Stratospheric Injection of Bromine from Very Short Lived Sources

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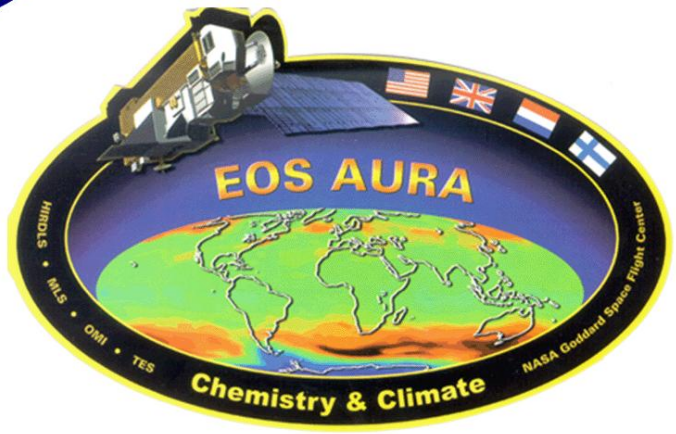
Alan Hills, Rebecca Hornbrook, Daniel Riemer Dexian Chen, Grey Huey, David Tanner,
Andrew Weinheimer, Glenn Wolfe, Tom Hanisco, Sam Hall, Kirk Ullmann, Rafael Fernandez,
Alfonso Saiz-Lopez, Doug Kinnison, Jean-Francois Lamarque, Simon Tilmes, Tim Canty,
Shawn Honomichl, Laura Pan, Richard McPeters, P. K. Bhartia, Thomas Kurosu, George Mount,
Elena Spinei, William Simpson, Deanna Donohue, Bryan Johnson



VSL Br_y

- WMO/UNEP 2010 ⇨ 6 ppt (range 3 to 8 ppt)
- WMO/UNEP 2014 ⇨ 5 ppt (range 2 to 8 ppt)
- Salawitch et al. (2010) analysis of OMI BrO : 7 to 12 ppt

