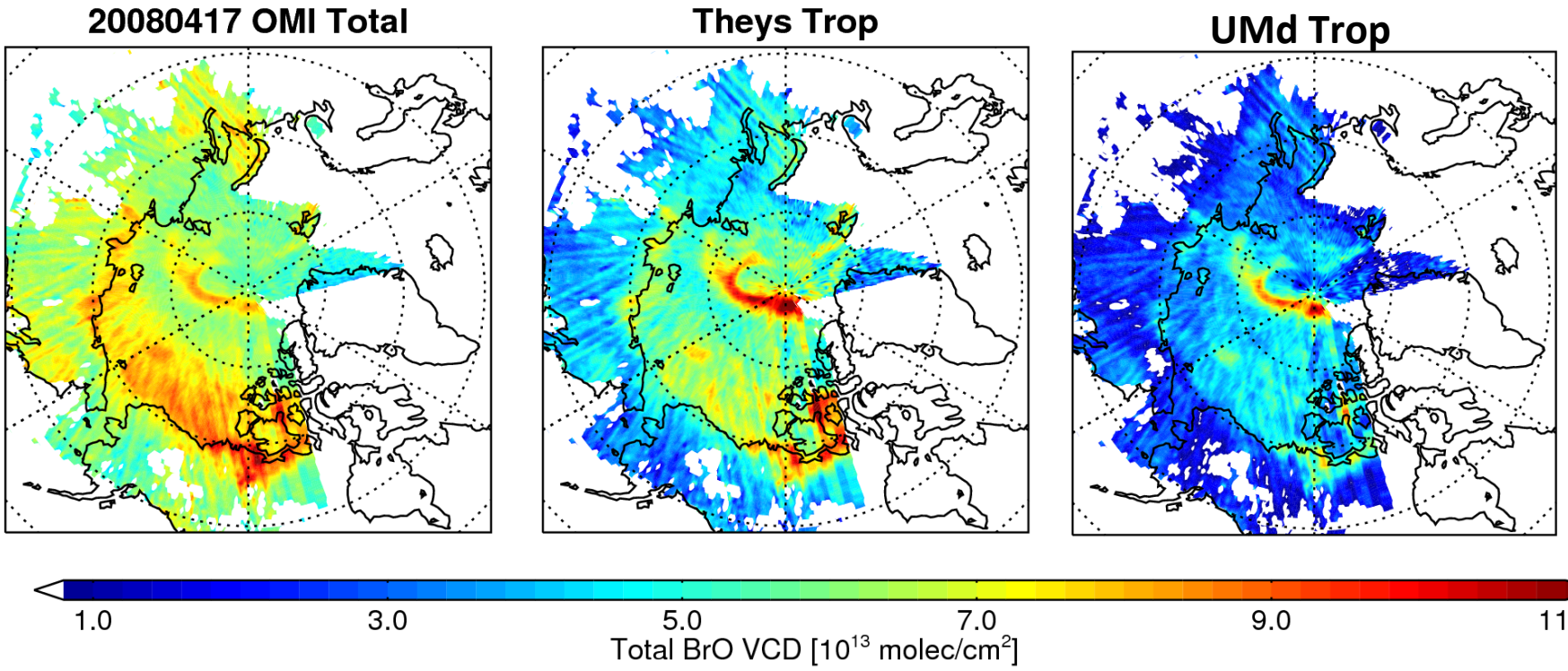
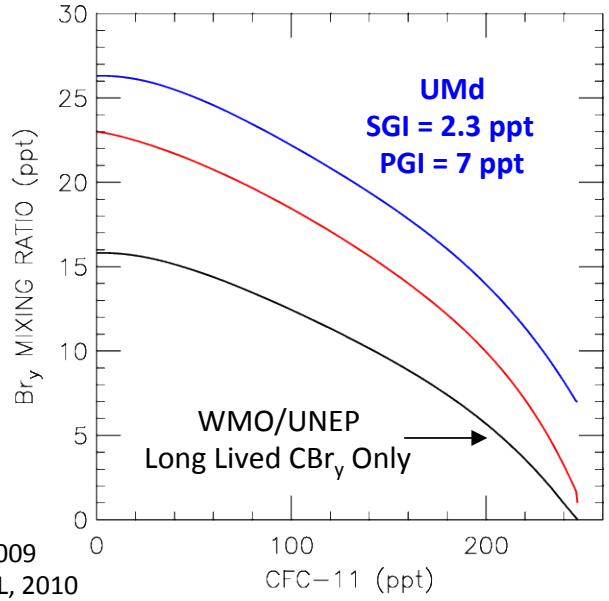
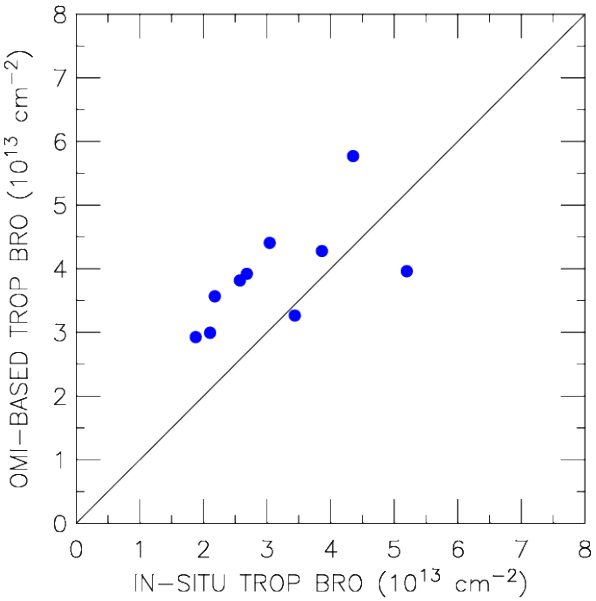
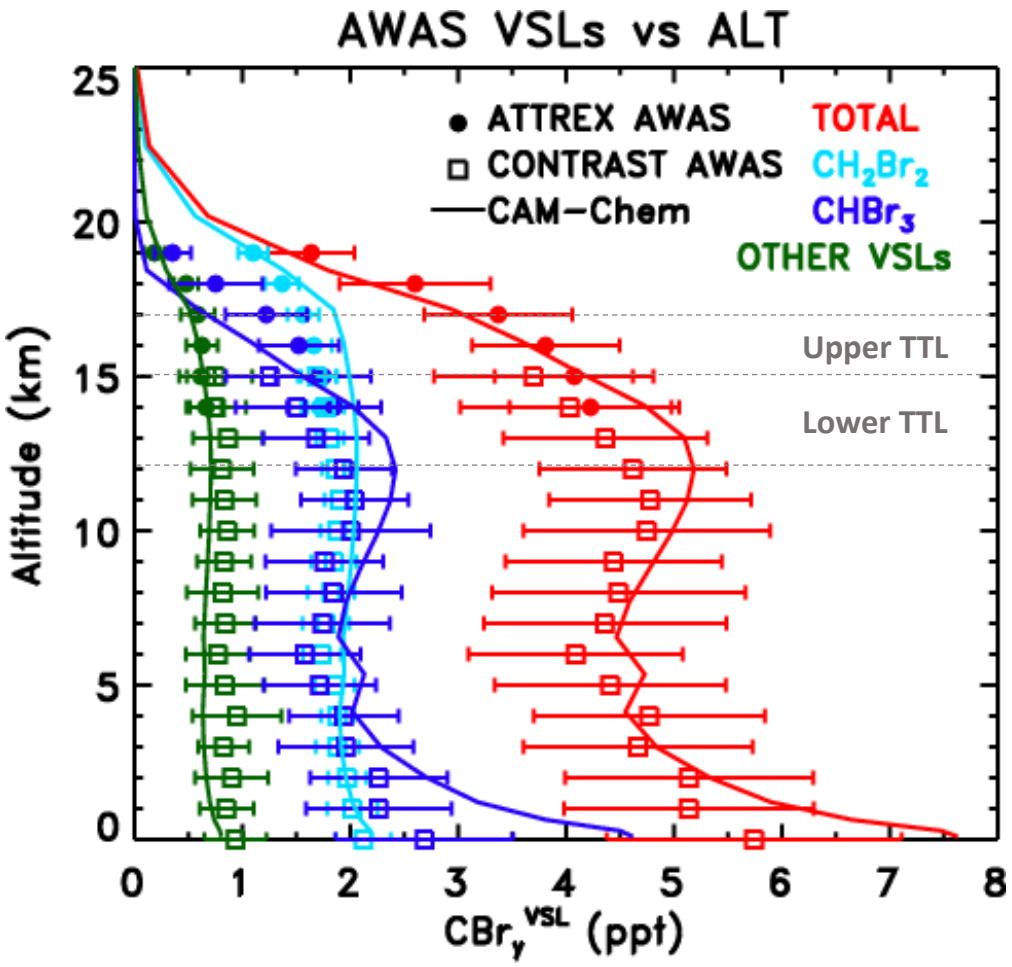






Theys et al., ACP, 2009
Salawitch et al., GRL, 2010
Choi et al.,ACP, 2014
Liao et al., ACP, 2014

VSLS: Very Short Lived Substance

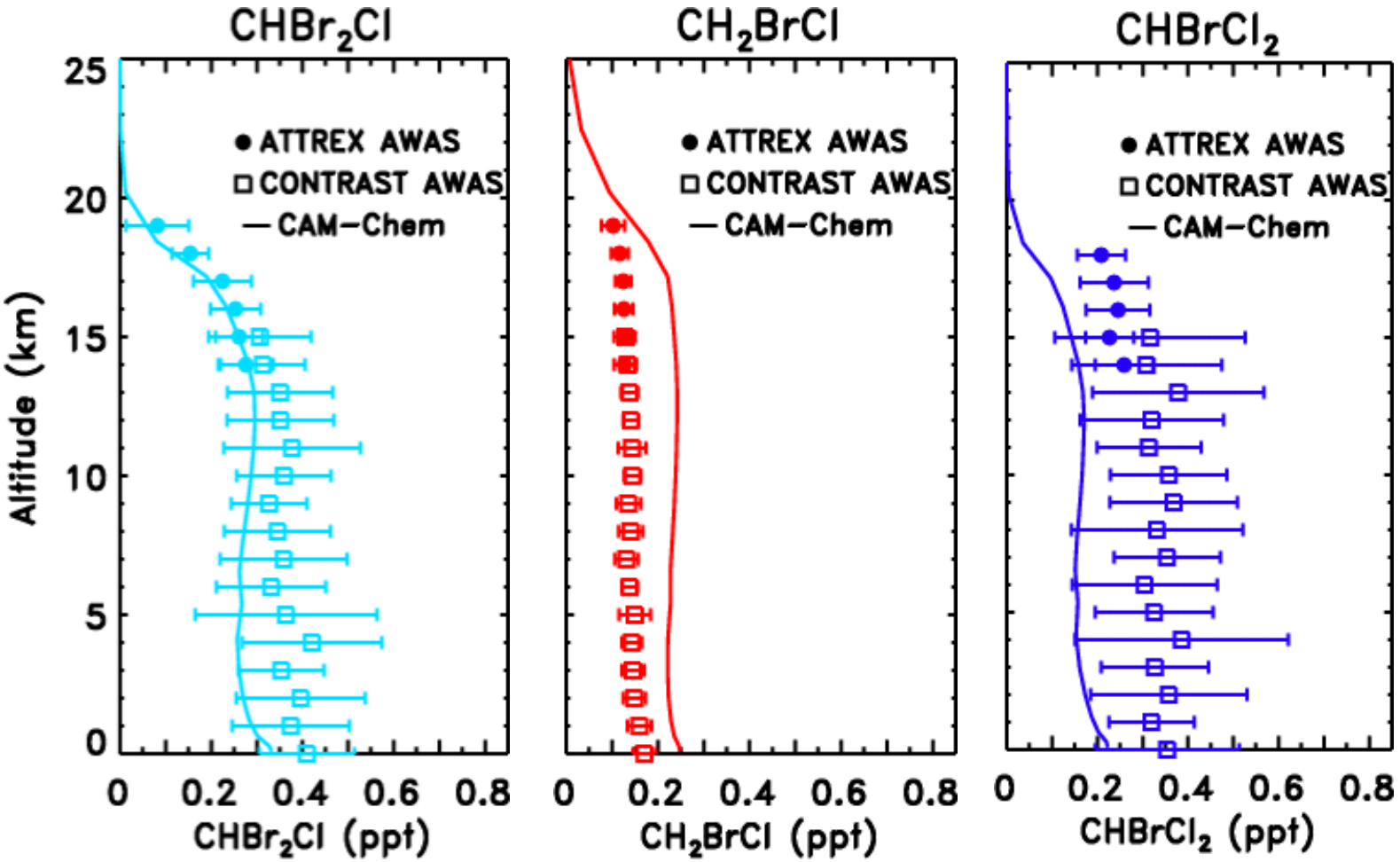


Measurements: AWAS

Model: Fernandez et al., ACP, 2014 Note: paper did not include CONTRAST data

Geographically & seasonally distributed oceanic sources of VSLS as described in Ordonez et al. (2012)

Closer look at minor VSLS

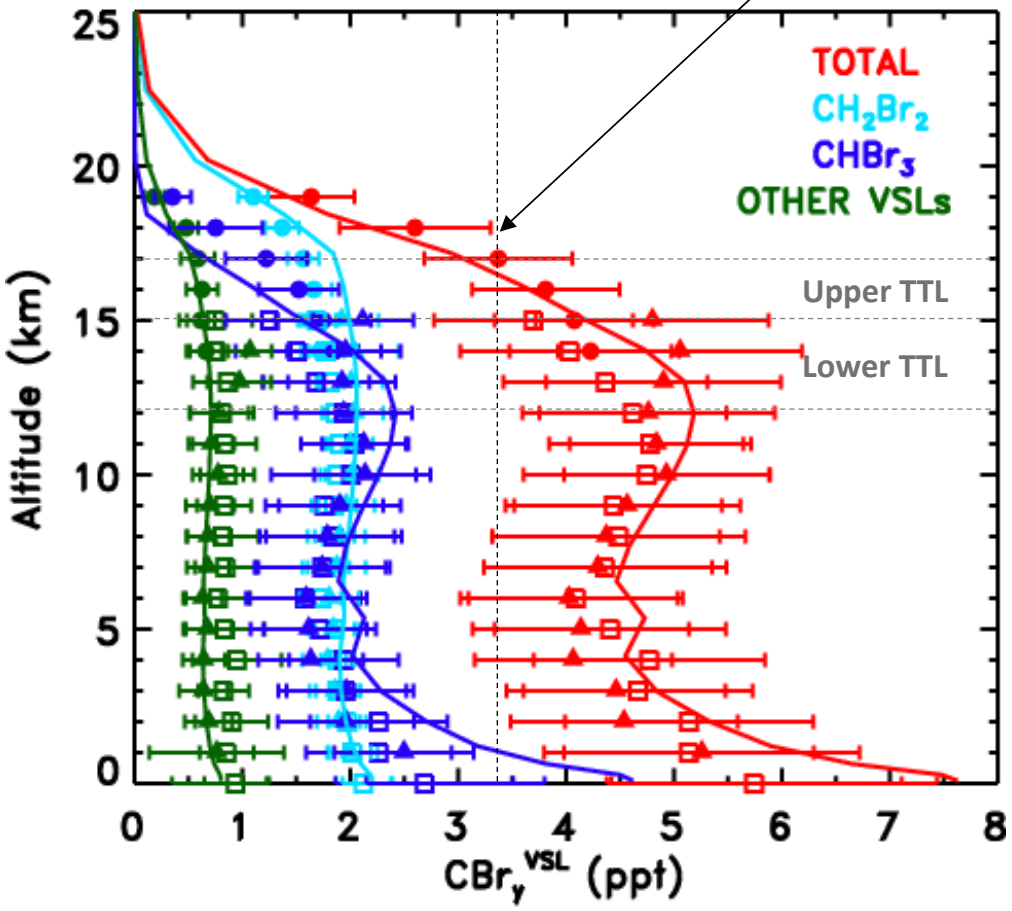


Measurements: AWAS

Model: Fernandez et al., ACP, 2014 Note: paper did not include CONTRAST data

Geographically & seasonally distributed oceanic sources of VSLS as described in Ordonez et al. (2012)

Source Gas Injection (SGI) of Br_y due to VSLS, aka $Br_y^{VSLS\ SGI} \approx 3.37 \pm 0.68$ ppt



Measurements: AWAS

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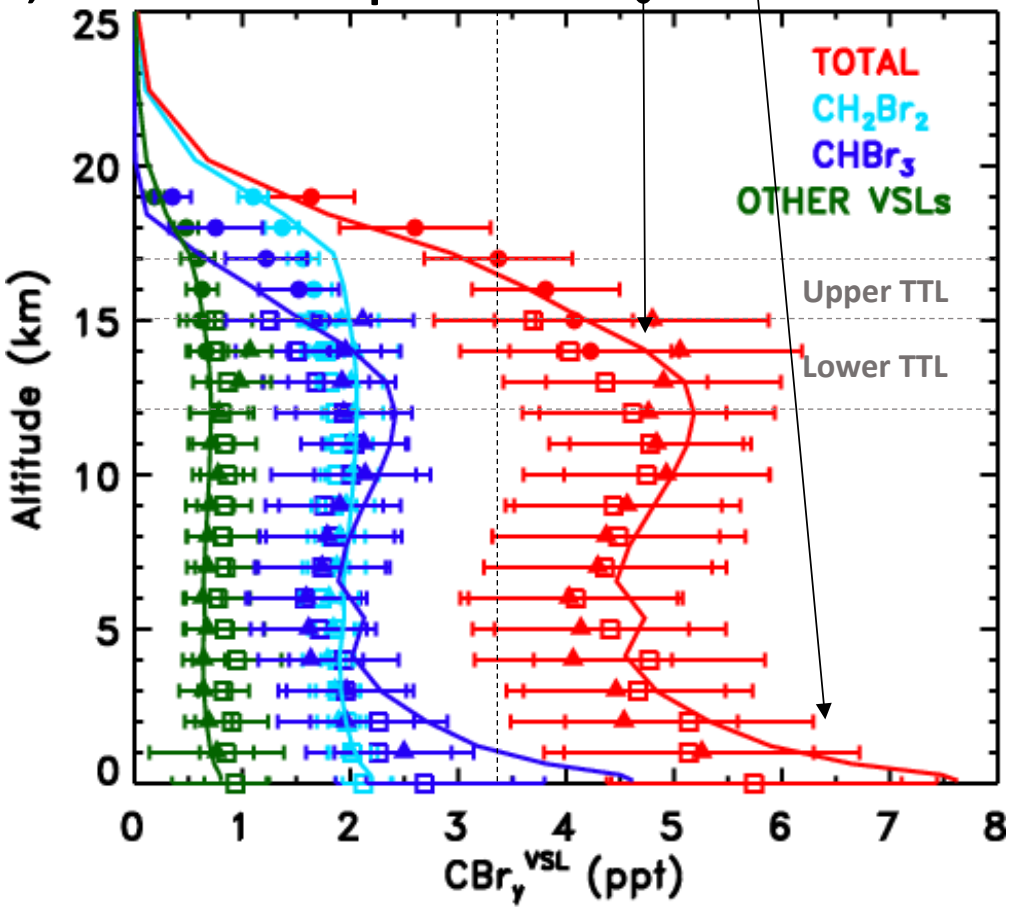
Product Gas Injection (PGI) depends on CBr_y near surface, lofting of bromine by saline aerosols, and het chem processes in TTL