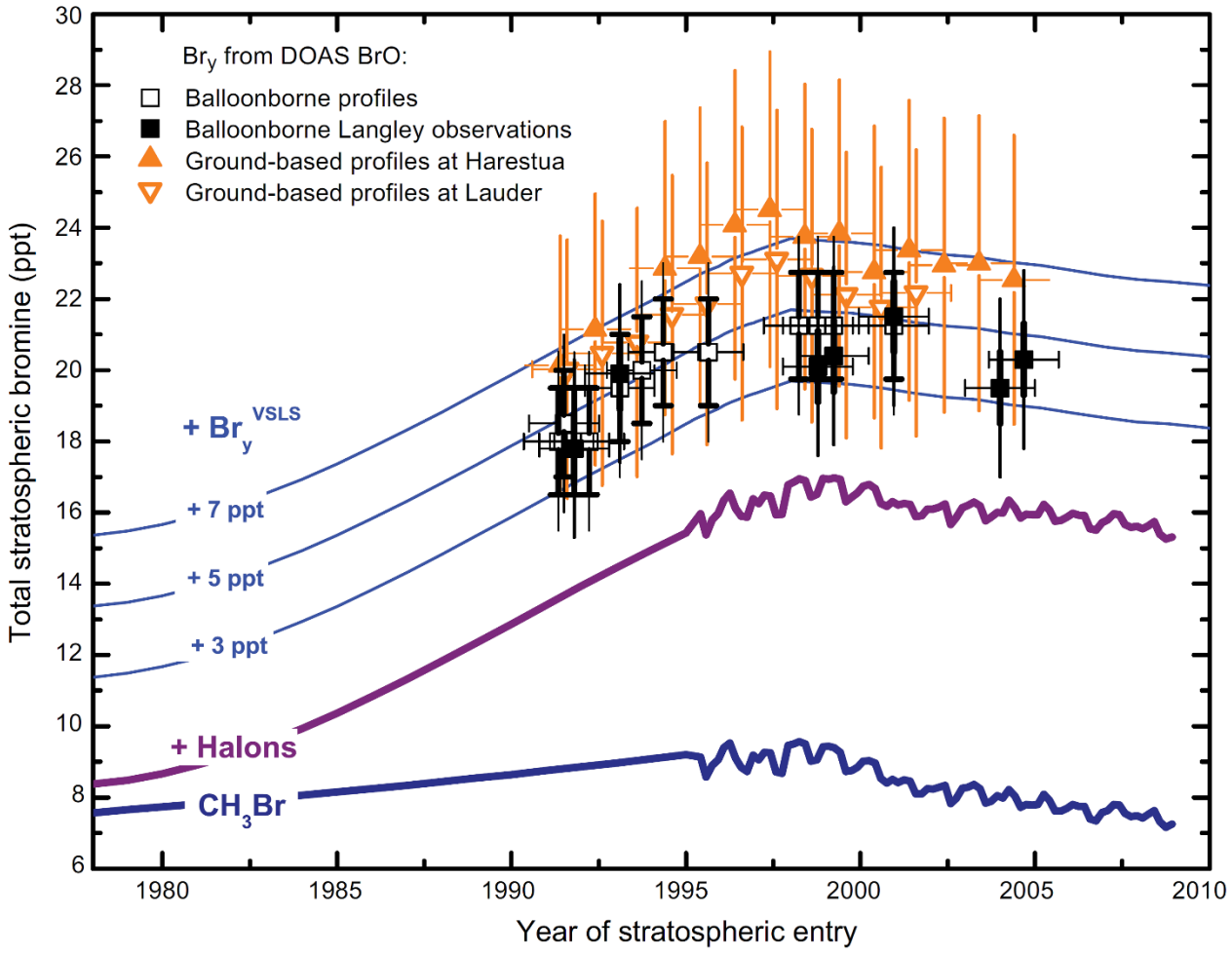
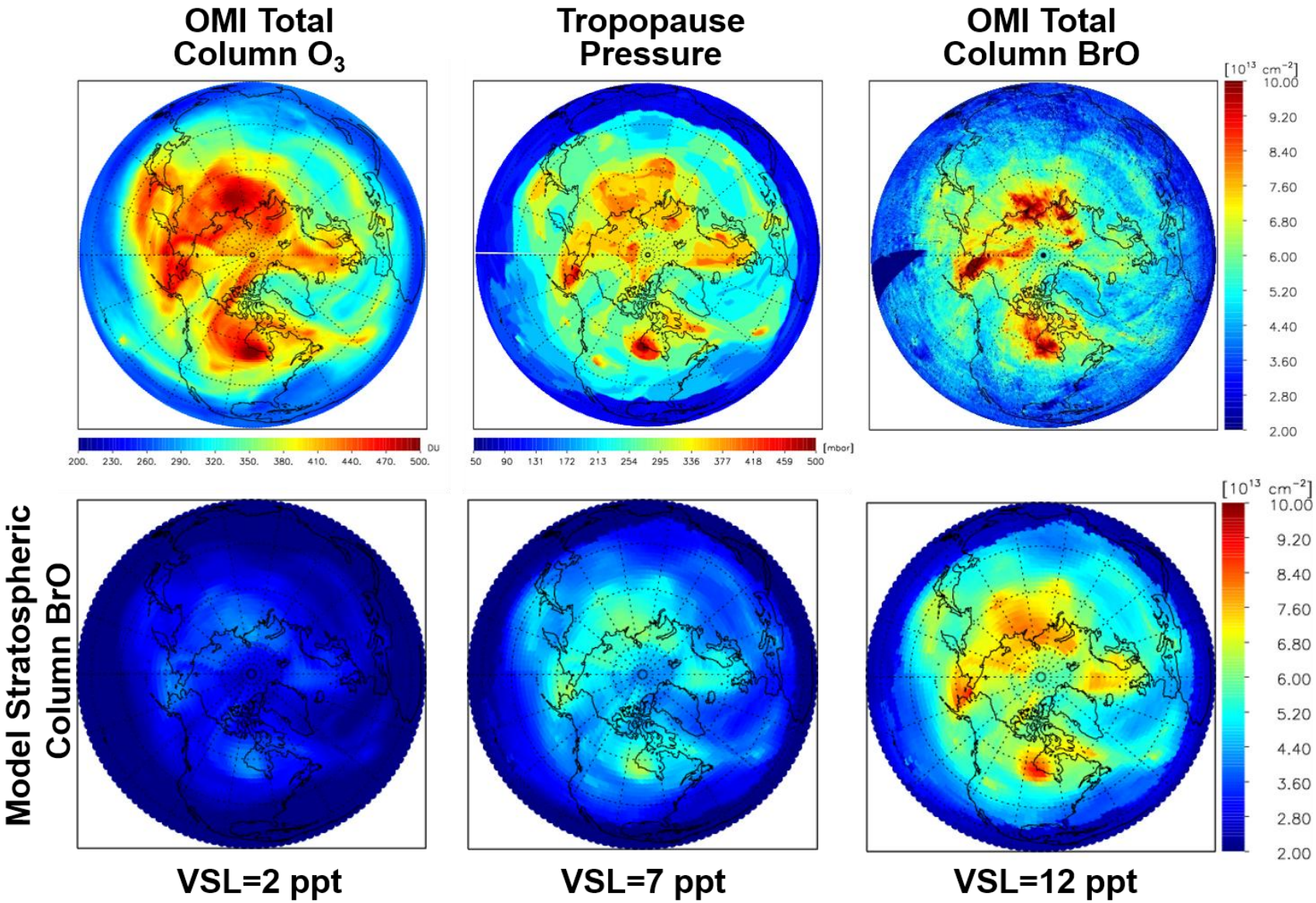


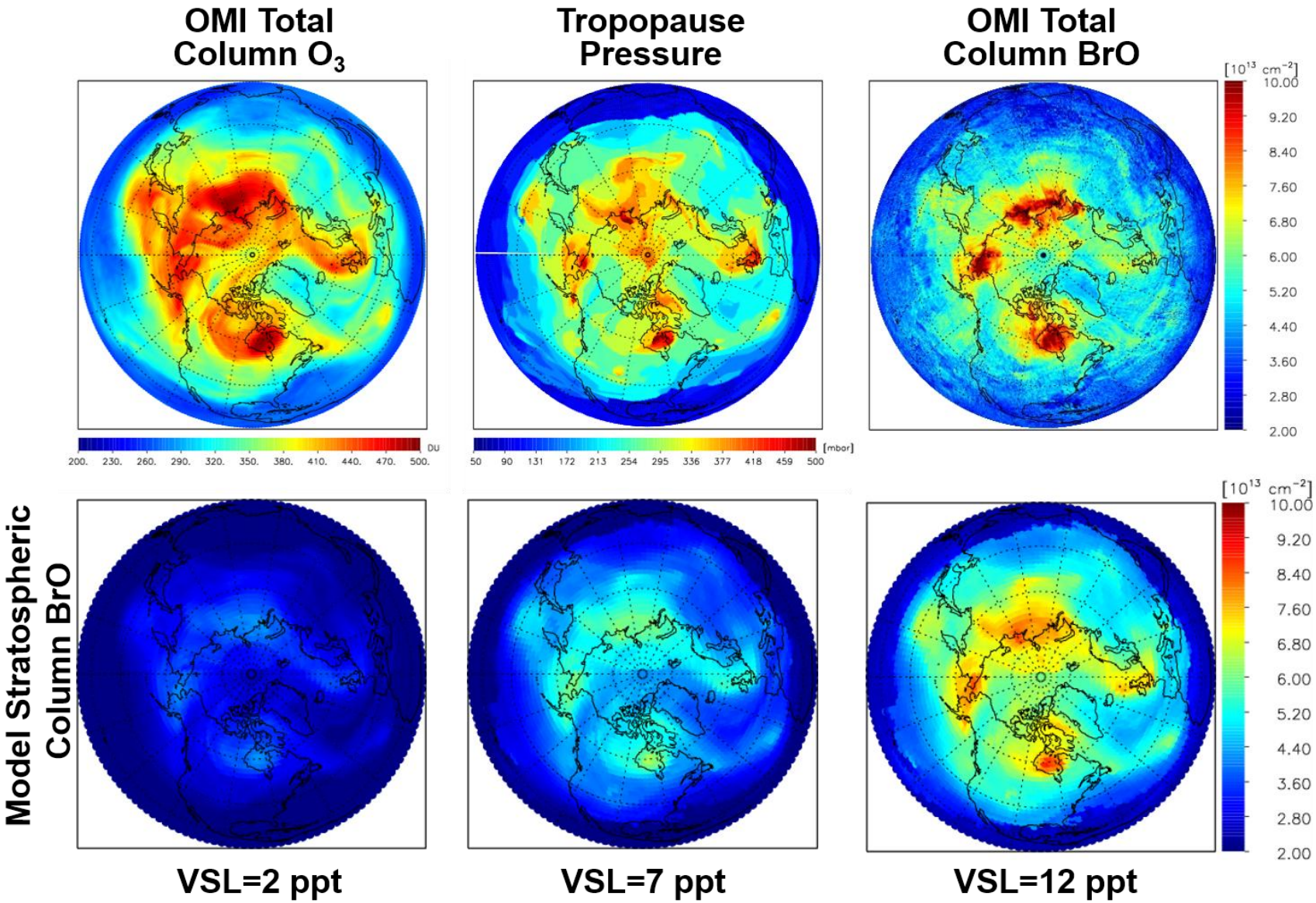
Figure 1-21, WMO/UNEP 2010

5 Apr 2008



Salawitch et al., GRL, 2010

6 Apr 2008