Measurements: AWAS

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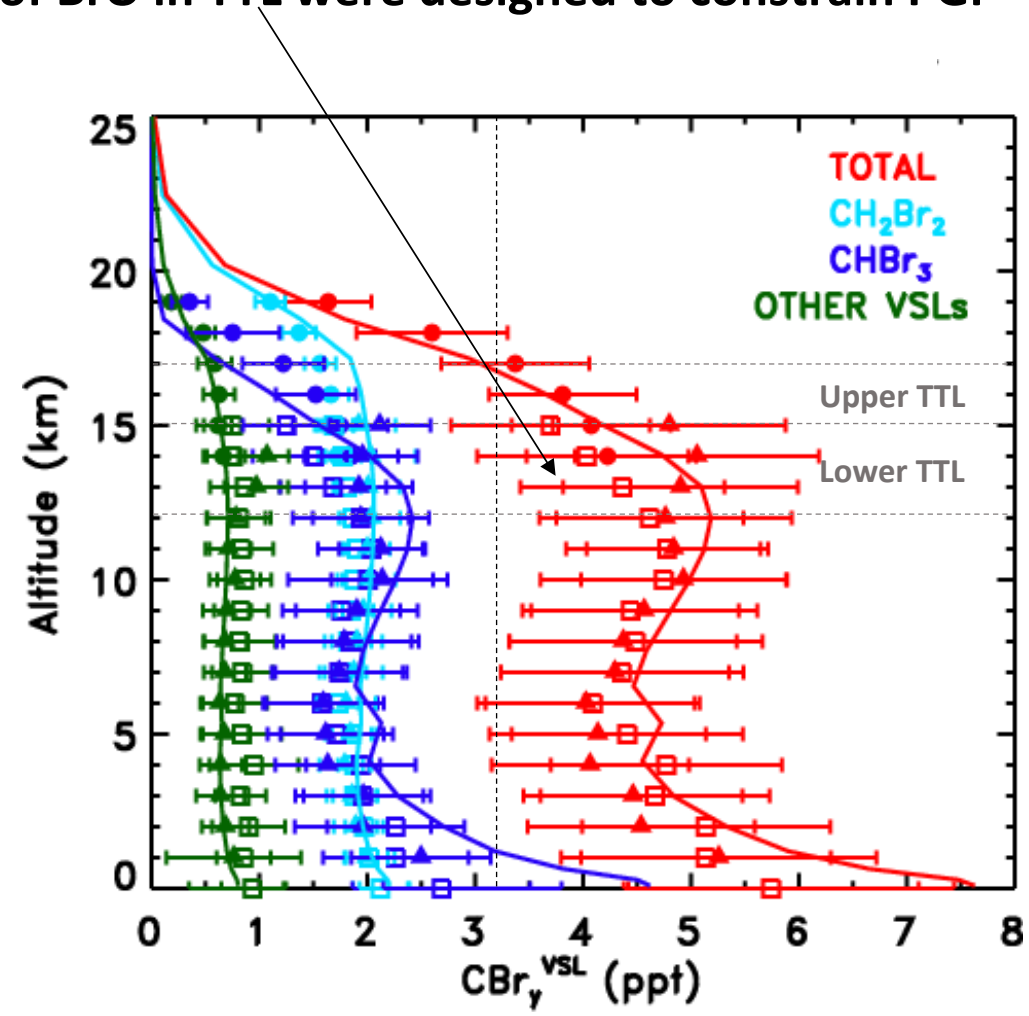
Geographically & seasonally distributed oceanic sources of VSLS as described in Ordonez et al. (2012)

Measurements of BrO in TTL were designed to constrain PGI



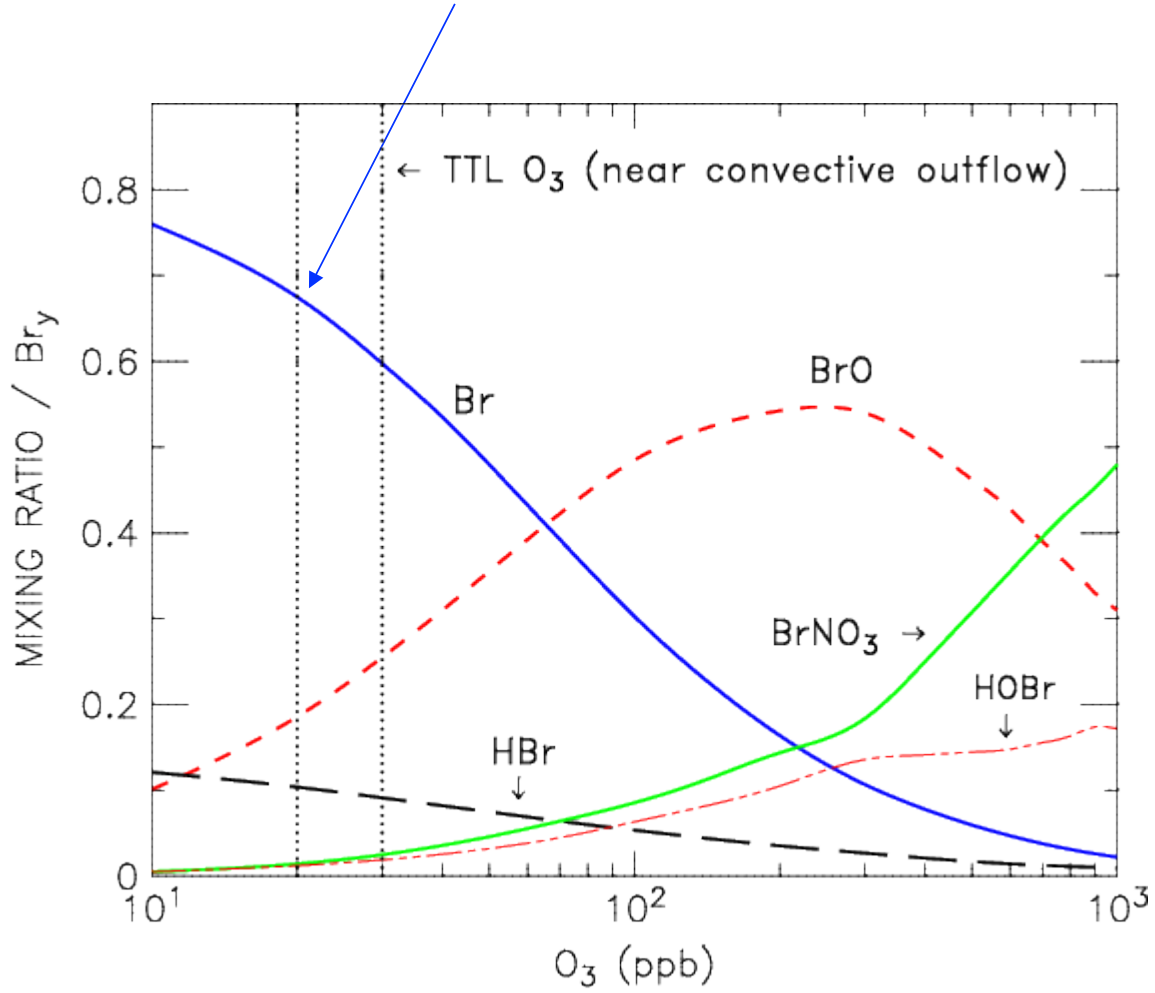
Measurements: AWAS

Model: Fernandez et al., ACP, 2014 Note: paper did not include CONTRAST data

Geographically & seasonally distributed oceanic sources of VSLS as described in Ordonez et al. (2012)

Measurements of BrO in TTL were designed to constrain PGI

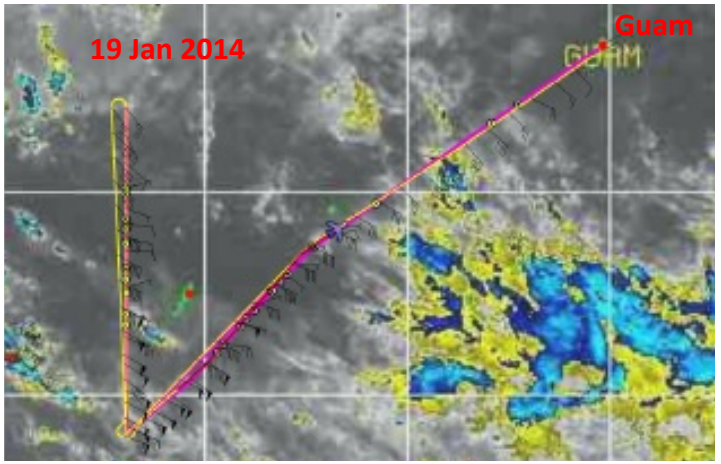
But theory indicates most of the product gas, if present in the gas phase, will be in the form of atomic-Br

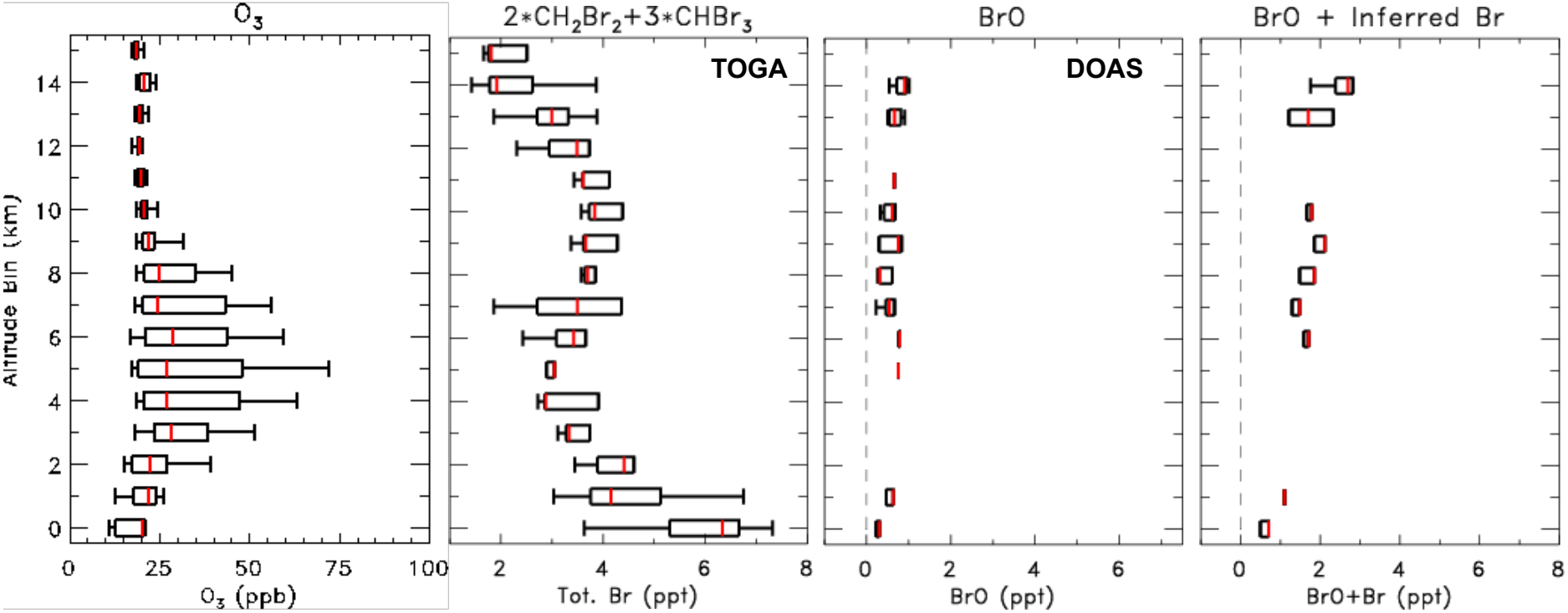


Fernandez et al., ACP, 2014

GV Flight	Description	AWAS	TOGA	DOAS	CIMS
RF01	Colo to HI		✓	✓	
RF02	HI to Guam		✓	✓	
RF03	SE survey		✓		
RF04	**SW survey**		✓	✓	
RF05	Local active convection	✓	✓		
RF06	North jet crossing, moderate stratosphere	✓	✓	✓	
RF07	Convective outflow	✓	✓		
RF08	Photochemical sunset	✓	✓		
RF09	**Convective outflow, PNG fly-by**	✓	✓		✓
RF10	CO River, ITCZ survey	✓	✓		✓
RF11	**Convective outflow to SW, GH flight**	✓	✓		✓
RF12	Convective outflow to SE, GH flight	✓	✓		✓
RF13	Photochemical sunrise	✓	✓		✓
RF14	Equator crossing, SH survey	✓	✓		✓
RF15	**North jet crossing, deep stratosphere**	✓	✓	✓	✓

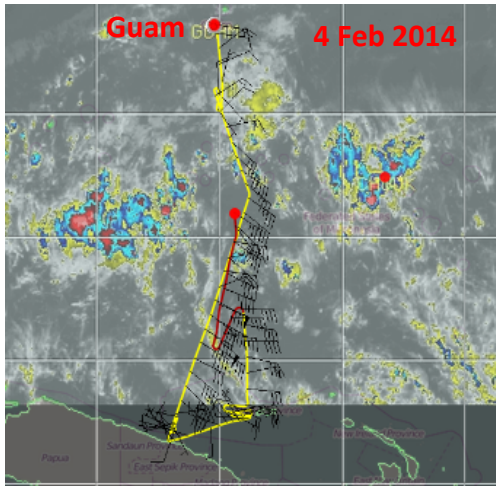
RF04: Southwest Survey

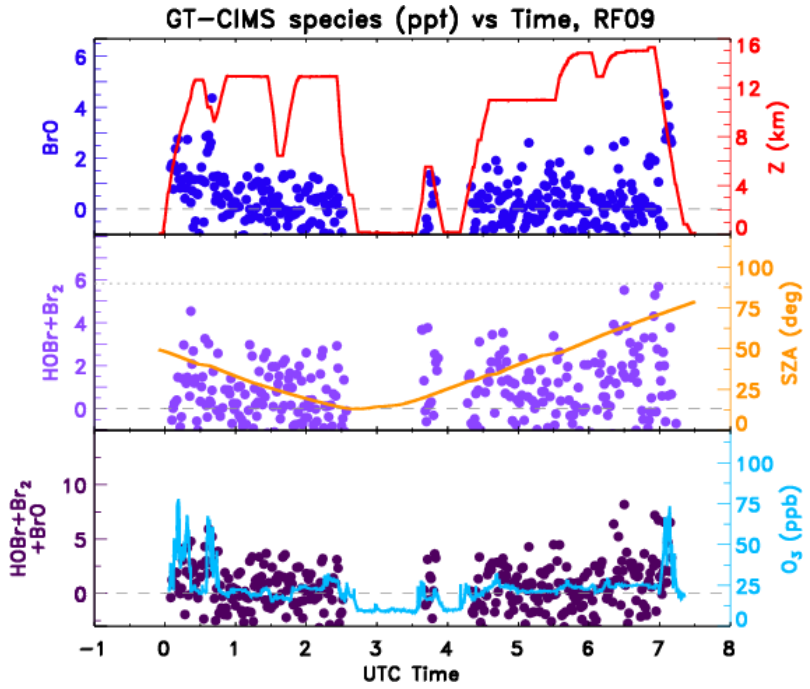




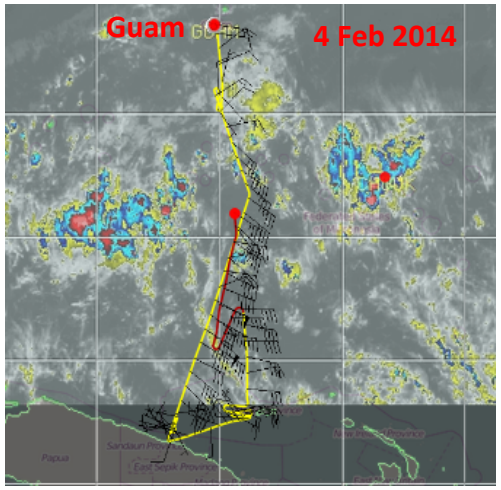
CT3LS, Boulder, Co, July 2015

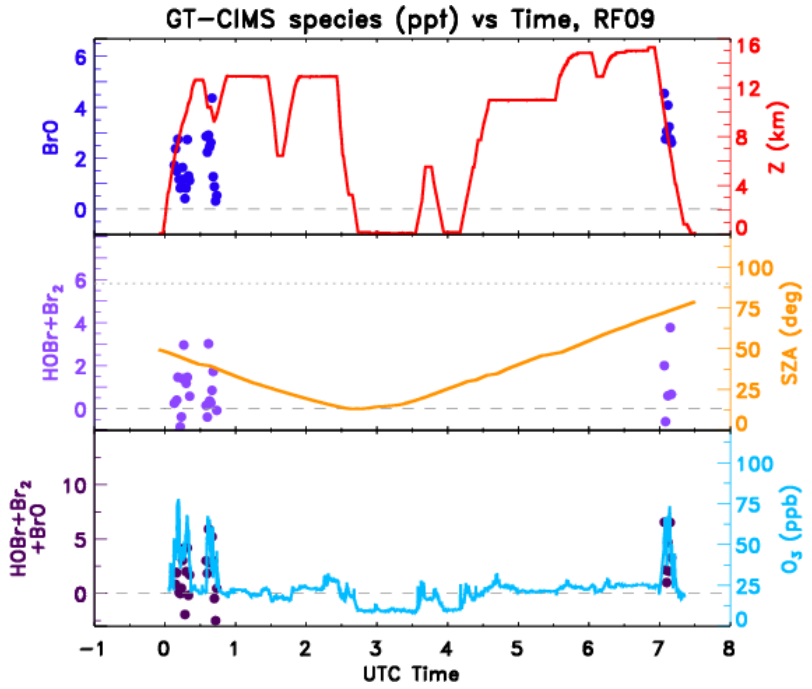
RF09: Convective Outflow and Equator Crossing





RF09: Convective Outflow and Equator Crossing





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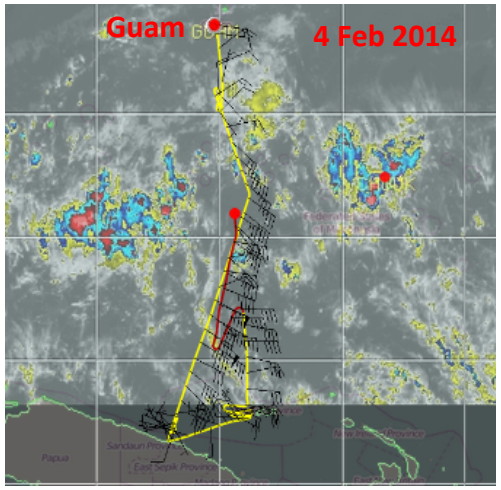