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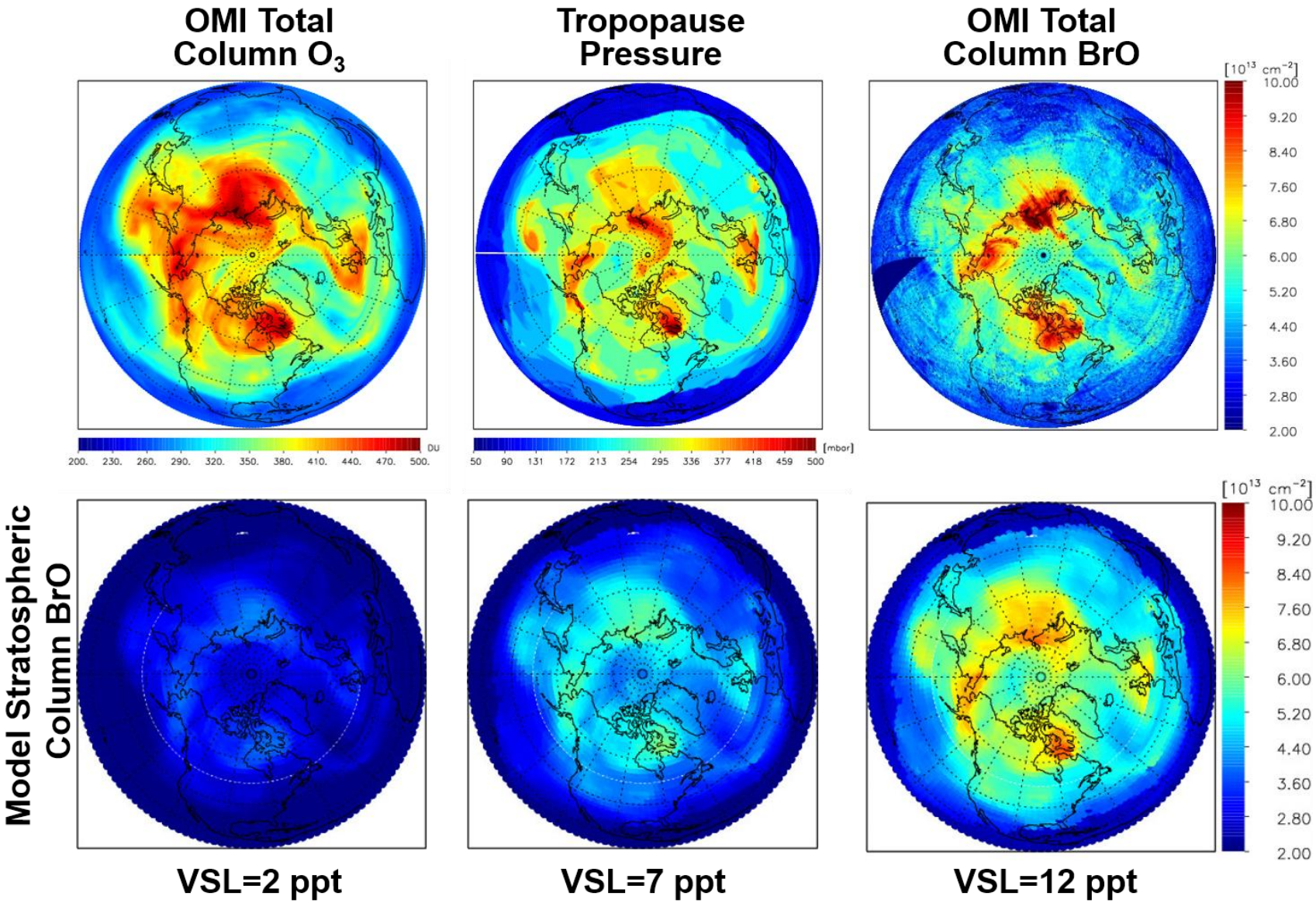
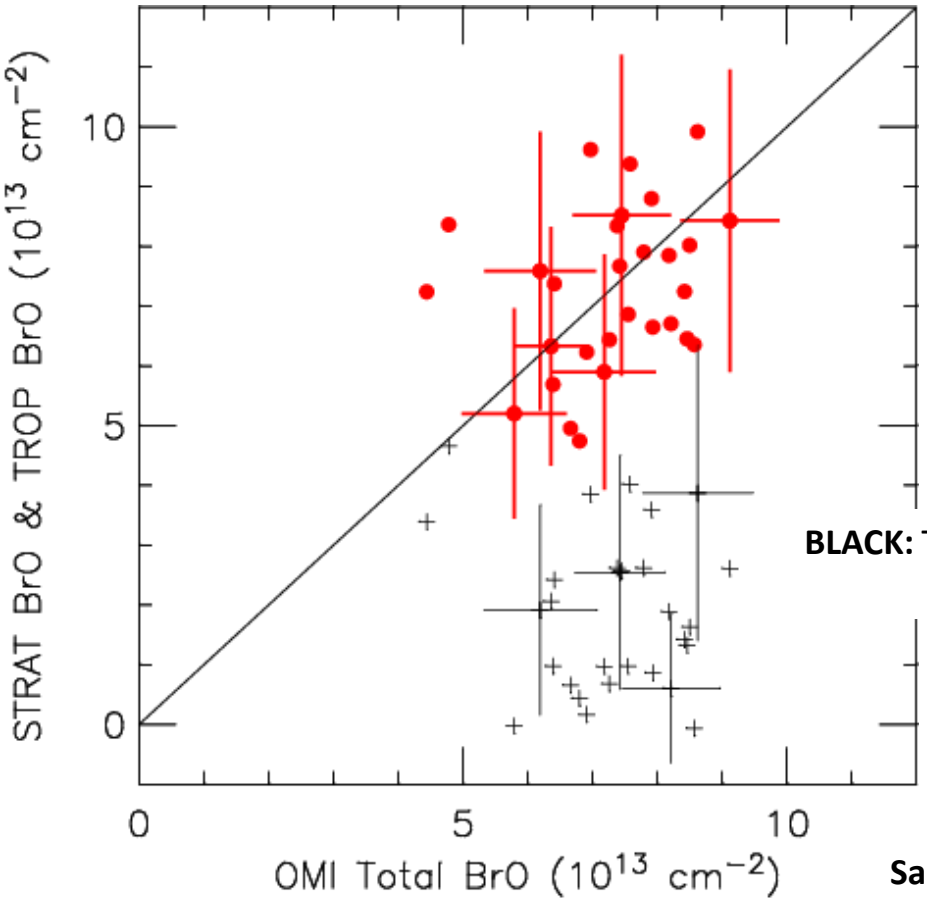