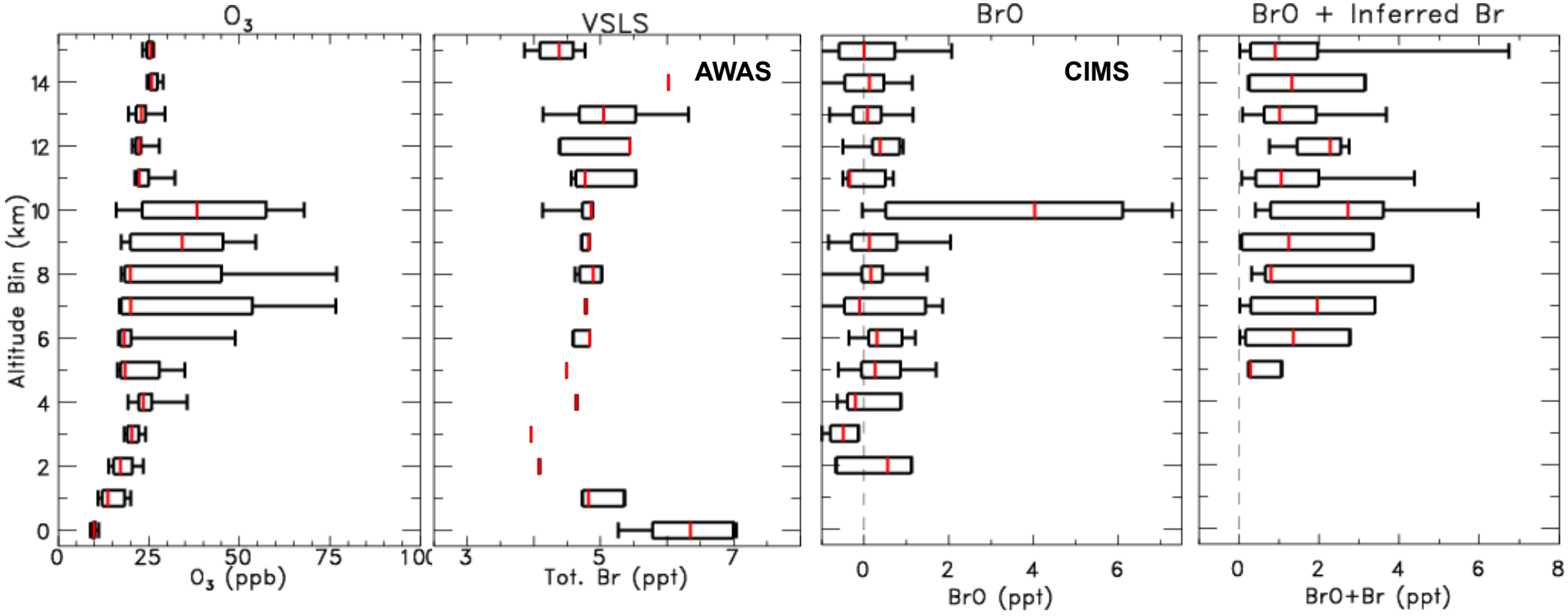

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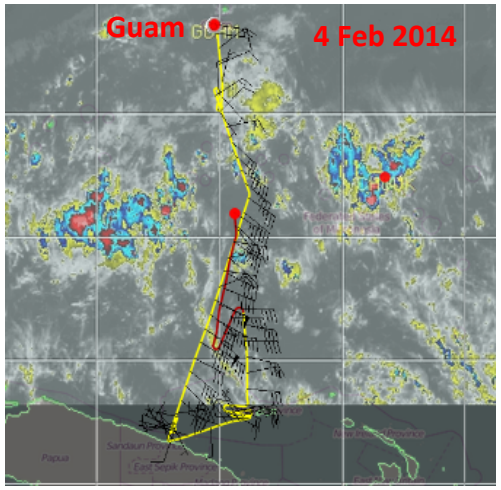
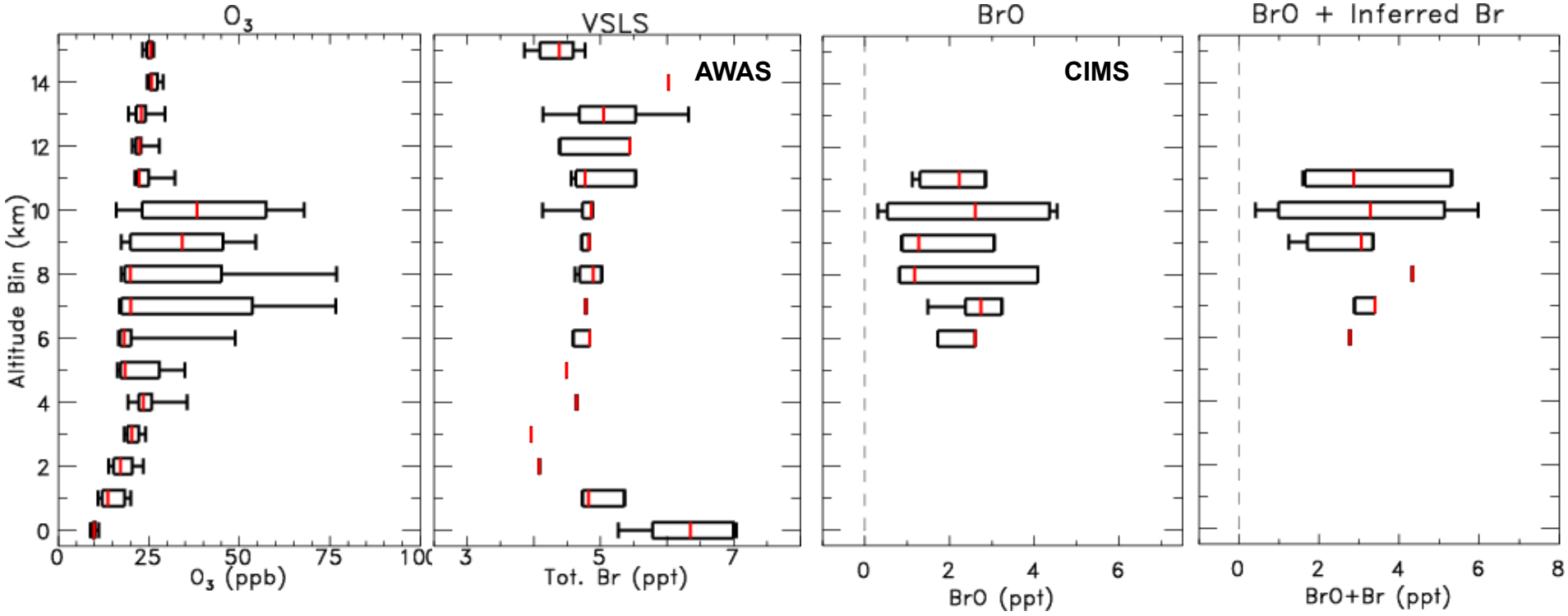
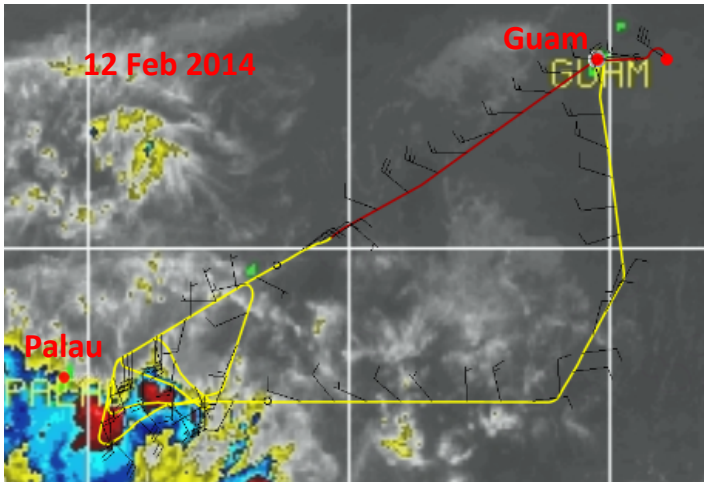
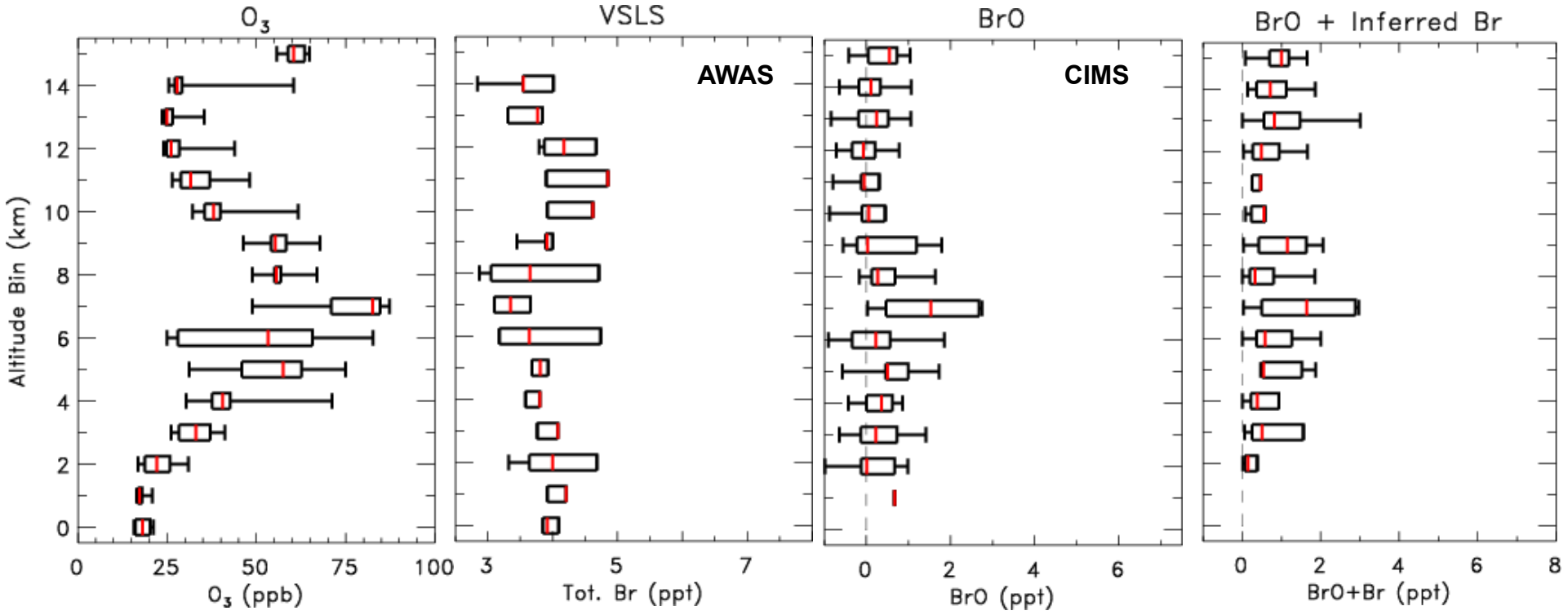




RF11: Convective outflow to SW, GH flight





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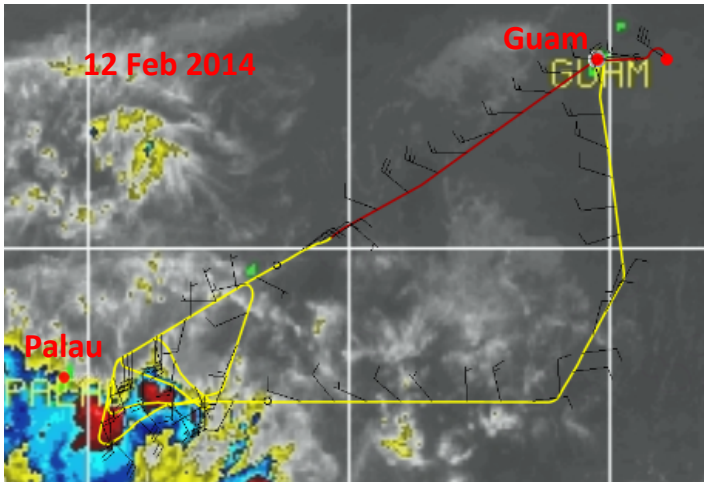
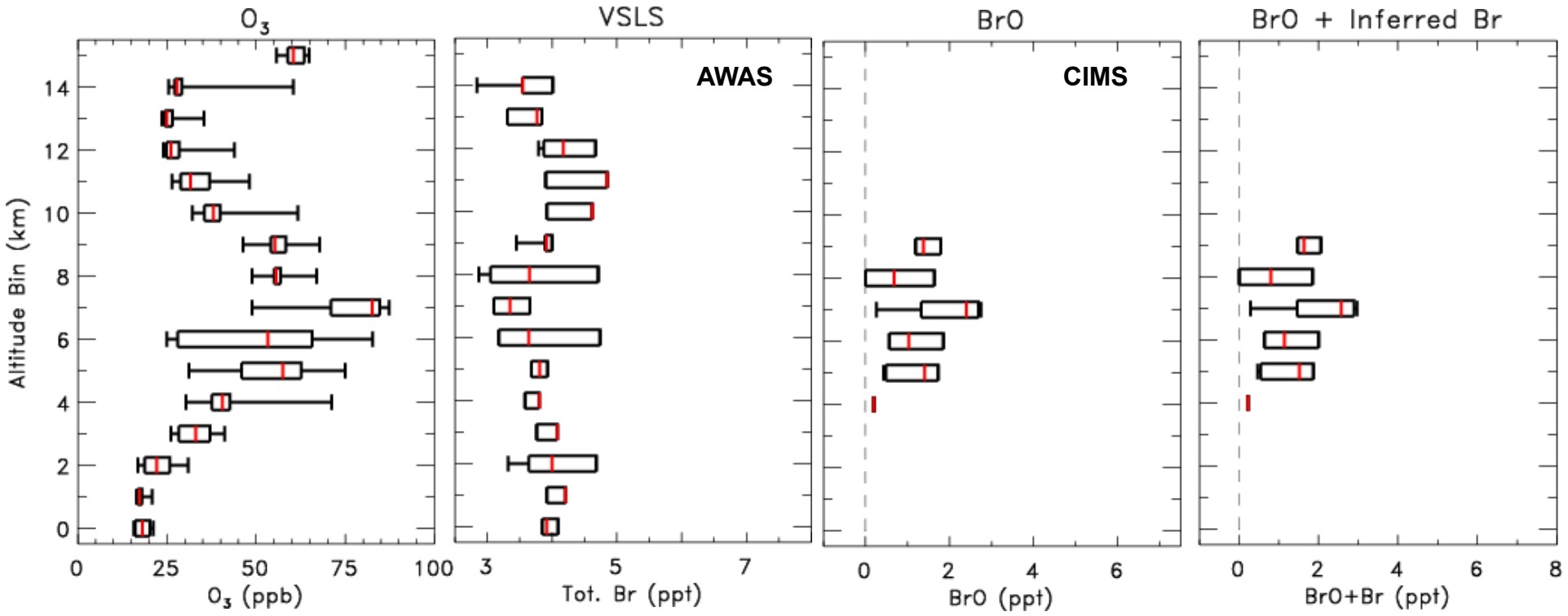
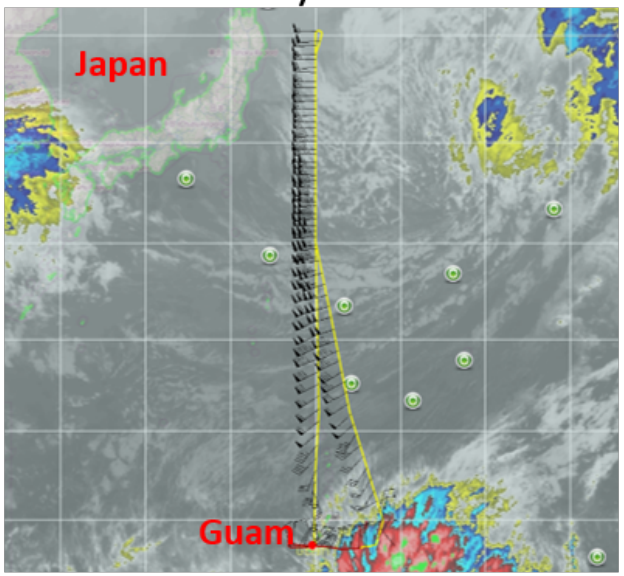