Salawitch et al., GRL, 2010

VSL Br_y estimated from ratio:

$$\frac{\text{STRAT BrO (model, fn of VSL } Br_y\text{) + Trop BrO (Aircraft Data)}}{\text{OMI Total Column BrO}}$$

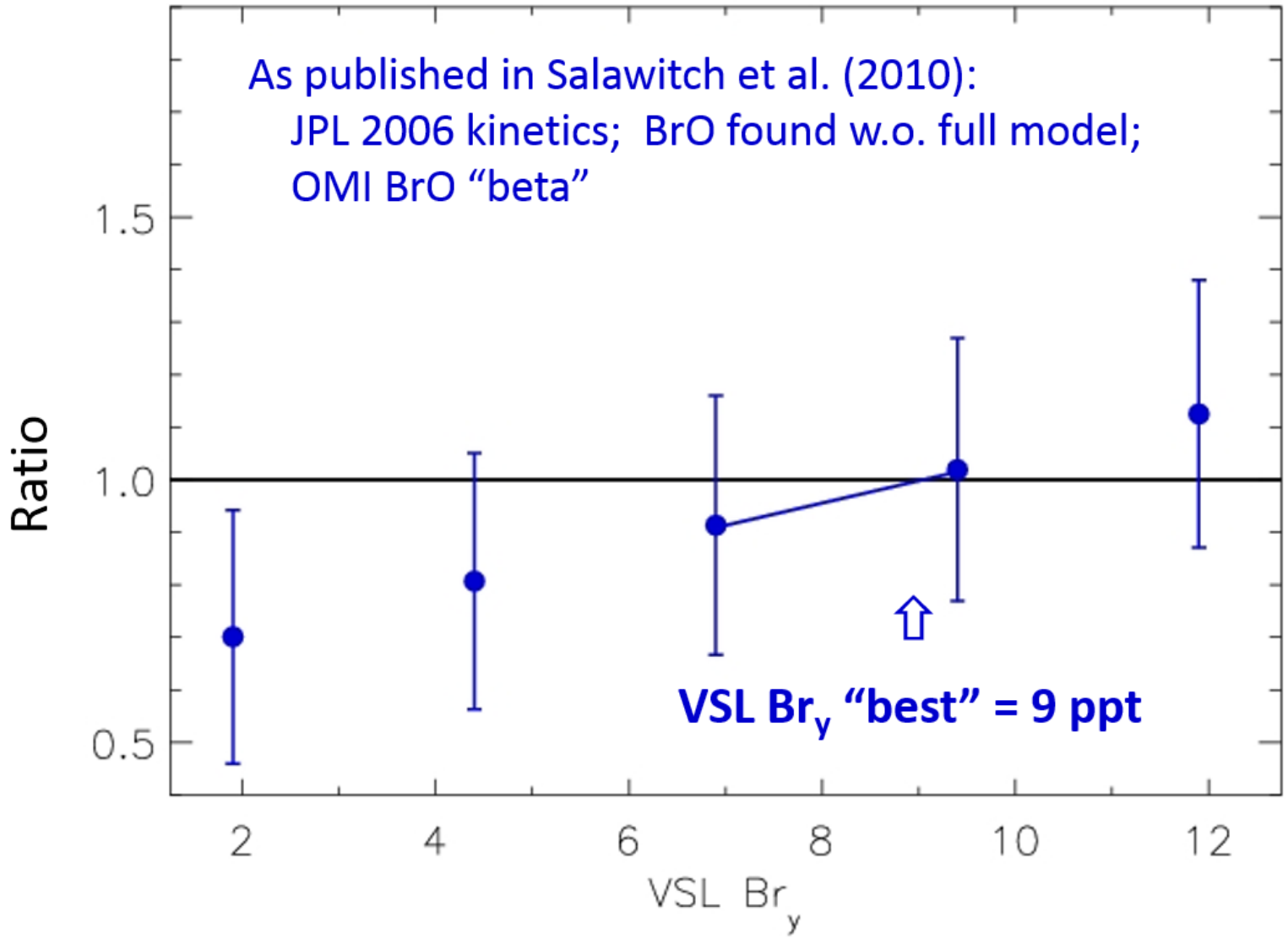
Trop BrO based on 29 profiles conducted during ARCTAS & ARCPAC ⇨



BLACK: Trop BrO, Huey (ARCTAS) & Neuman (ARCPAC)