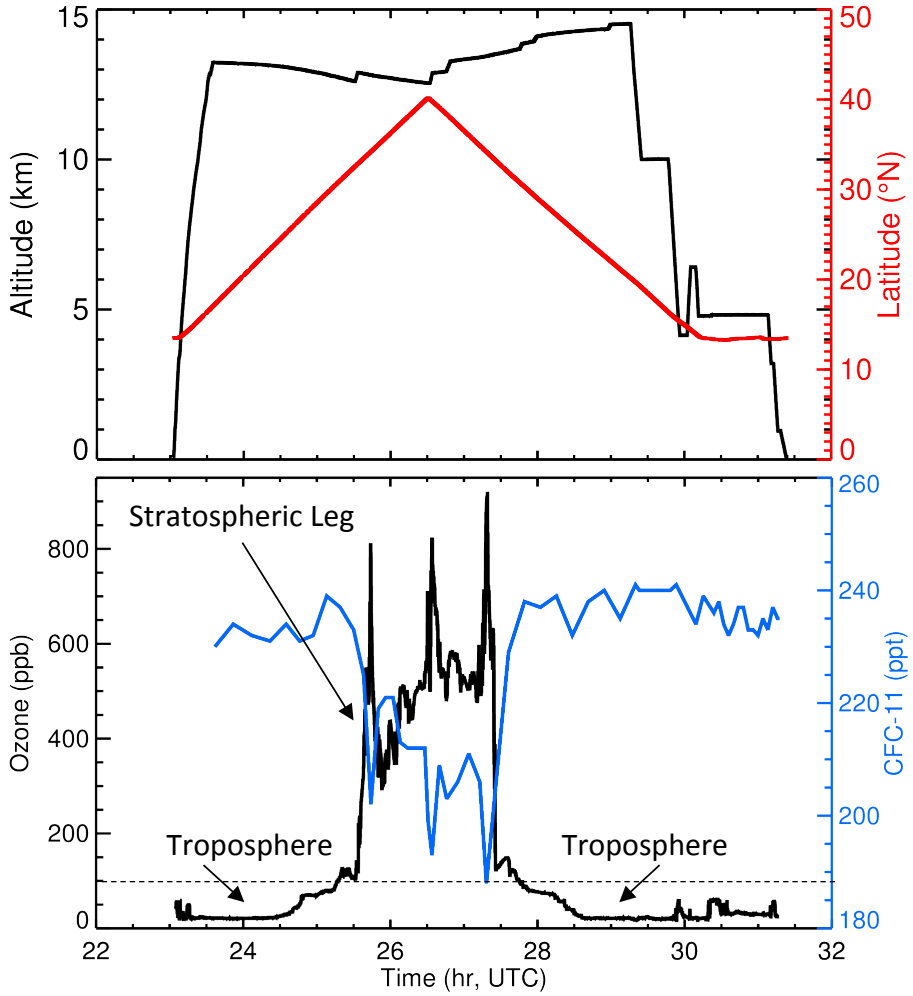


RF15: Northward Jet Crossing, Deep Stratosphere

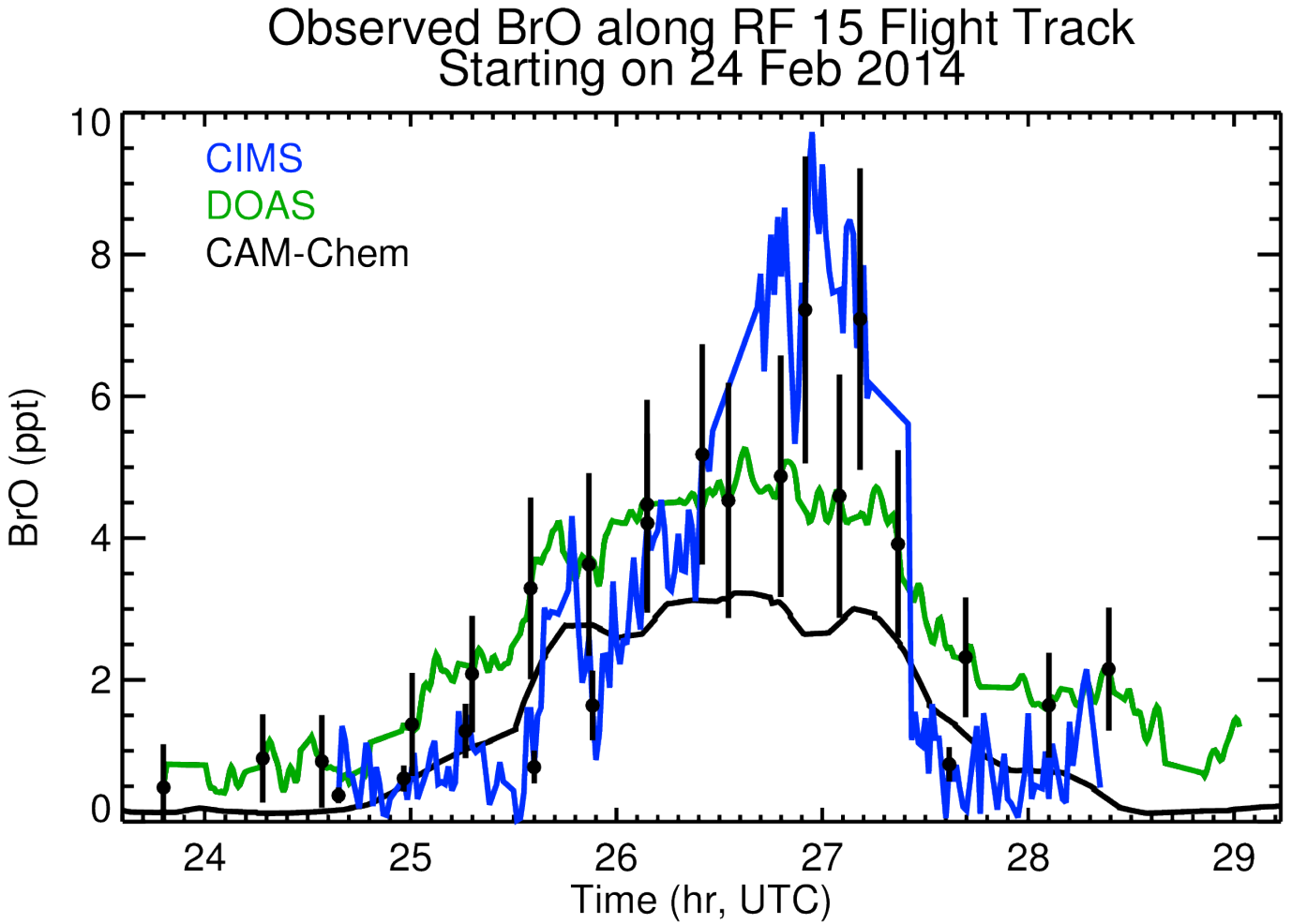
RF15: 25 Feb 2014

Northern Survey: reached 385 K

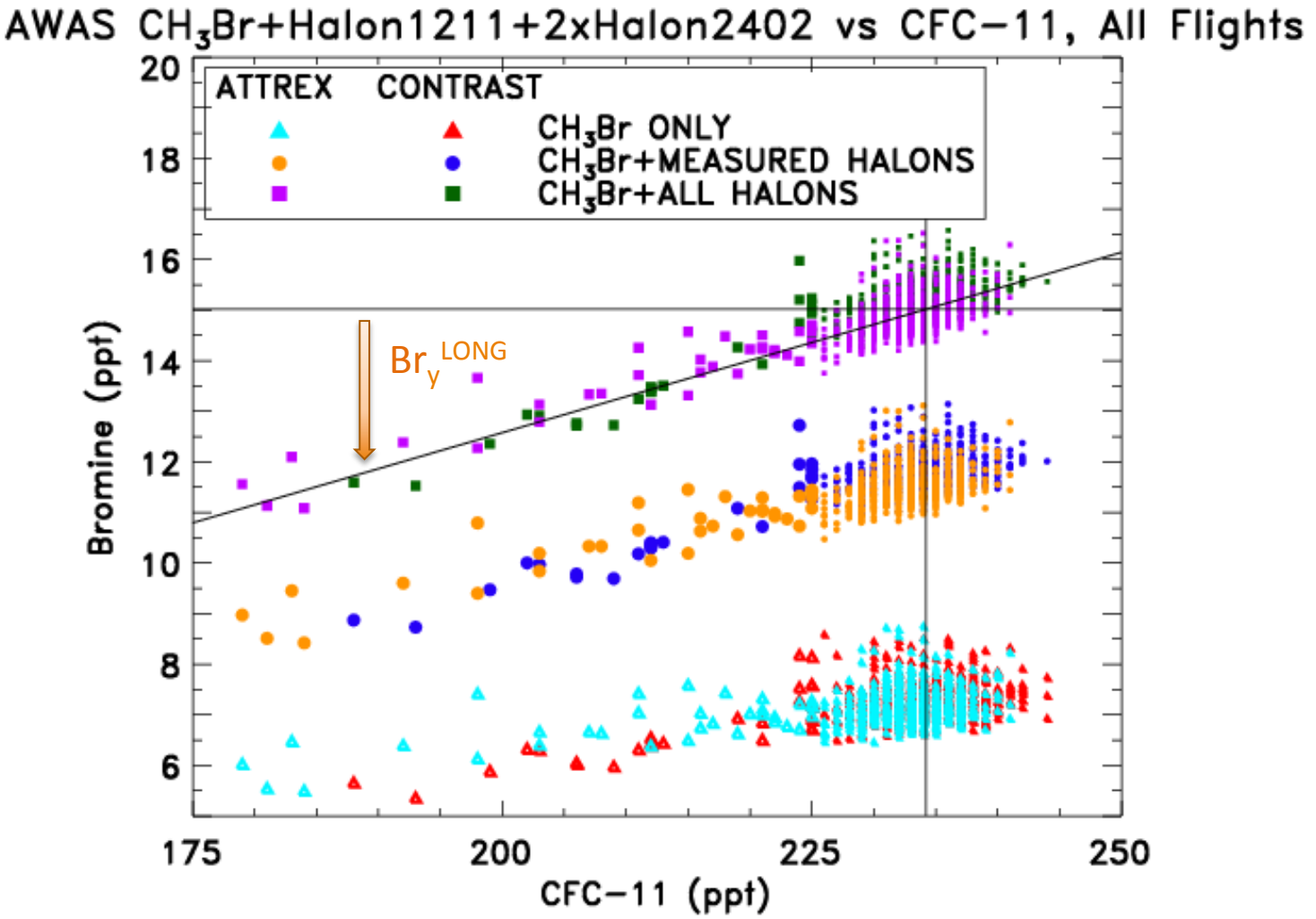




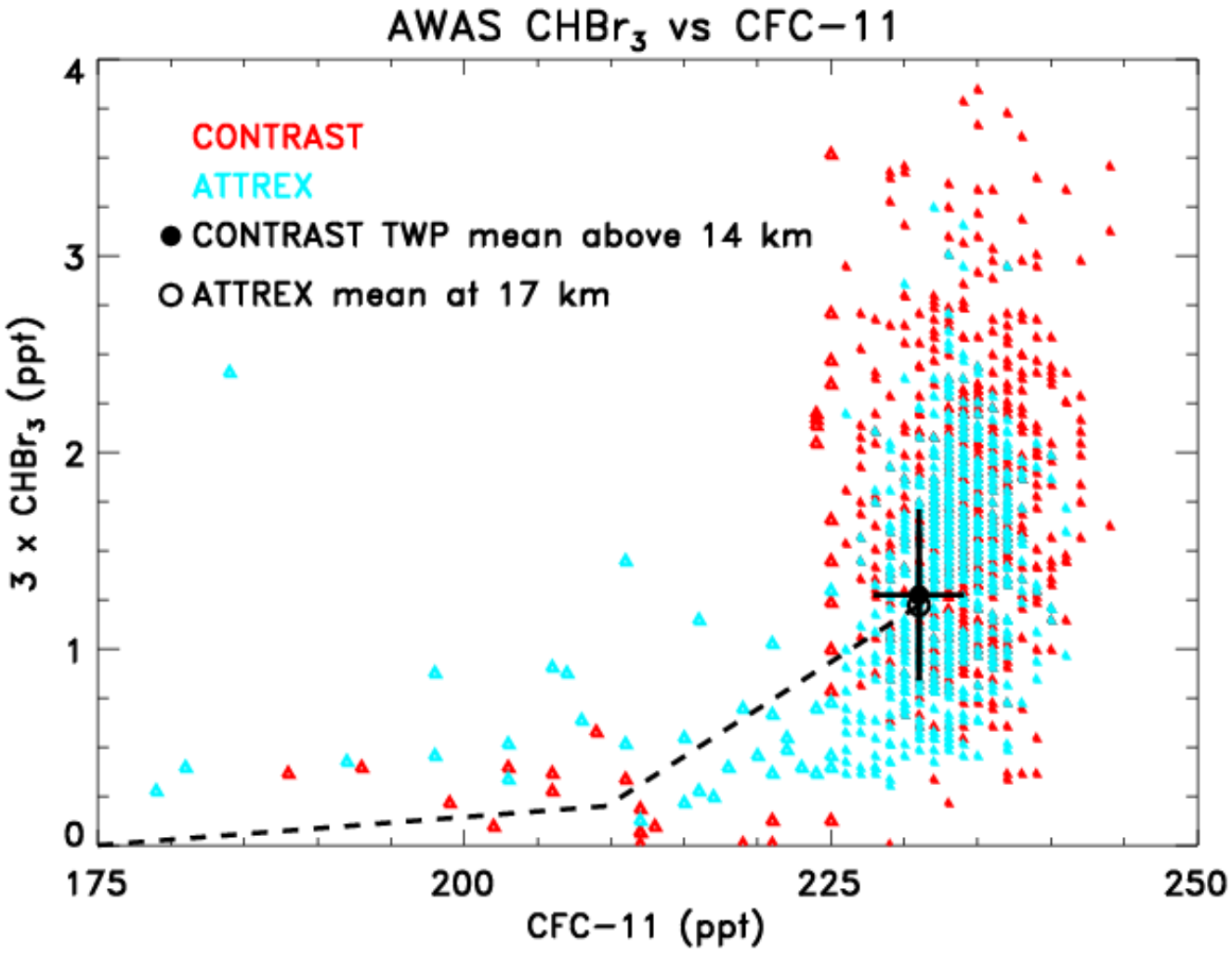
RF15: Northward Jet Crossing, Deep Stratosphere



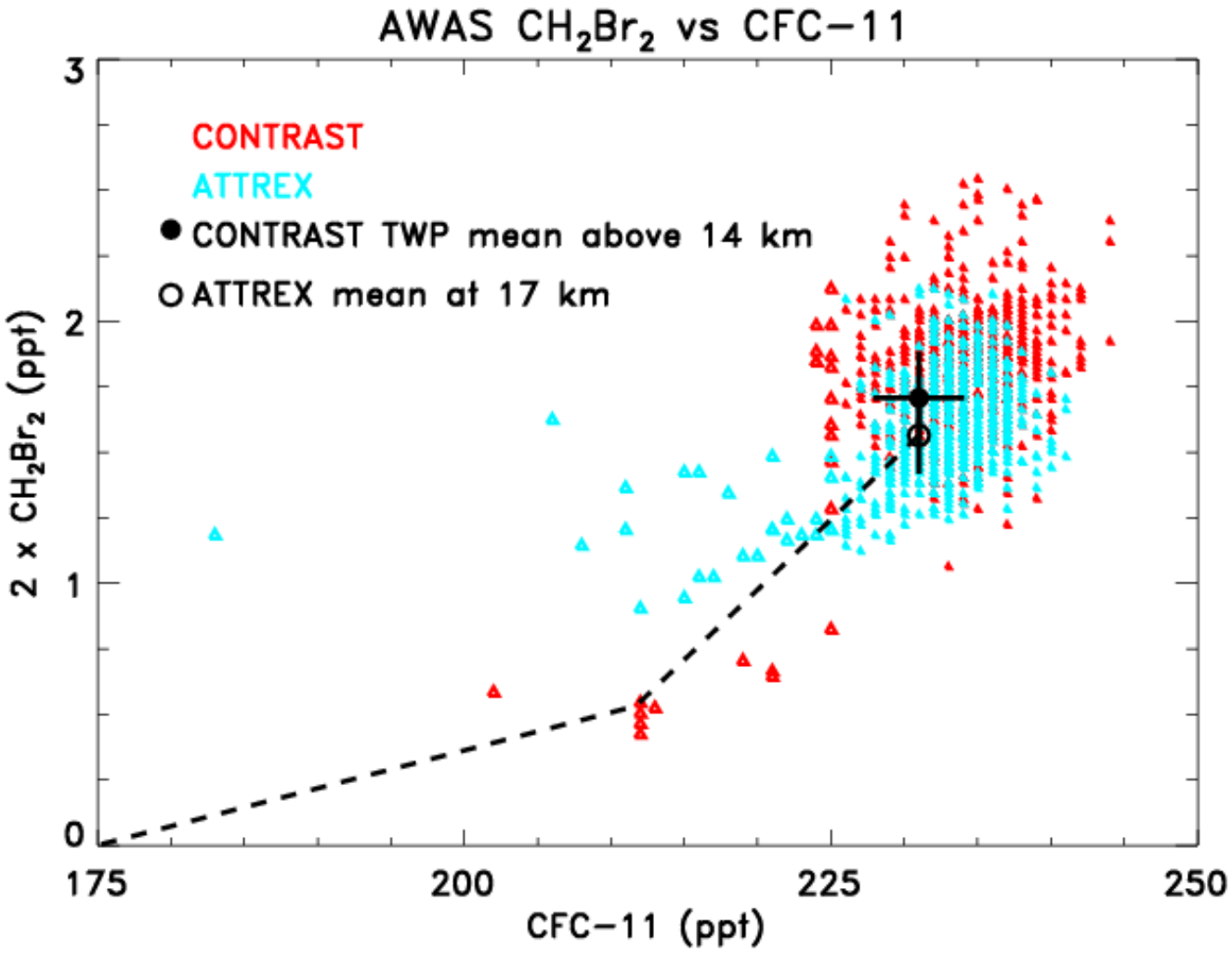
Long Lived CBr_y: ATTREX & CONTRAST



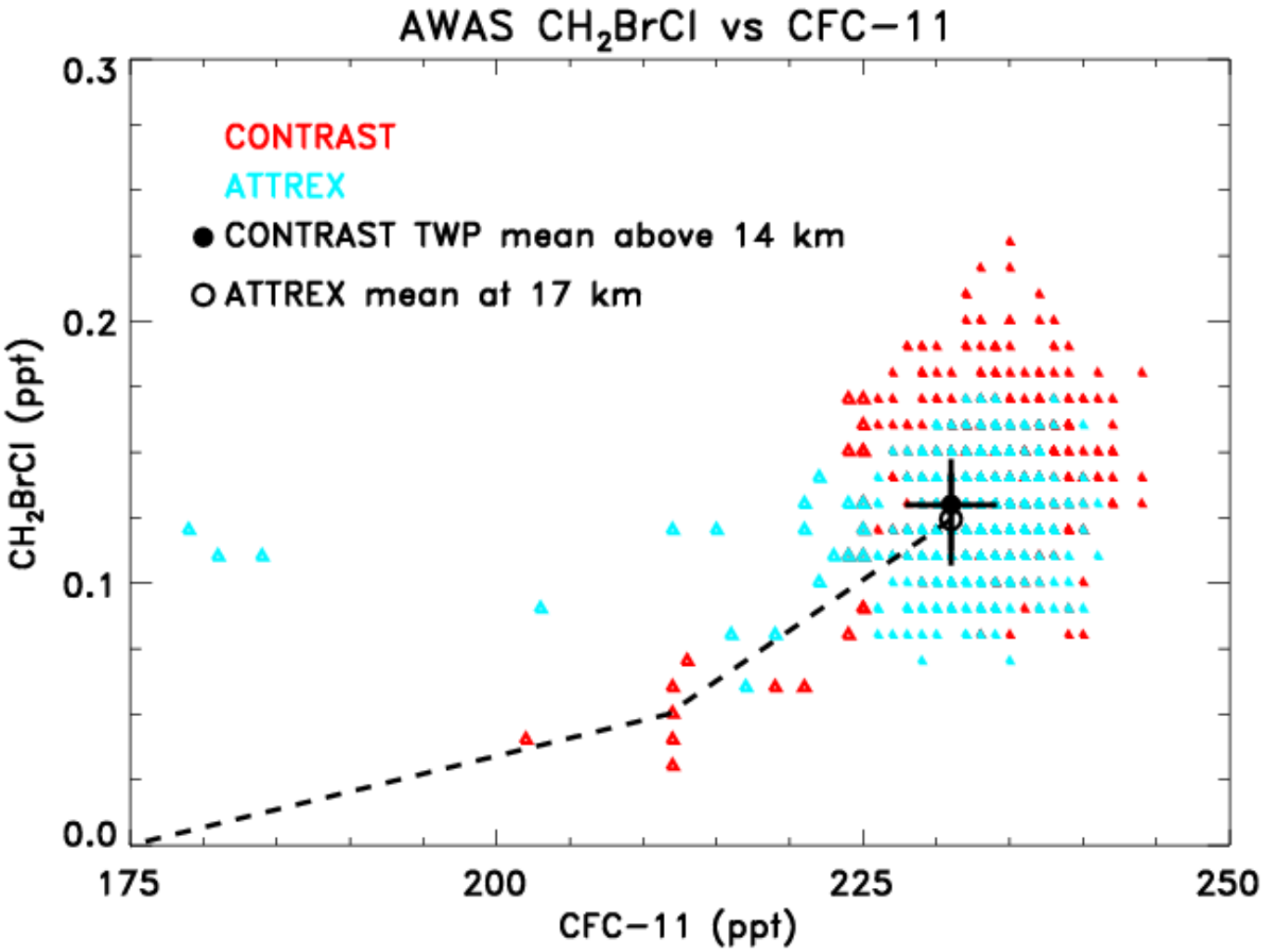
$CHBr_3$: ATTREX & CONTRAST



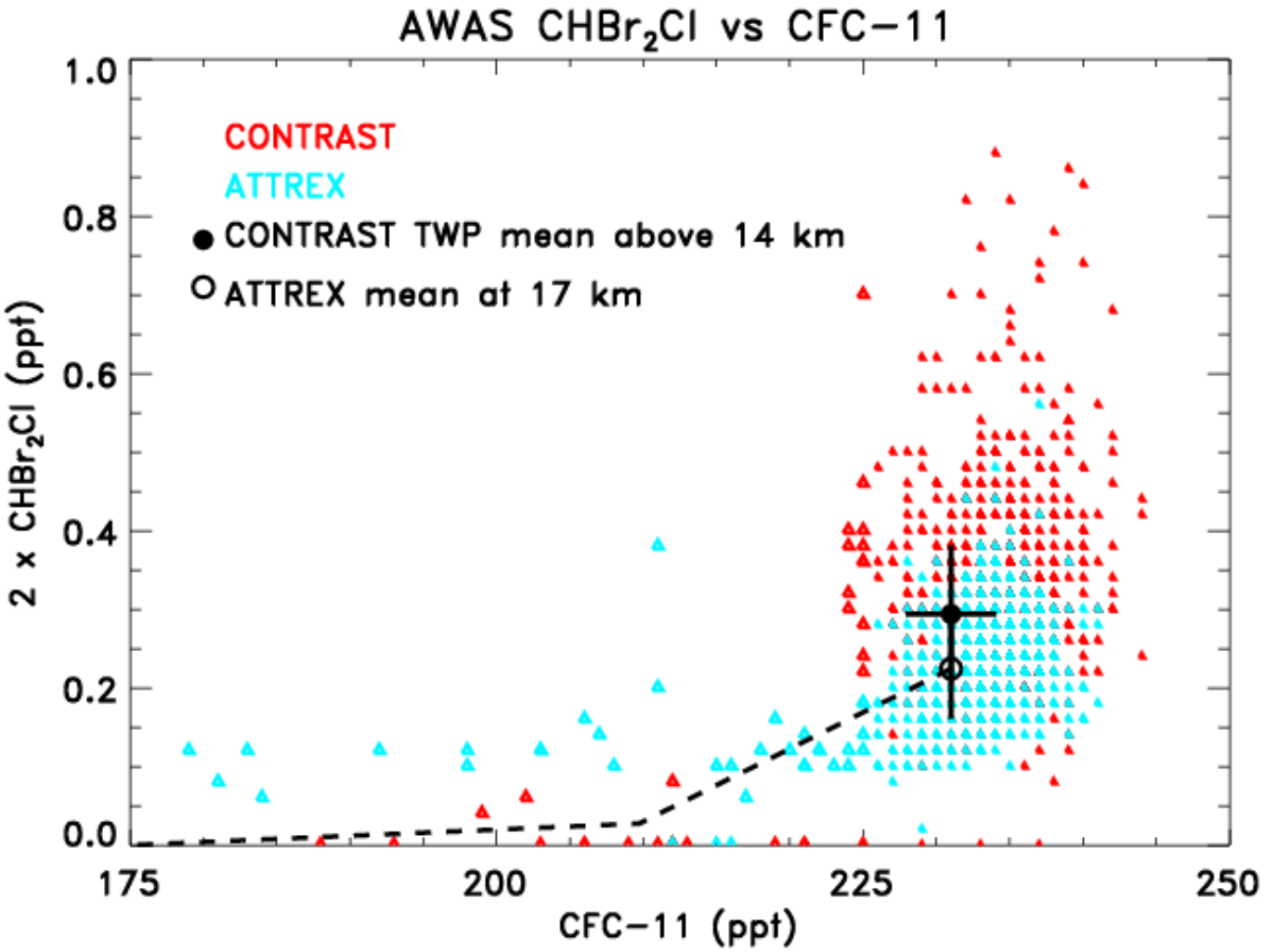
CH_2Br_2 : ATTREX & CONTRAST



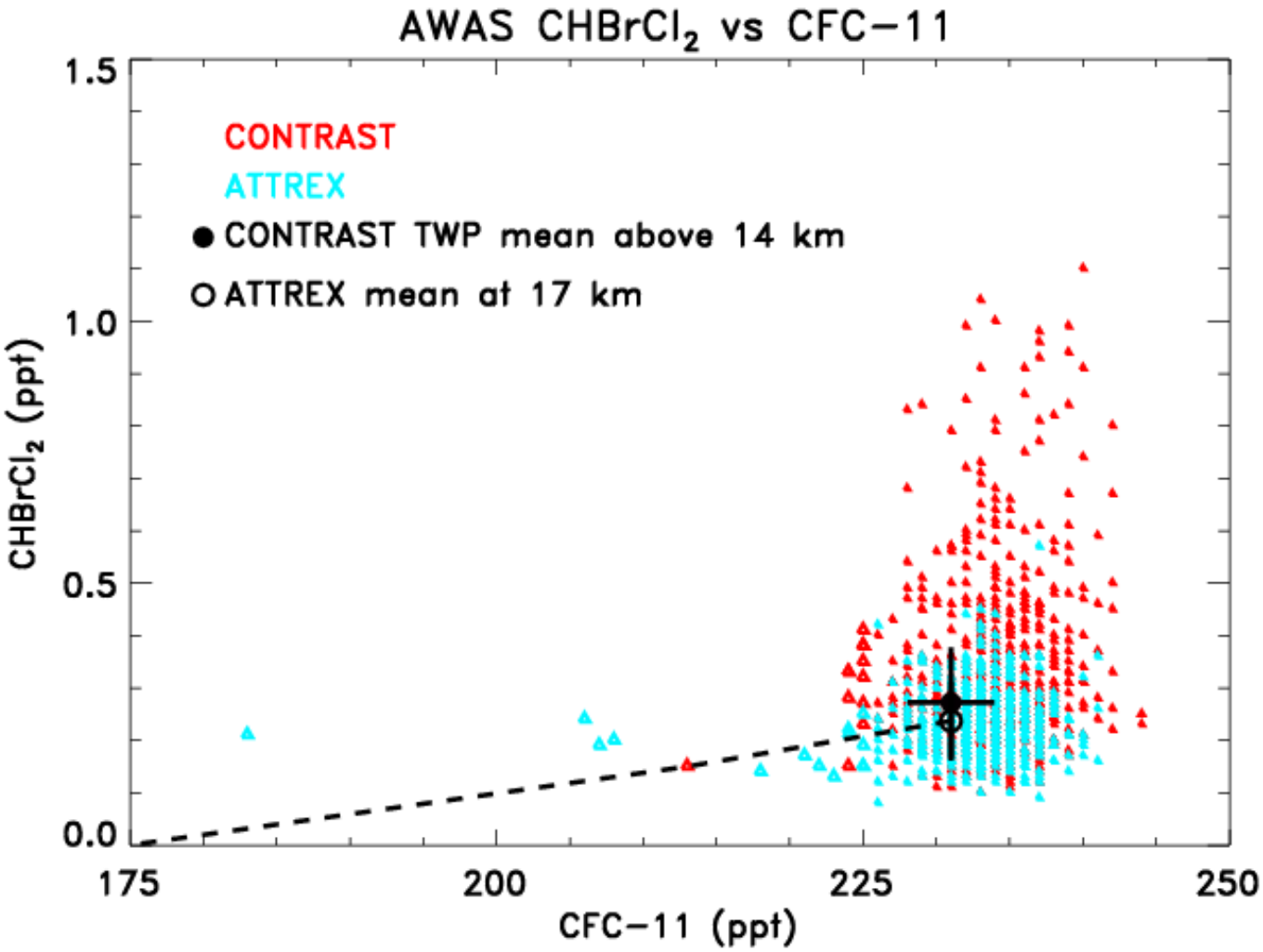
CH_2BrCl: ATTREX & CONTRAST



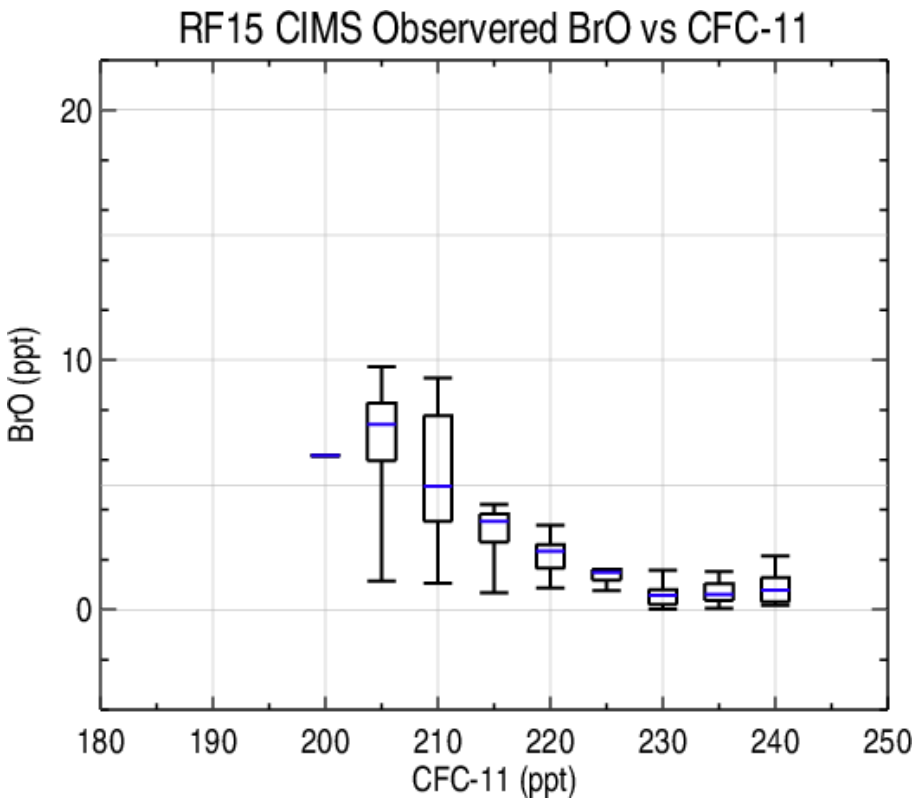
$CHBr_2Cl$: ATTREX & CONTRAST

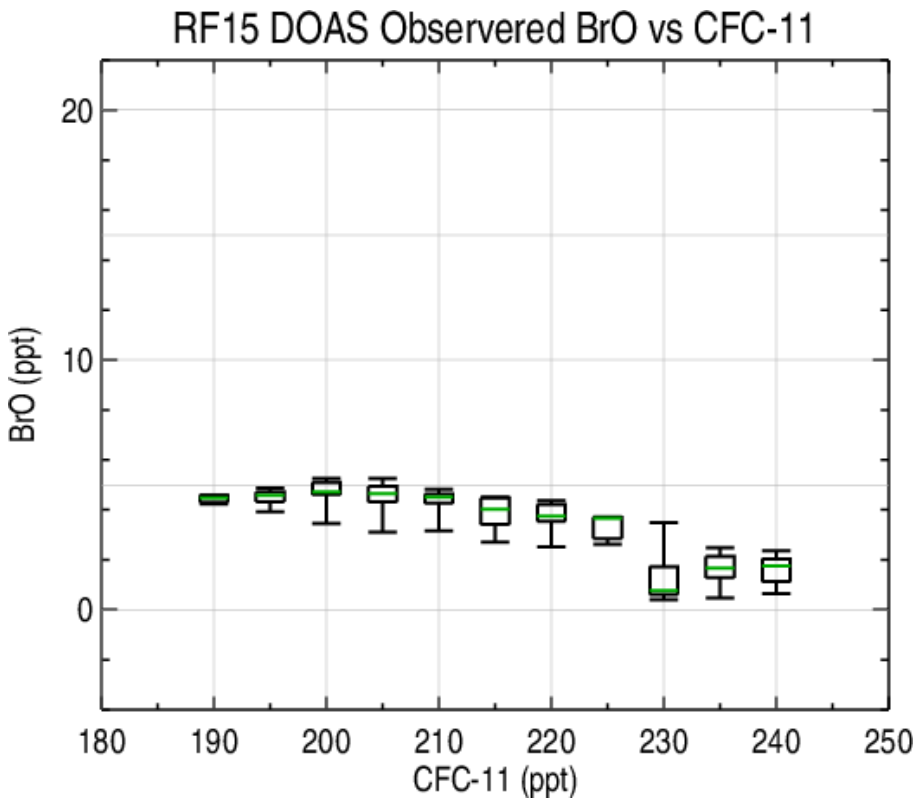


$CHBCl_2$: ATTREX & CONTRAST



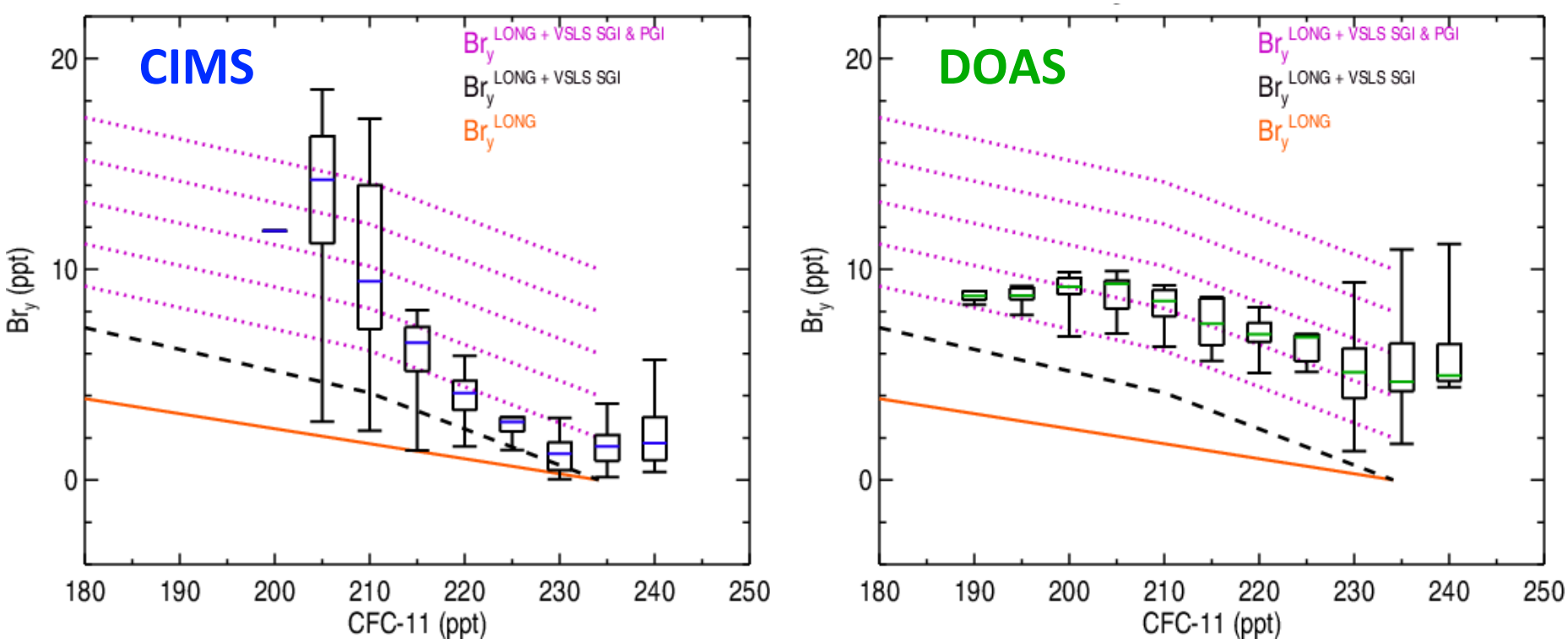
RF15: Northward Jet Crossing, Deep Stratosphere





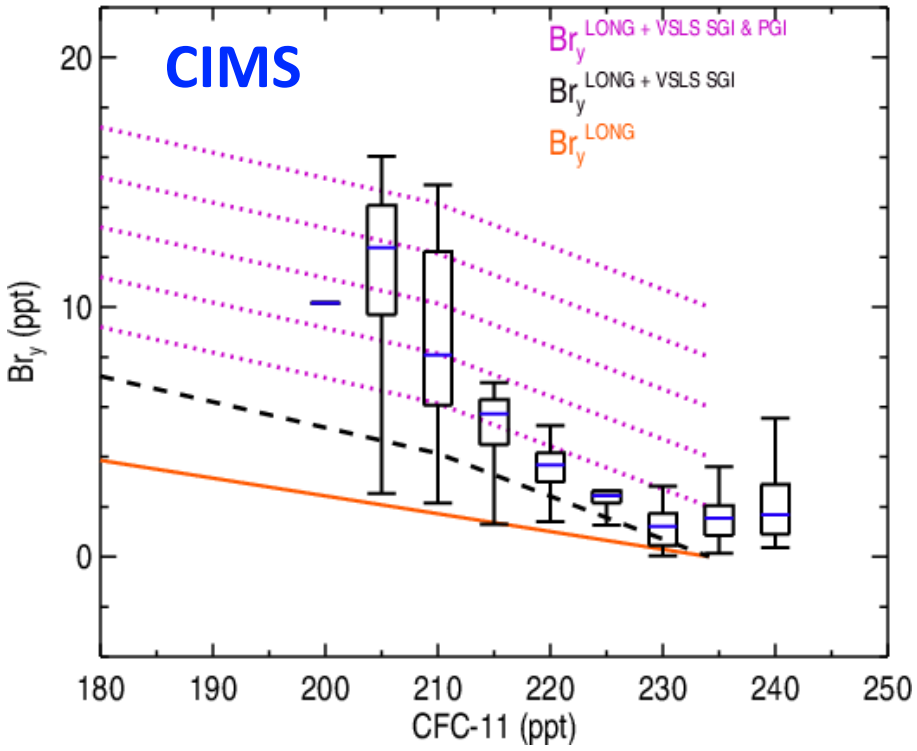
RF15: Northward Jet Crossing, Deep Stratosphere

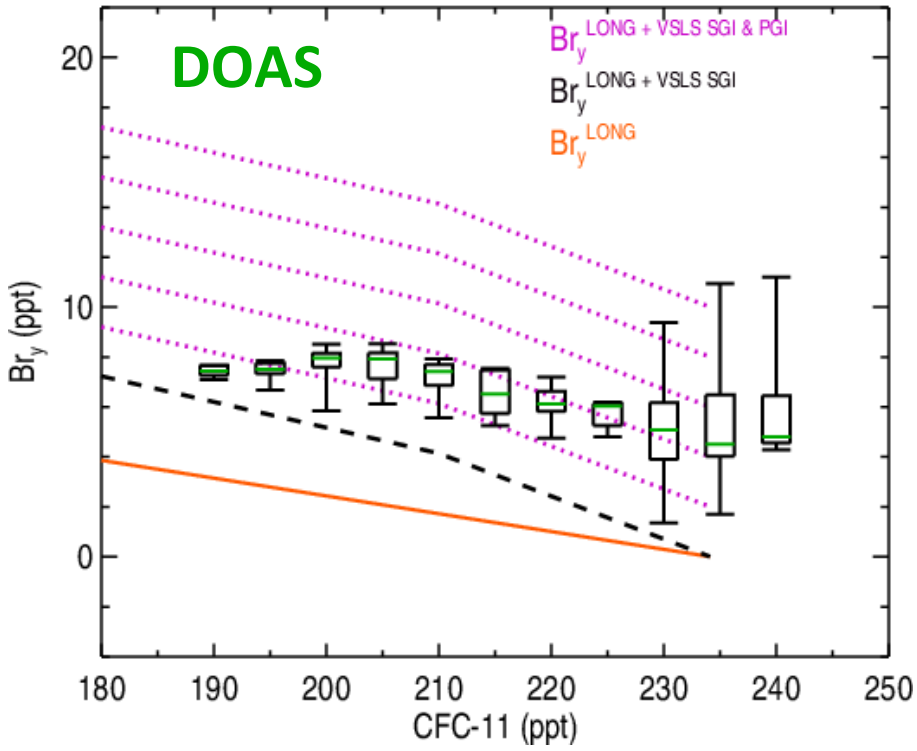
JPL 2011 Kinetics



RF15: Northward Jet Crossing, Deep Stratosphere

Kreycy et al., ACP, 2013 Kinetics





Conclusions

1. $CBr_y^{CH3Br\ \&\ Halons}$ & $CBr_y^{SGI\ VSLS}$ for 2014 well quantified by ATTREX:

CH_3Br & Halons	: 15 ppt
SGI VSLS	: 3.4 ± 0.7 ppt
	18.4 ppt

2. At low O_3, BrO+Br titrates to Br. Nonetheless, BrO measured by CIMS & DOAS on CONTRAST indicate the presence of *significant levels of "product" (i.e., Br_y) throughout tropical troposphere*

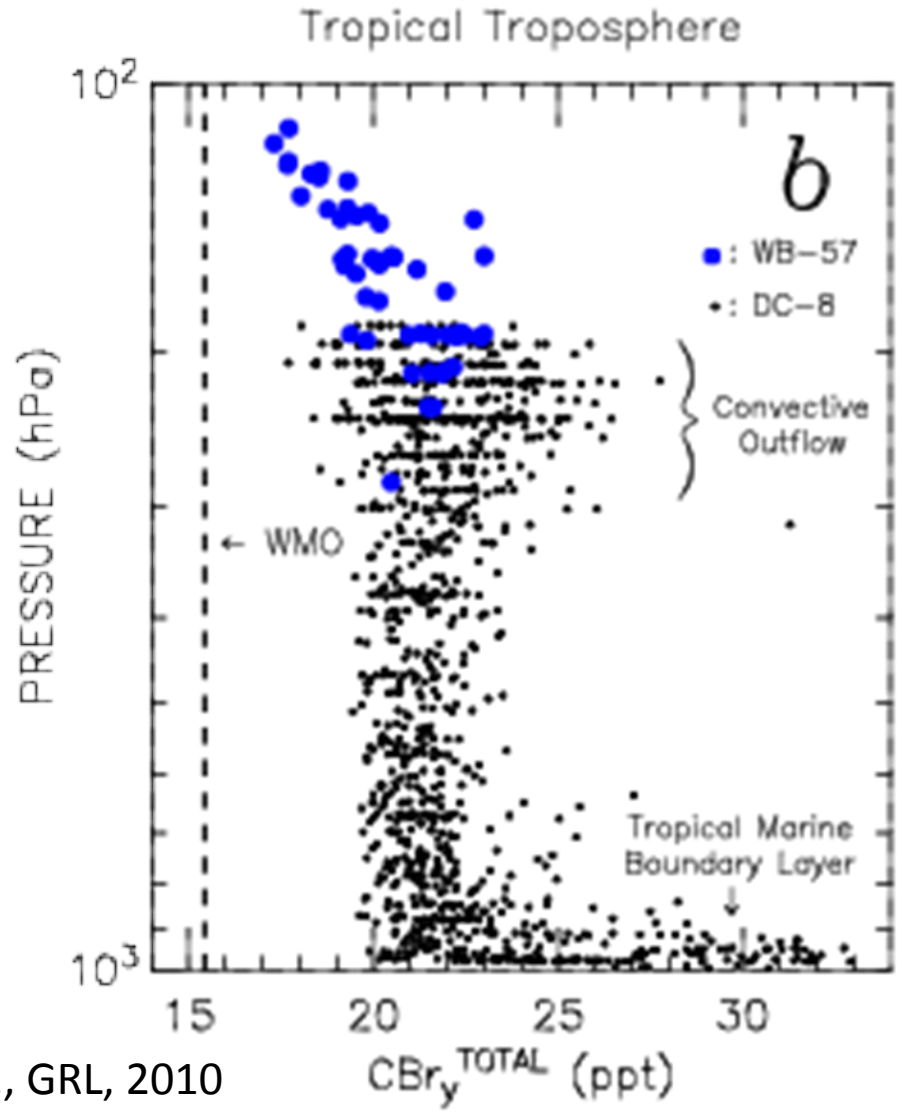
3. $Br_y^{PGI\ VSLS/others}$ estimate based on CIMS & DOAS BrO from RF15:

   CIMS: 0 to 10 ppt, strong fn of CFC-11

   DOAS: 3 to 5 ppt, nearly constant wrt CFC-11

4. WMO/UNEP (2014) stated "5 (range 2 to 8) ppt" for VSLS Br_y

TWP mission data suggests these estimates too low, by at least 1 to 2 ppt



Salawitch et al., GRL, 2010

TC^4 data, collected in vicinity of Costa Rica

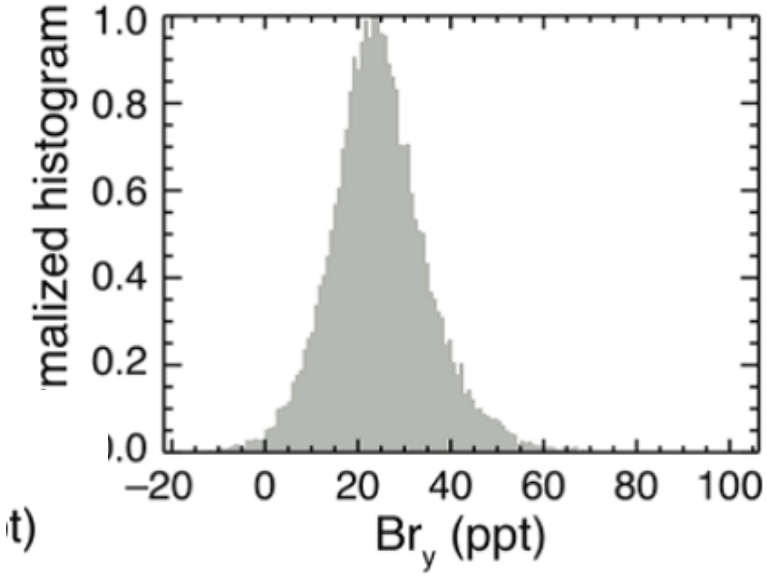
Parella et al., AMT, 2013

Atmos. Meas. Tech., 6, 2549–2561, 2013
www.atmos-meas-tech.net/6/2549/2013/
doi:10.5194/amt-6-2549-2013

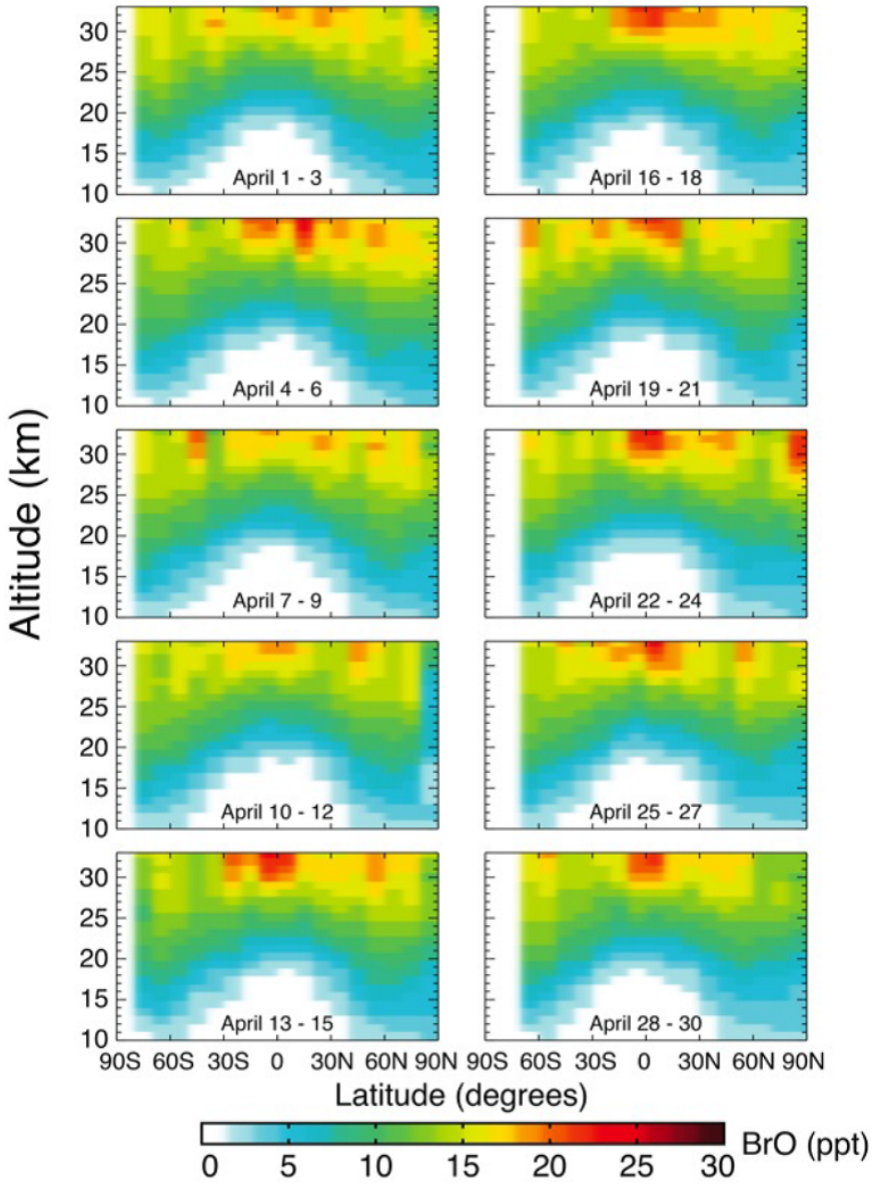
New retrieval of BrO from SCIAMACHY limb: an estimate of the stratospheric bromine loading during April 2008