Salawitch et al., GRL, 2010

Ratio = measured BrO total column / modeled BrO total column



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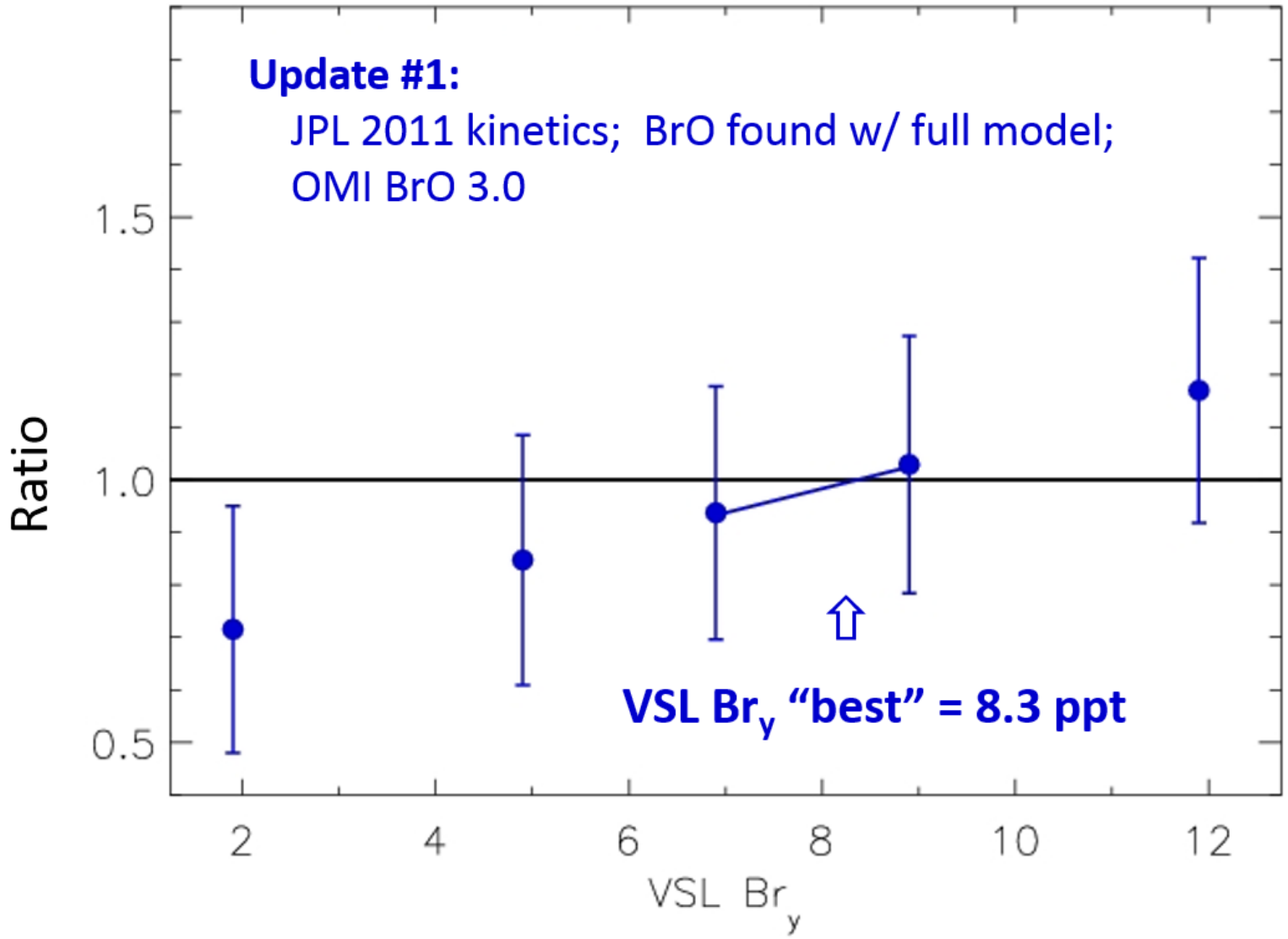