J. P. Parrella[1], K. Chance[2], R. J. Salawitch[3,4,5], T. Canty[3], M. Dorf[6], and K. Pfeilsticker[6]

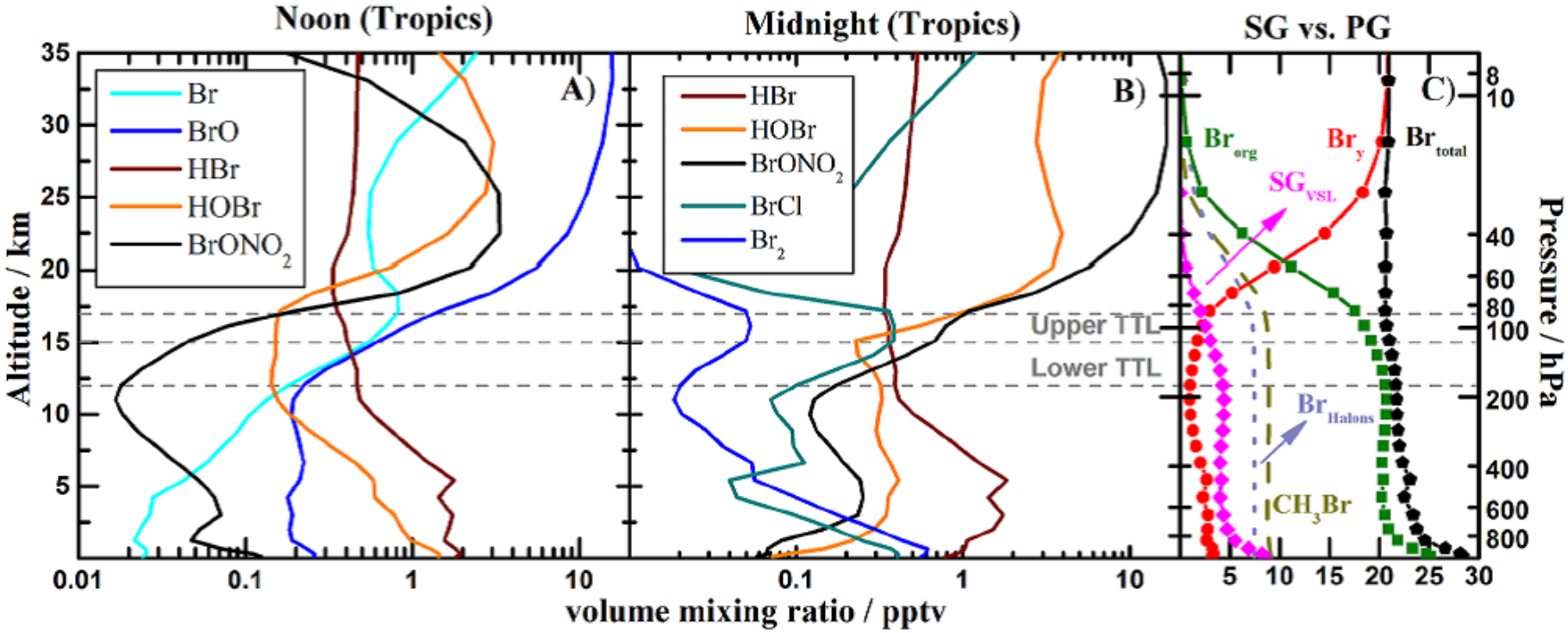
Abstract. We present a new retrieval of stratospheric BrO (bromine monoxide) from channel 2 SCIAMACHY (SCanning Imaging Absorption spectrometer for Atmospheric CHartographY) limb observations. Retrievals are shown to agree with independent balloon observations to within one standard deviation of the retrieval noise. We retrieve BrO profiles for all of April 2008, and apply simulated [BrO]/[Br_y] (bromine monoxide : stratospheric inorganic bromine) ratios to estimate the stratospheric Br_y loading. We find 23.5 ± 6 ppt Br, suggesting 7 ppt Br from short-lived bromocarbons to be at the high end of the current best estimate (3–8 ppt). The 6 ppt Br uncertainty estimate is dominated by the 21 % uncertainty in the simulated [BrO] / [Br_y] ratio due to propagation of errors from the underlying chemical kinetics.



Parella et al., AMT, 2013

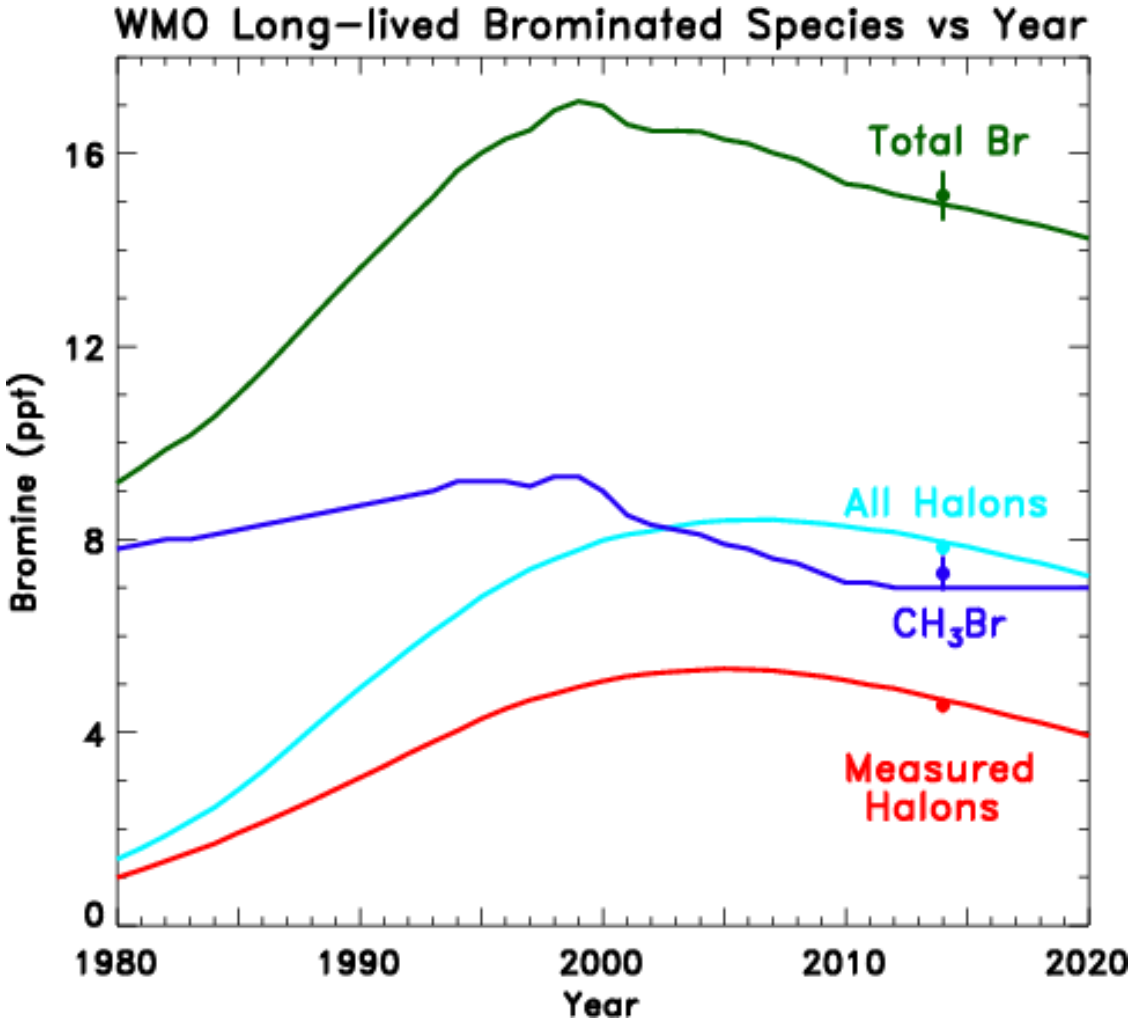


CT3LS, Boulder, Co, July 2015



Fernandez et al., ACP, 2014

Lines: Table 5A-2, WMO/UNEP 2014
Points: CONTRAST Tropical Western Pacific, AWAS
Note: AWAS reported measurements for only two halons, 1211 & 2402
"All Halons" is found by adding WMO value for halon 1301 to the AWAS measurements



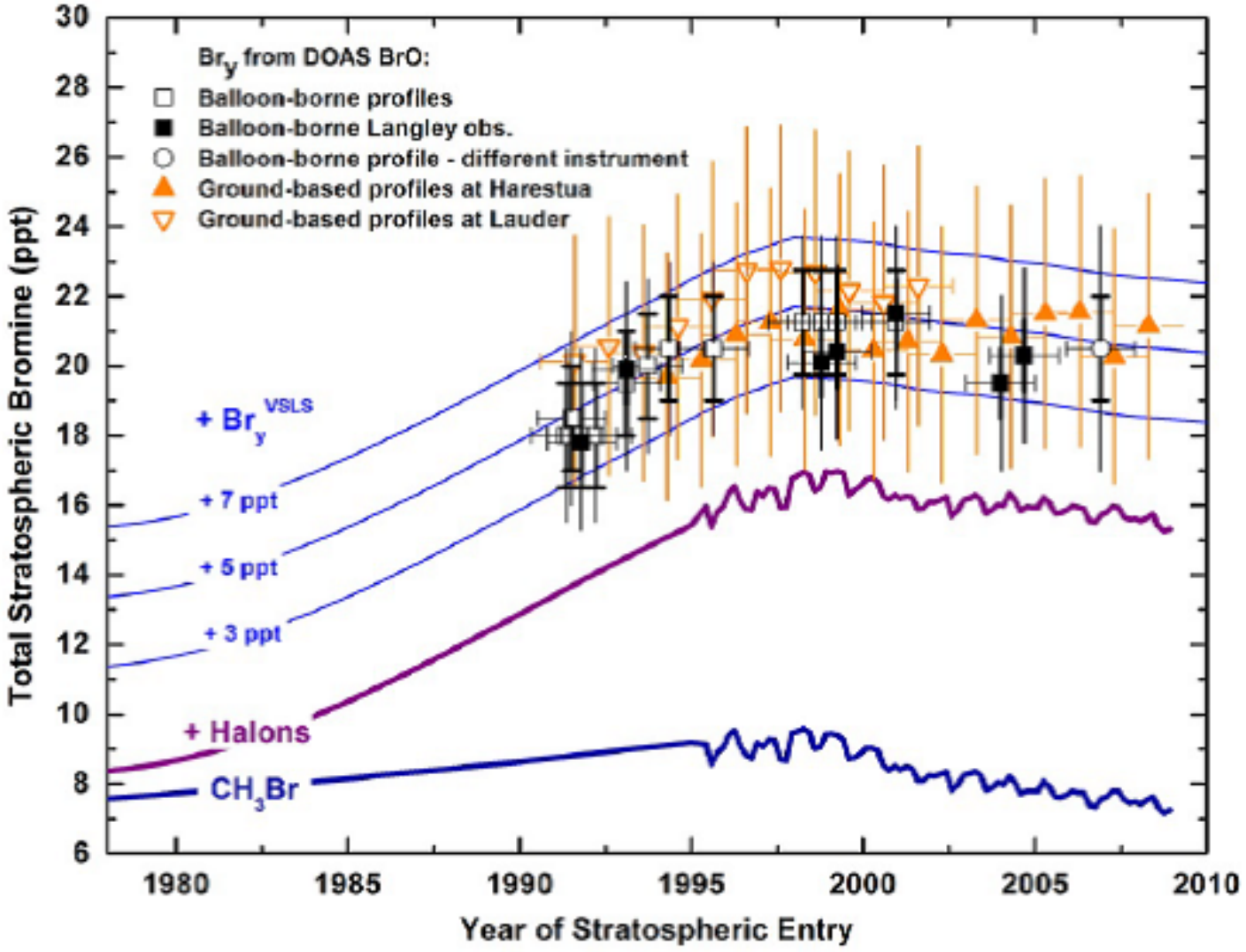
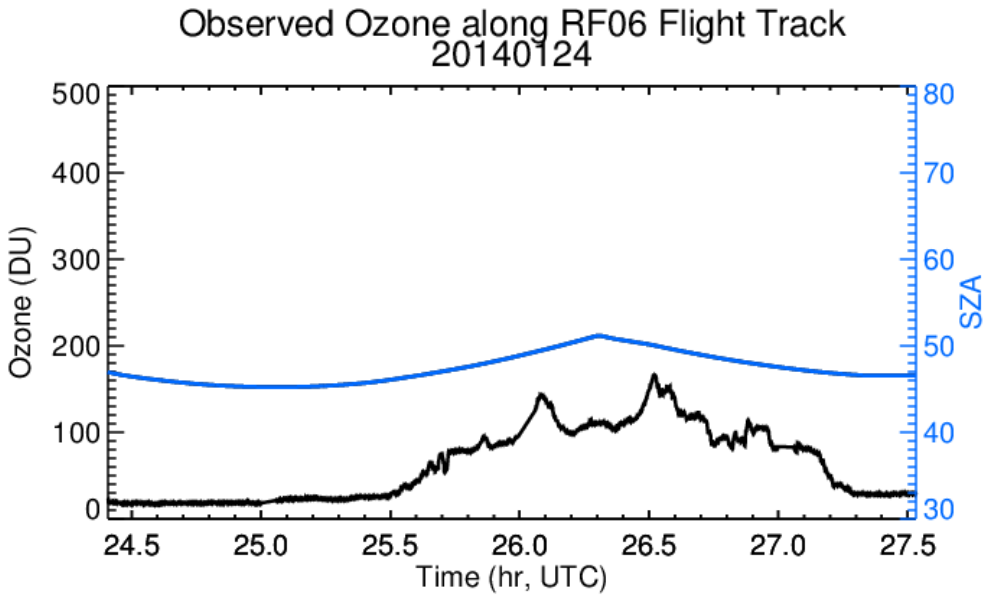
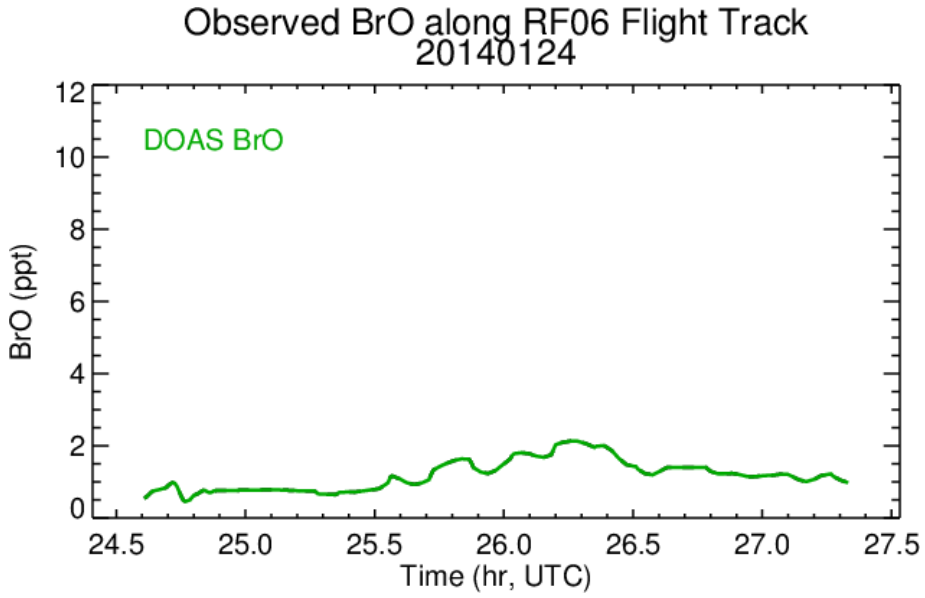
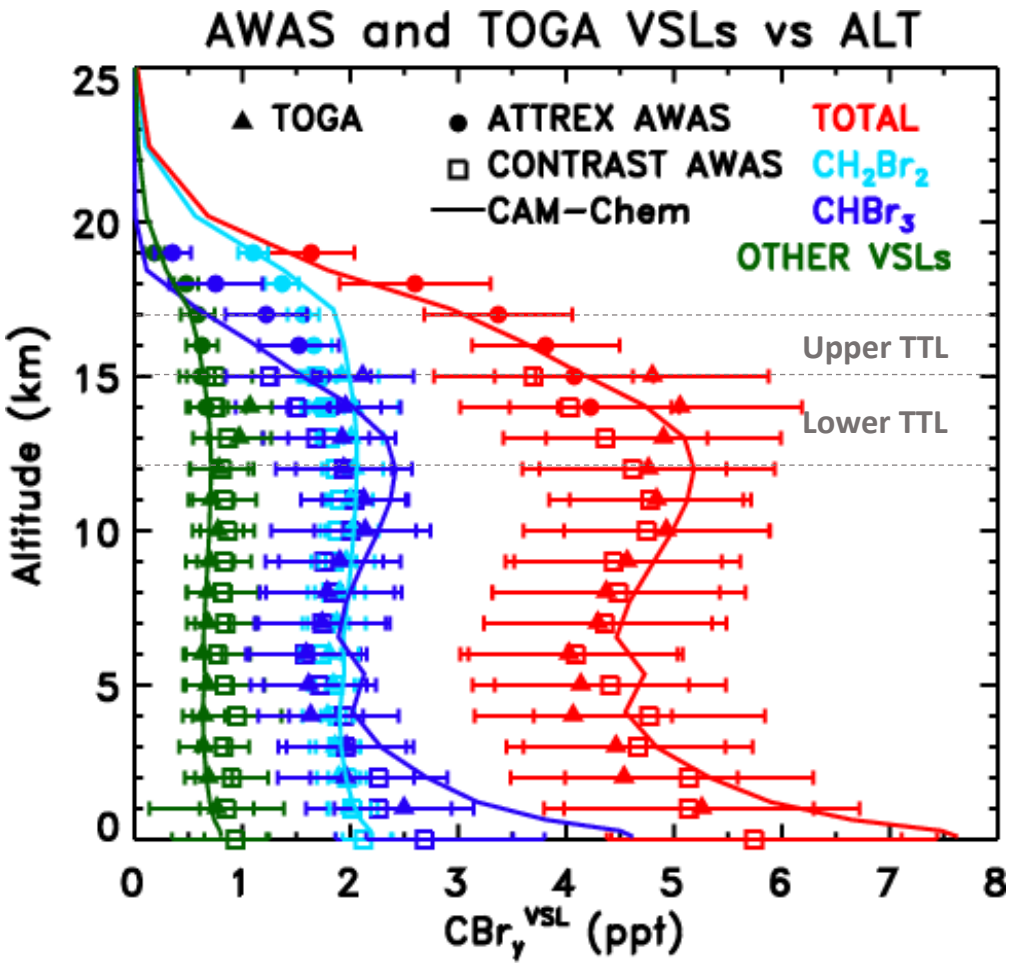


Figure 1-20, WMO/UNEP (2014)


Observed Ozone along RF06 Flight Track
20140124
Ozone (DU)
SZA
Time (hr, UTC)
500
400
300
200
100
0
80
70
60
50
40
30
24.5
25.0
25.5
26.0
26.5
27.0
27.5


Observed BrO along RF06 Flight Track
20140124
DOAS BrO
BrO (ppt)
Time (hr, UTC)
12
10
8
6
4
2
0
24.5
25.0
25.5
26.0
26.5
27.0
27.5

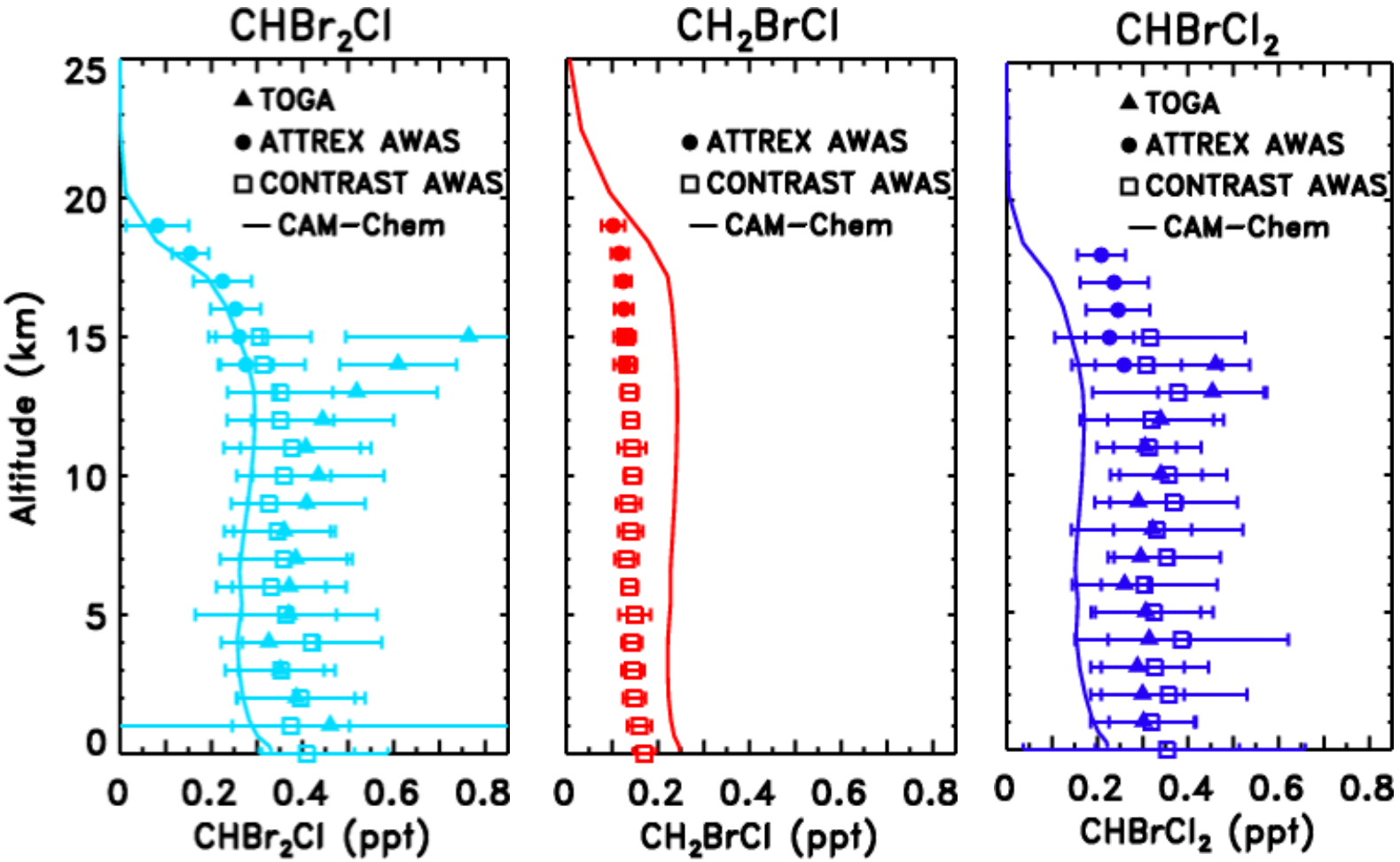


Measurements: AWAS & **TOGA**

Model: Fernandez et al., ACP, 2014 Note: paper did not include CONTRAST data

Geographically & seasonally distributed oceanic sources of VSLS as described in Ordonez et al. (2012)

Closer look at minor VSLS

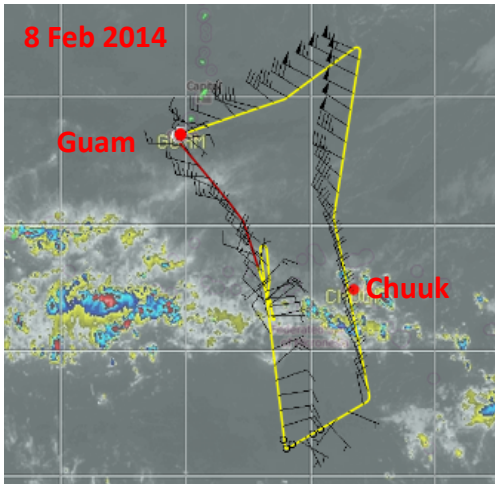


Measurements: AWAS

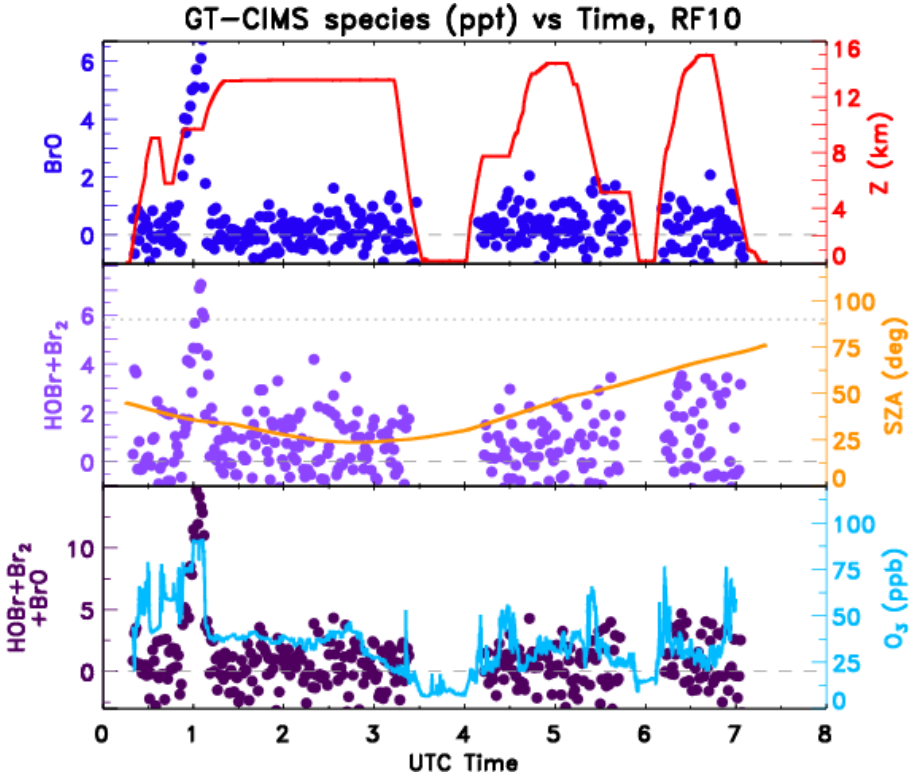
Model: Fernandez et al., ACP, 2014 Note: paper did not include CONTRAST data

Geographically & seasonally distributed oceanic sources of VSLS as described in Ordonez et al. (2012)

RF10: Subtropical Jet Pollution and ITCZ

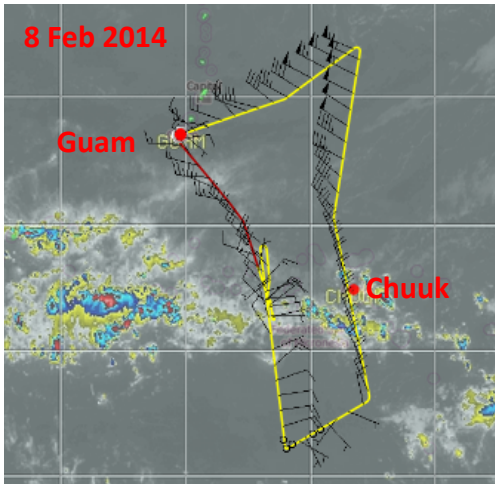


EQ

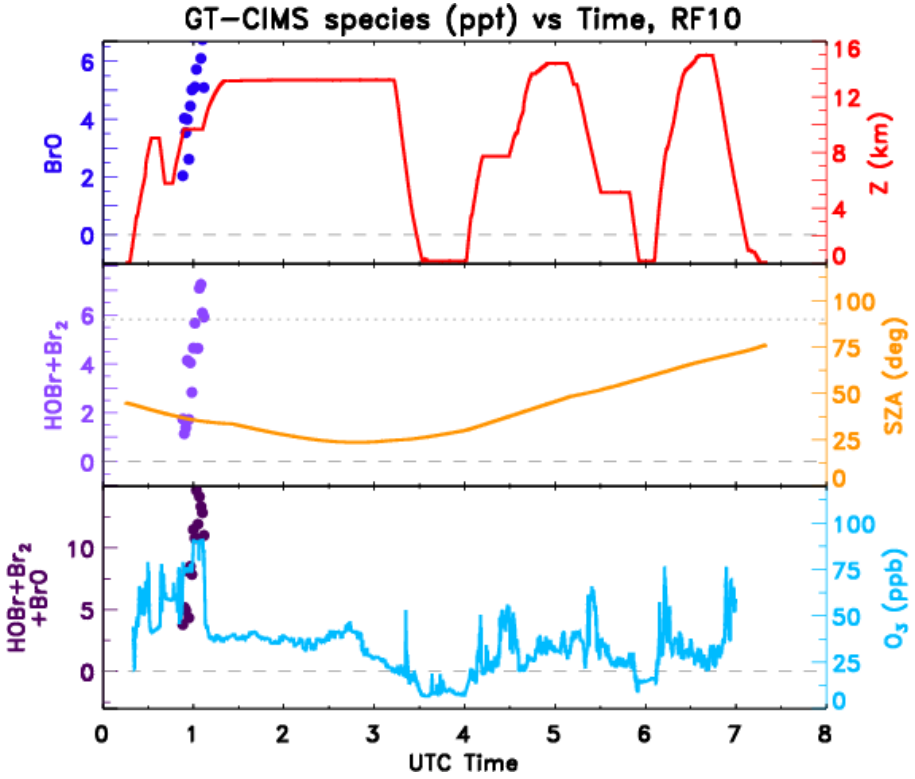


CT3LS, Boulder, Co, July 2015

RF10: Subtropical Jet Pollution and ITCZ

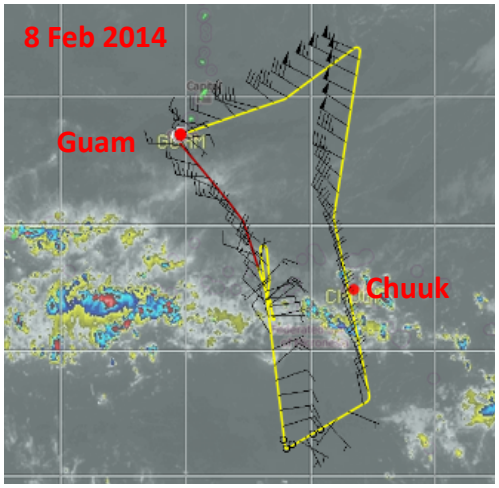


EQ

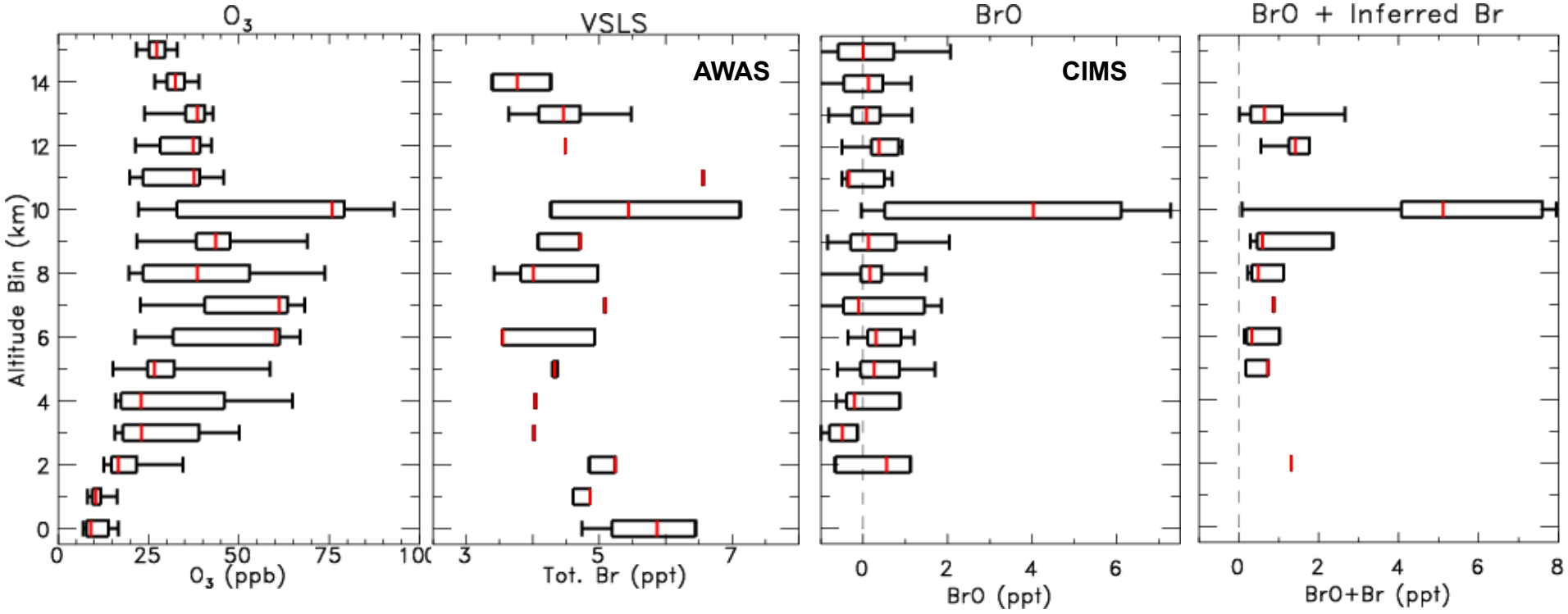


CT3LS, Boulder, Co, July 2015

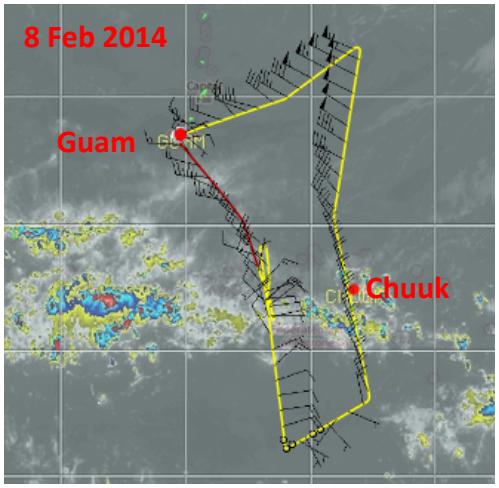
RF10: Subtropical Jet Pollution and ITCZ