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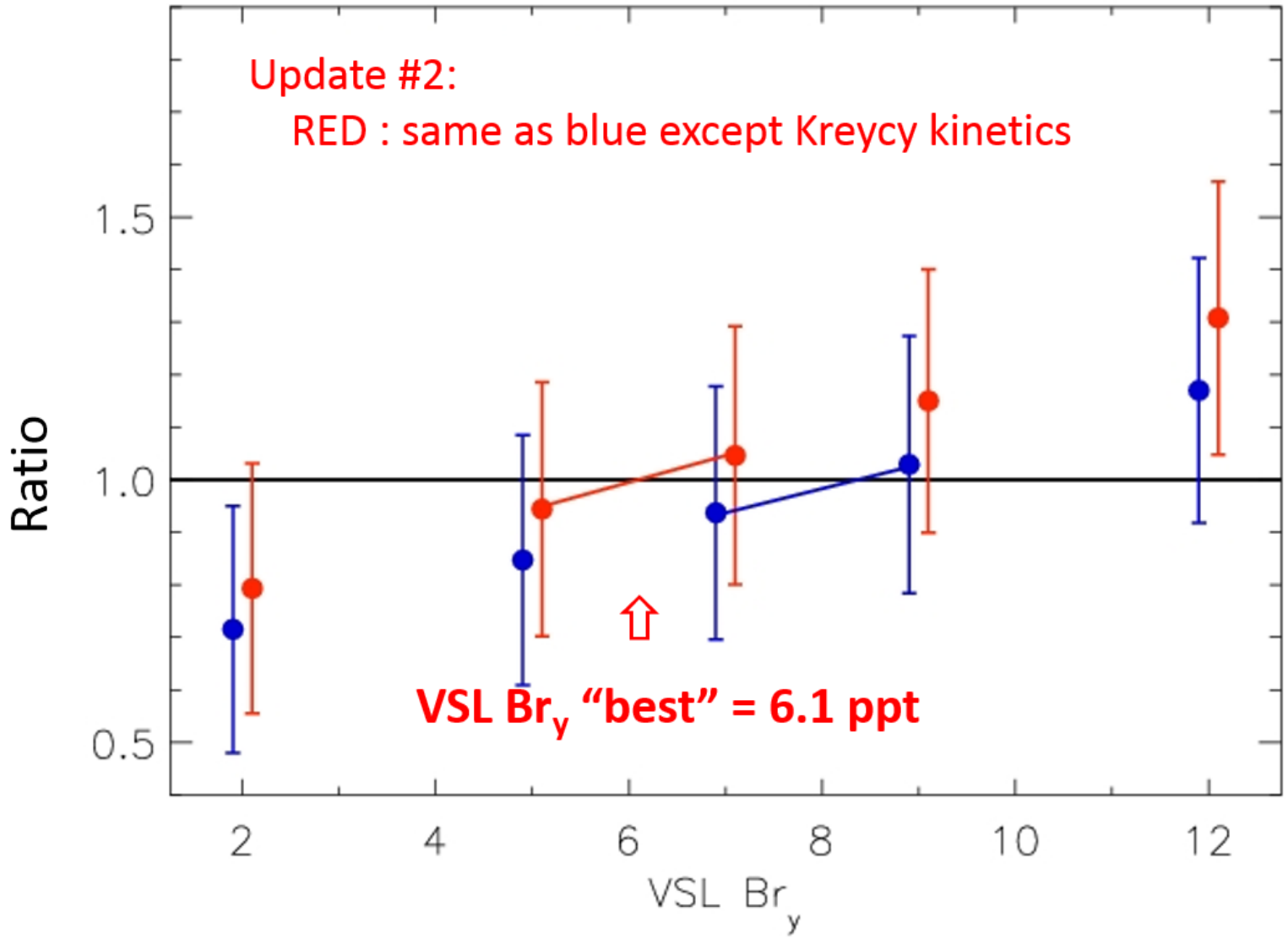

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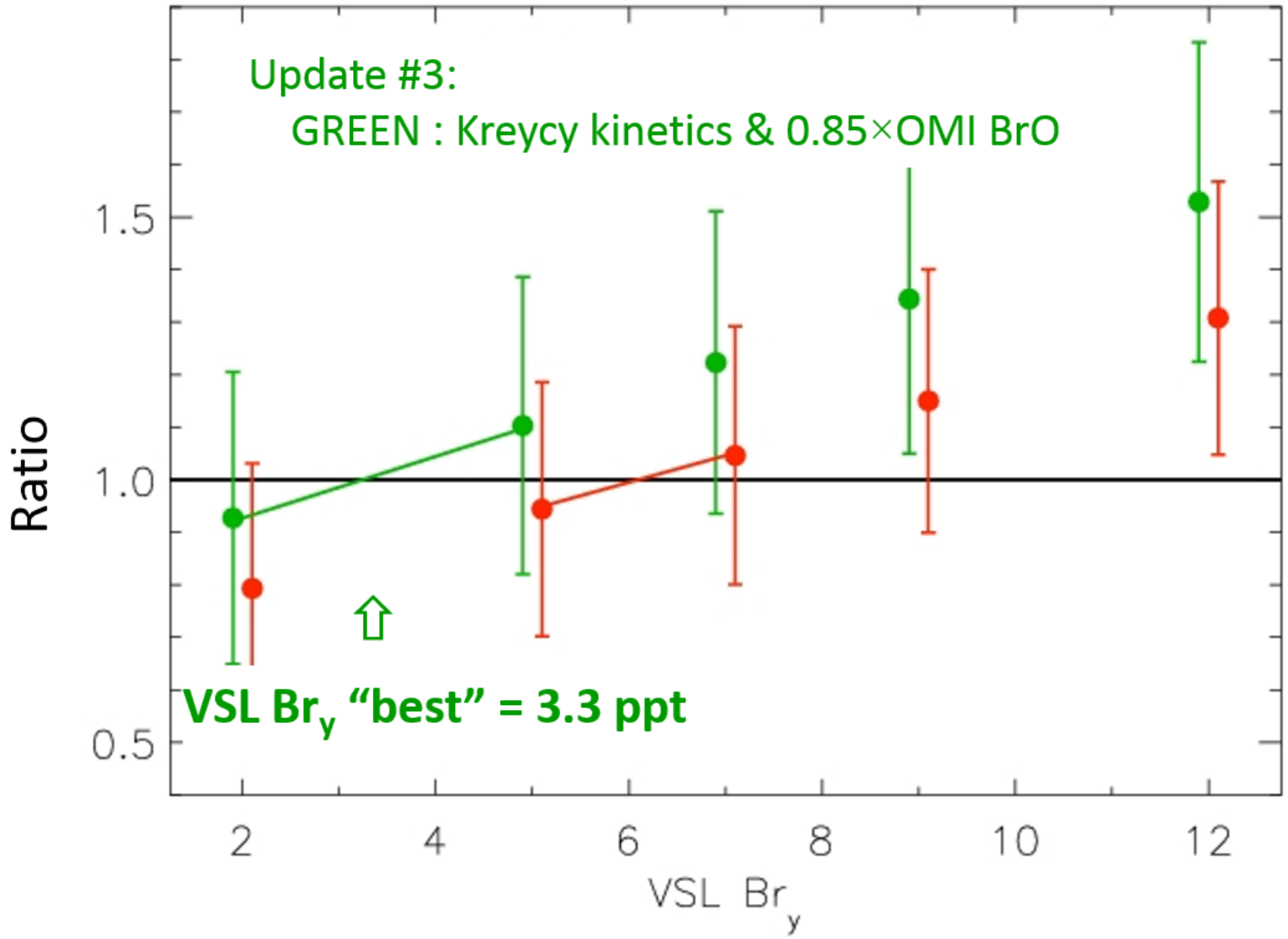