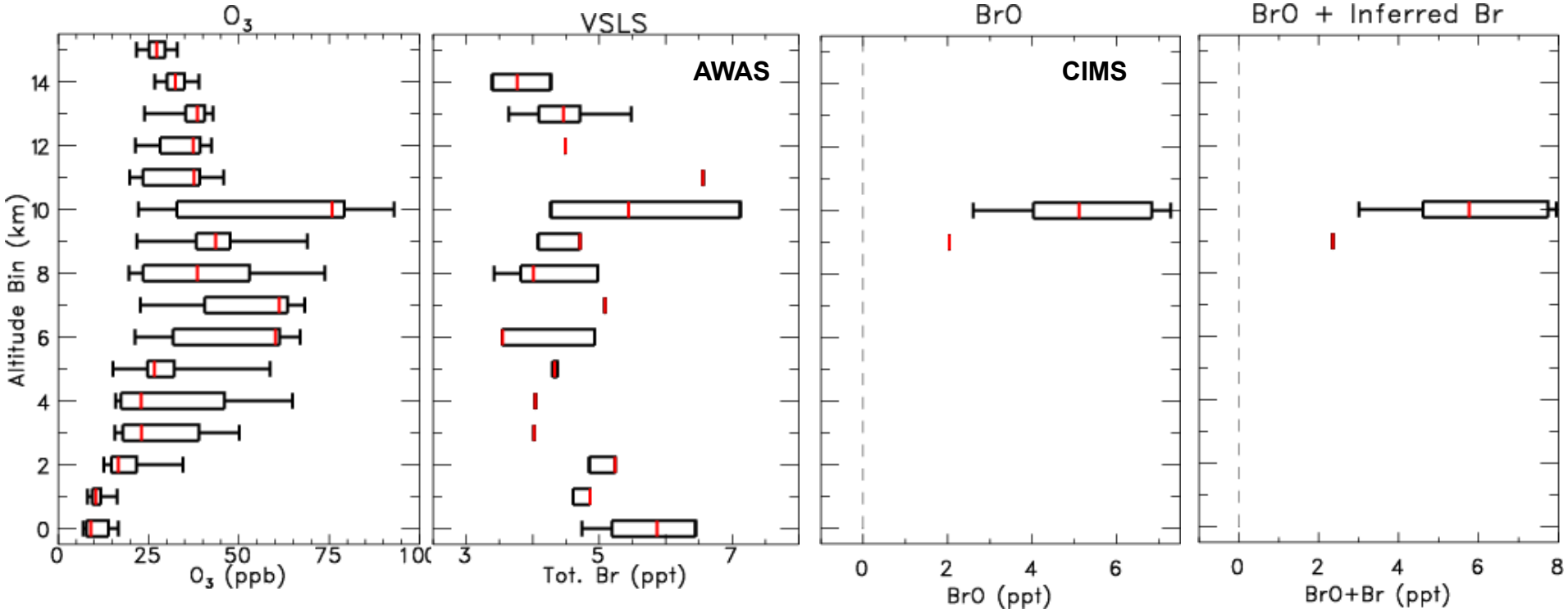
EQ



RF10: Subtropical Jet Pollution and ITCZ

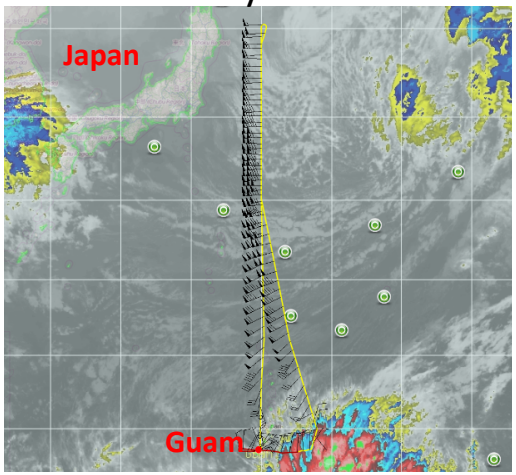


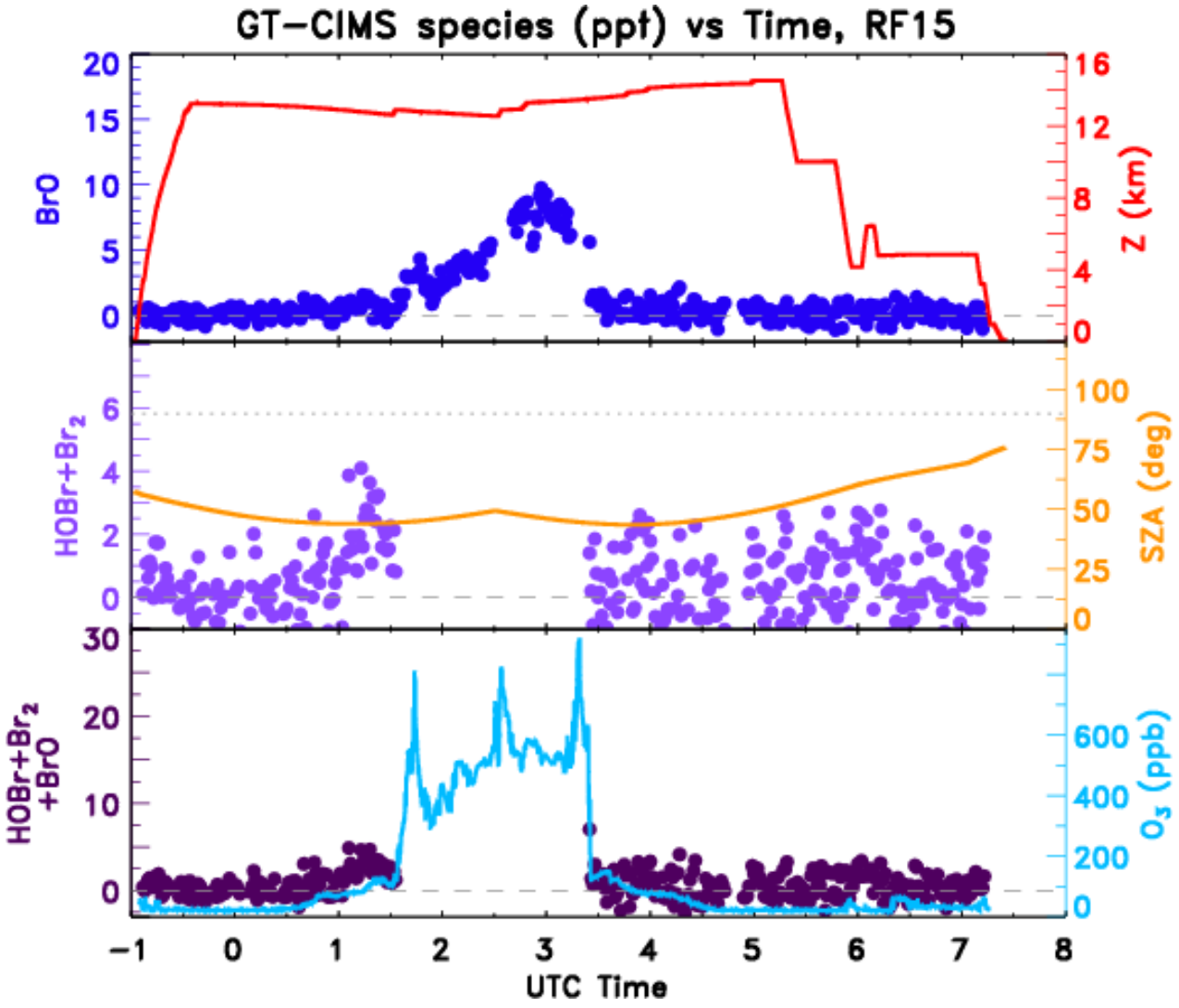
EQ



RF15: Northward Jet Crossing, Deep Stratosphere

RF15: 25 Feb 2014
Northern Survey: reached 385 K





RF15: Northward Jet Crossing, Deep Stratosphere

RF15: 25 Feb 2014
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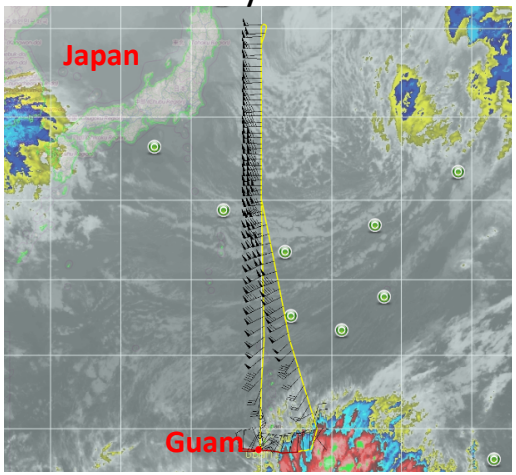
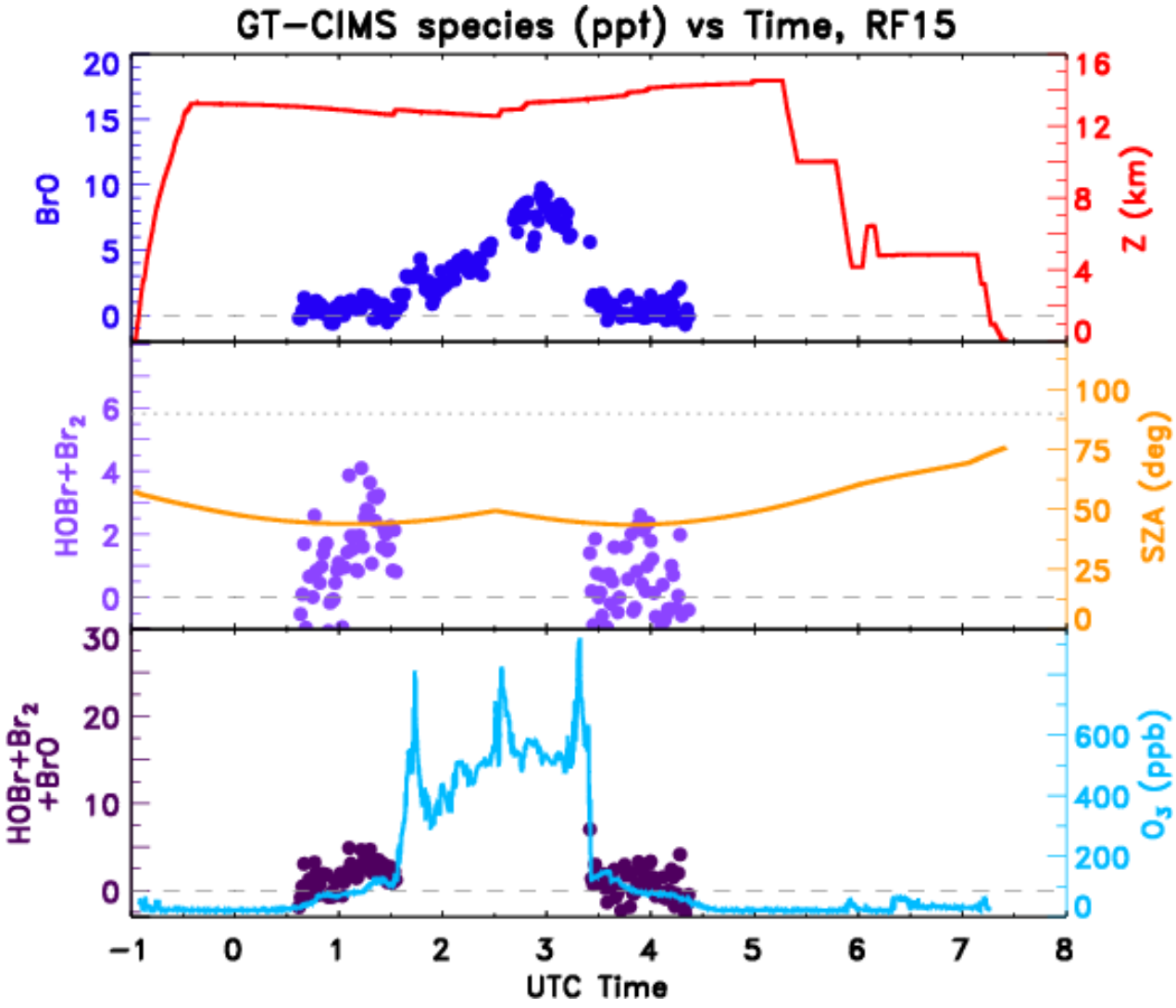
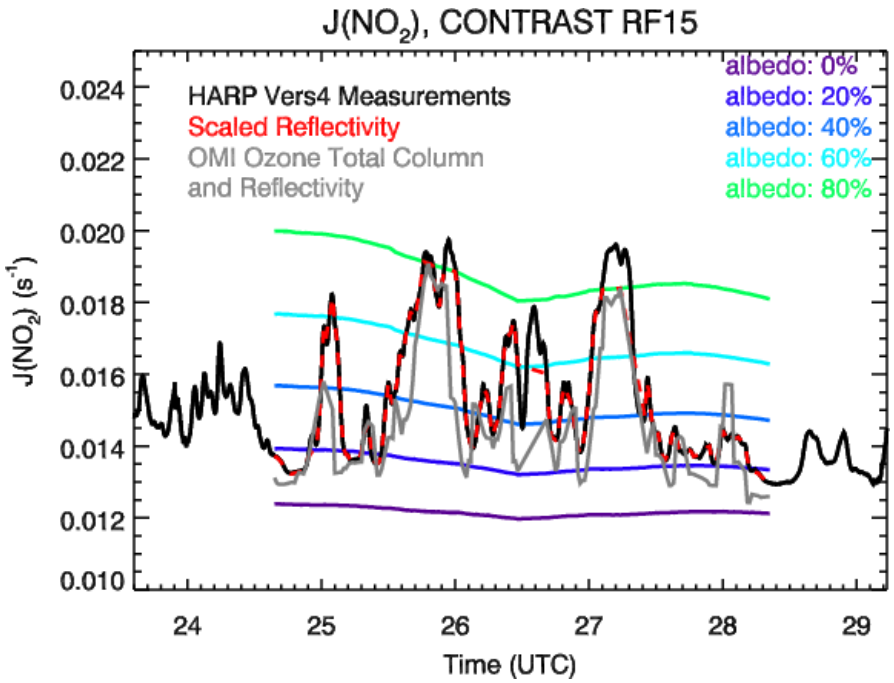


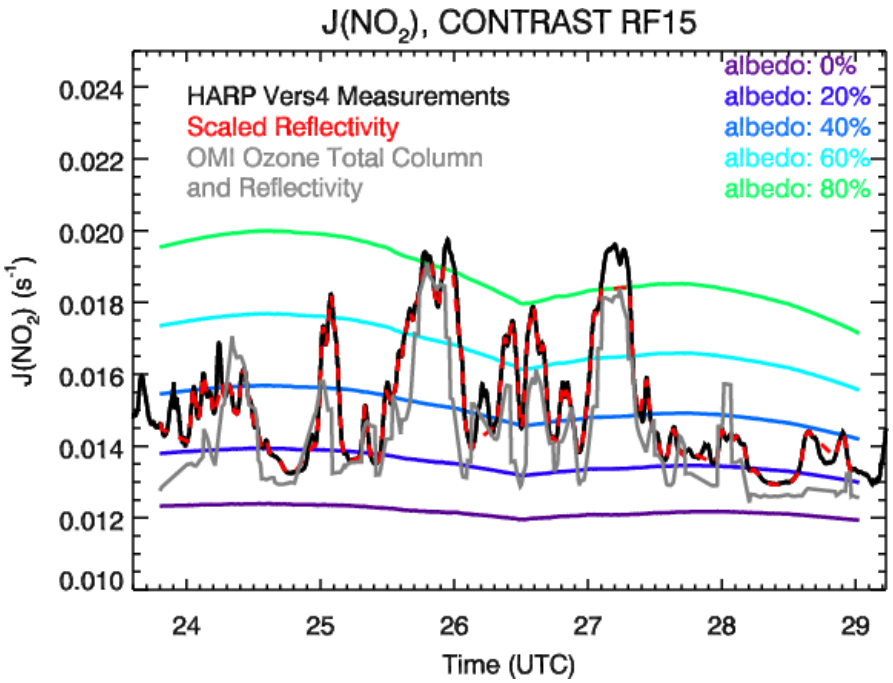


RF15 Modeling Backup

With CIMS time steps

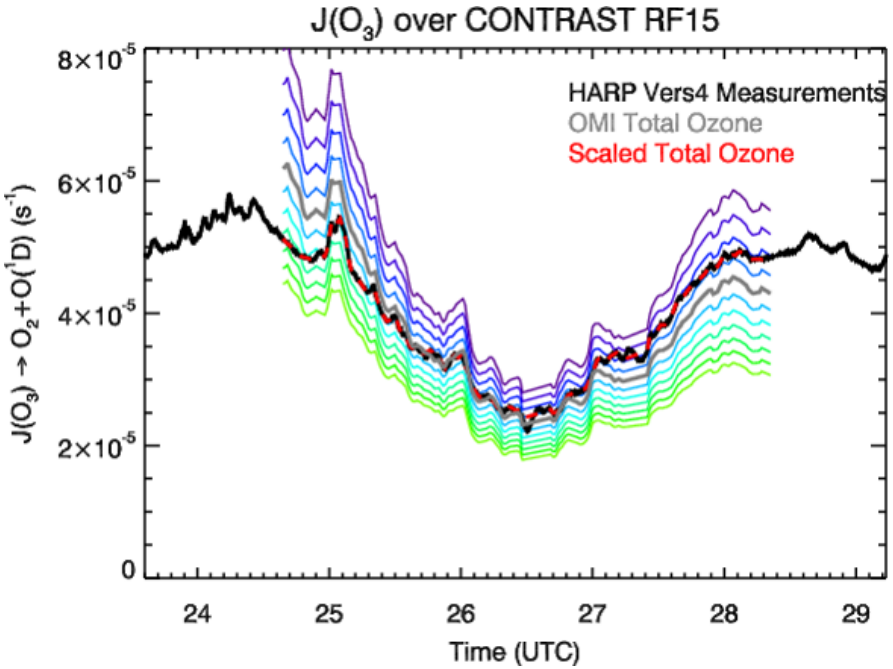


With DOAS time steps

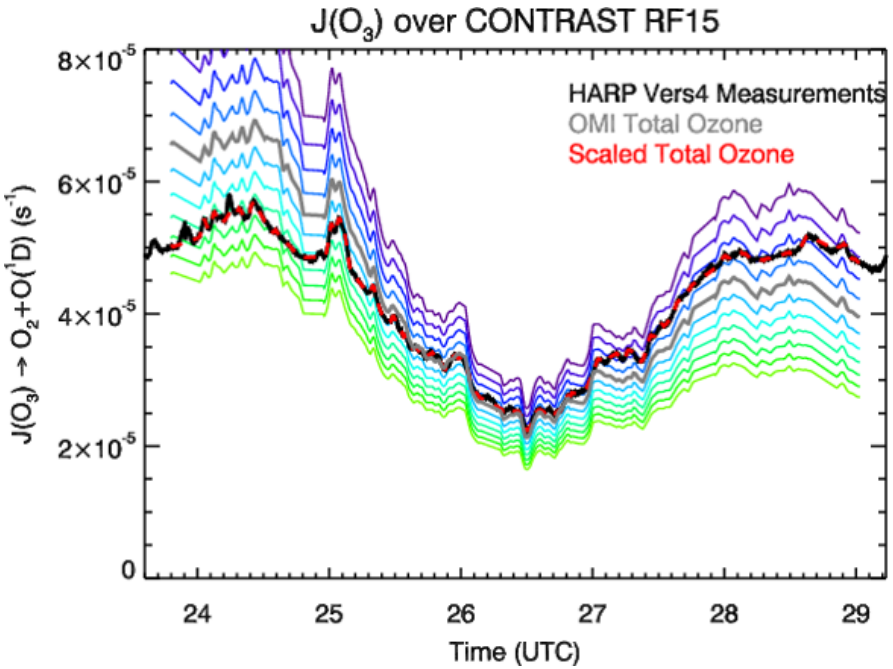


RF15 Modeling Backup

With CIMS time steps



With DOAS time steps



Backup Slide #1

$BrONO_2$ formation:

$BrO + NO_2 + M \Rightarrow k$

$BrONO_2$ loss:

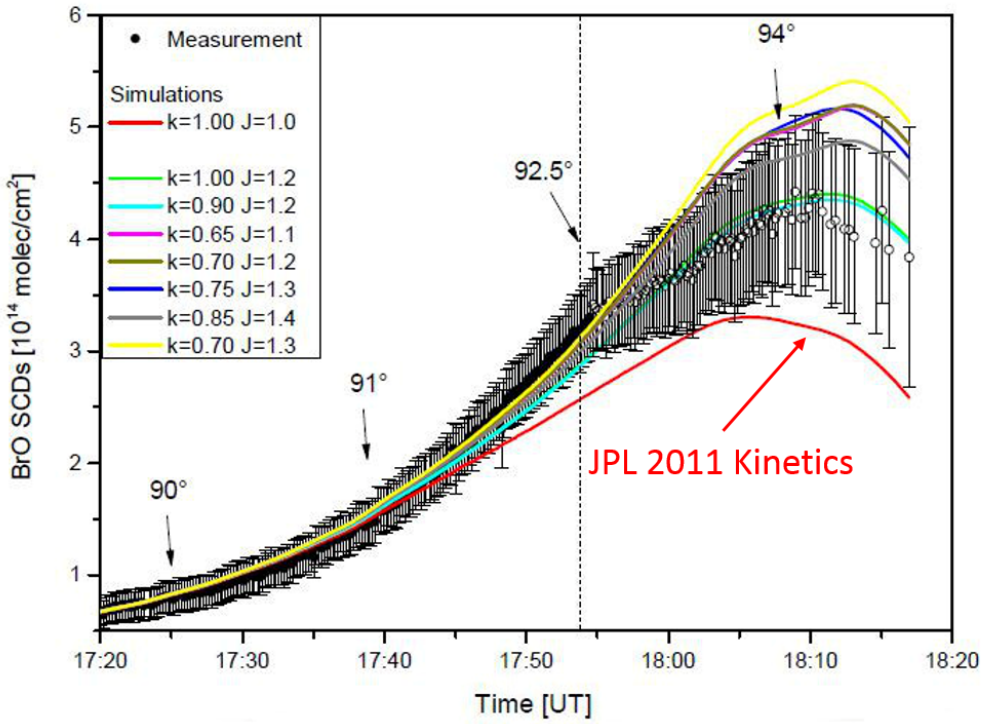
$BrONO_2 + h\nu \Rightarrow J$

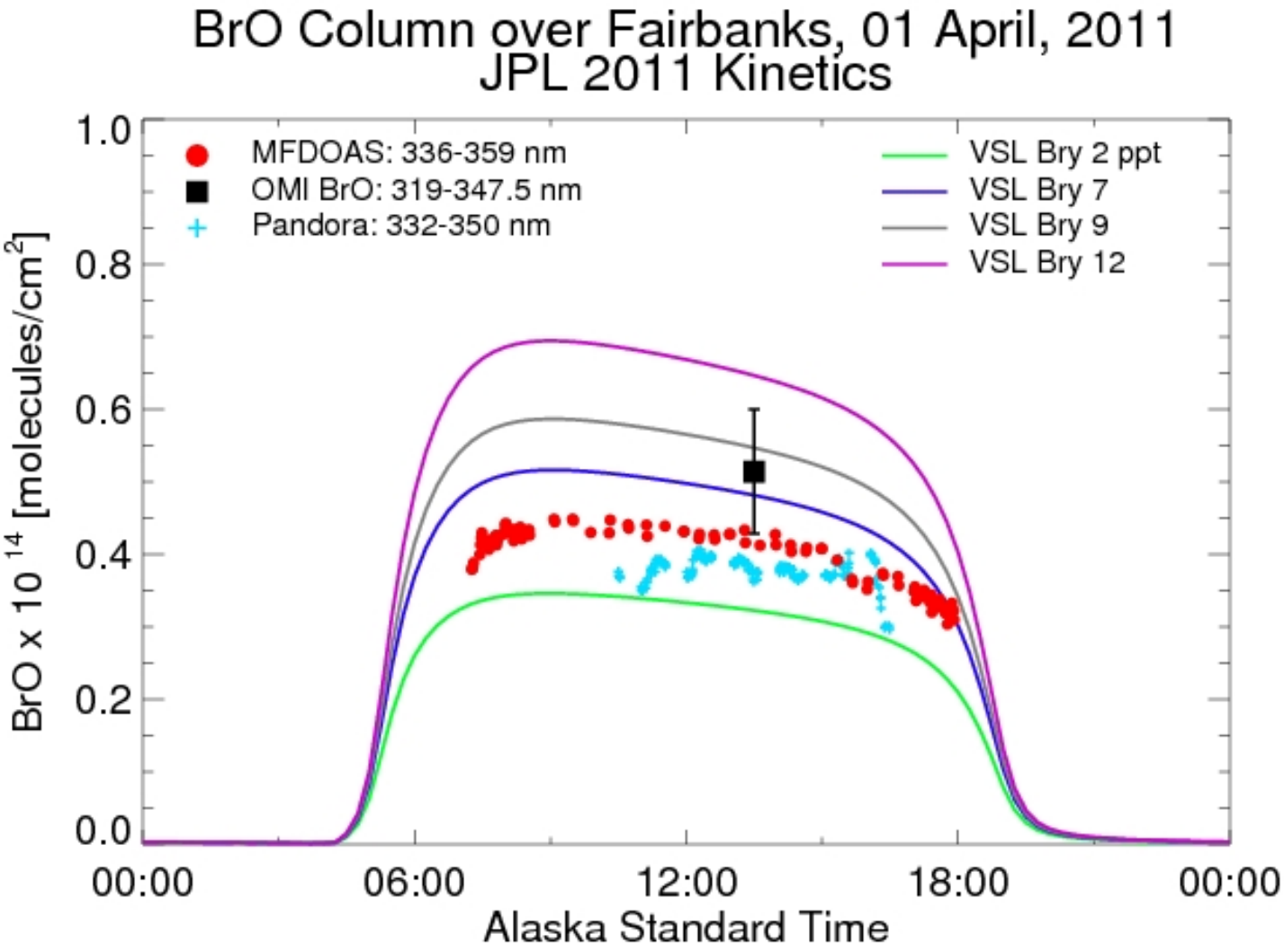
Kreycy et al. (2013) proposed k & J are misrepresented in JPL (2011) and that the ratio **J / k should rise by 27%**

This suggestion ***could*** be consistent with laboratory measurements of:

$BrONO_2$ formation rate constant

$BrONO_2$ cross section




BrO Column over Fairbanks, 01 April, 2011
JPL 2011 Kinetics
MFDOAS: 336-359 nm
OMI BrO: 319-347.5 nm
Pandora: 332-350 nm
VSL Bry 2 ppt
VSL Bry 7
VSL Bry 9
VSL Bry 12
BrO x 10 14 [molecules/cm2]
1.0
0.8
0.6
0.4
0.2
0.0
00:00
06:00
12:00
18:00
00:00
Alaska Standard Time