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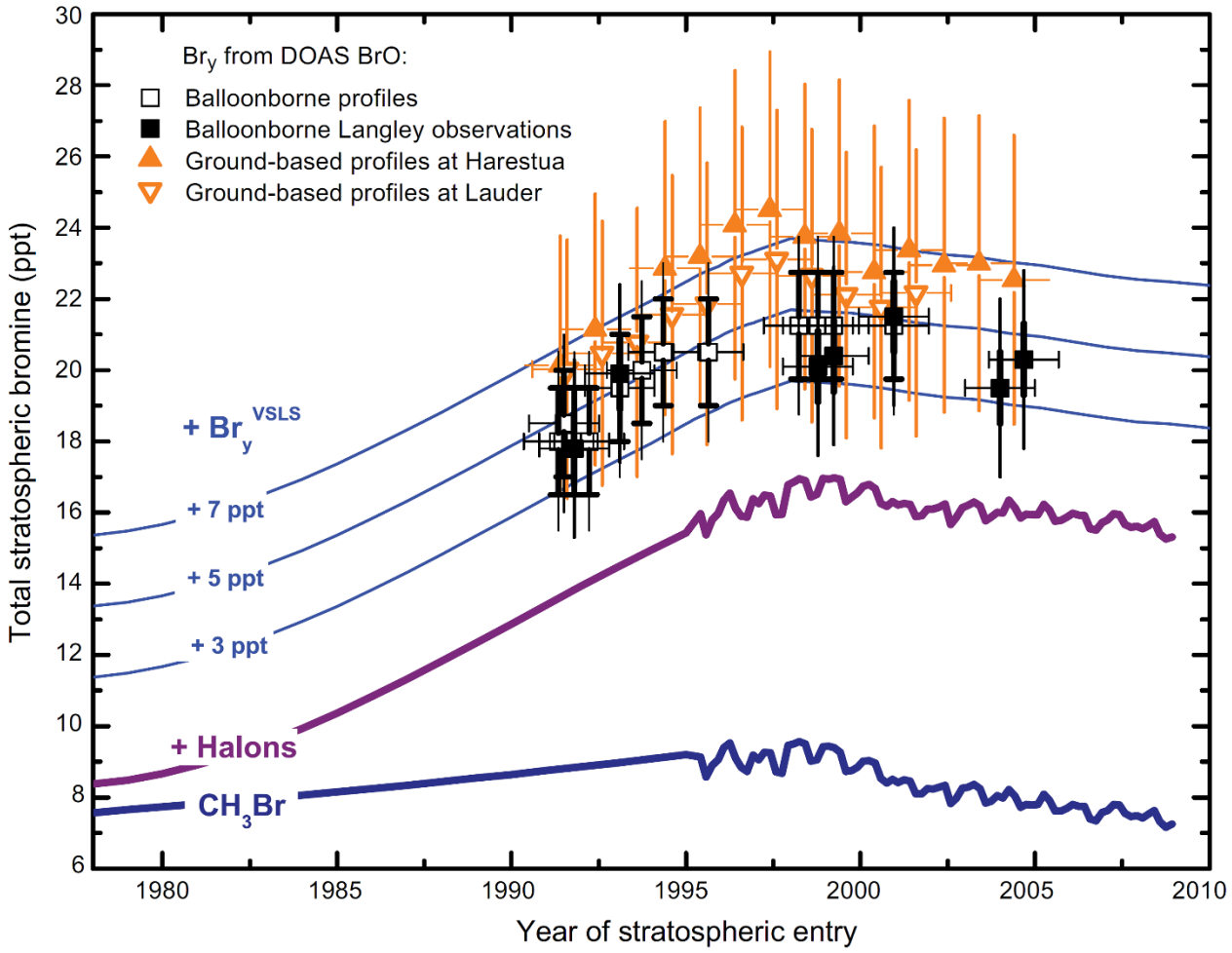
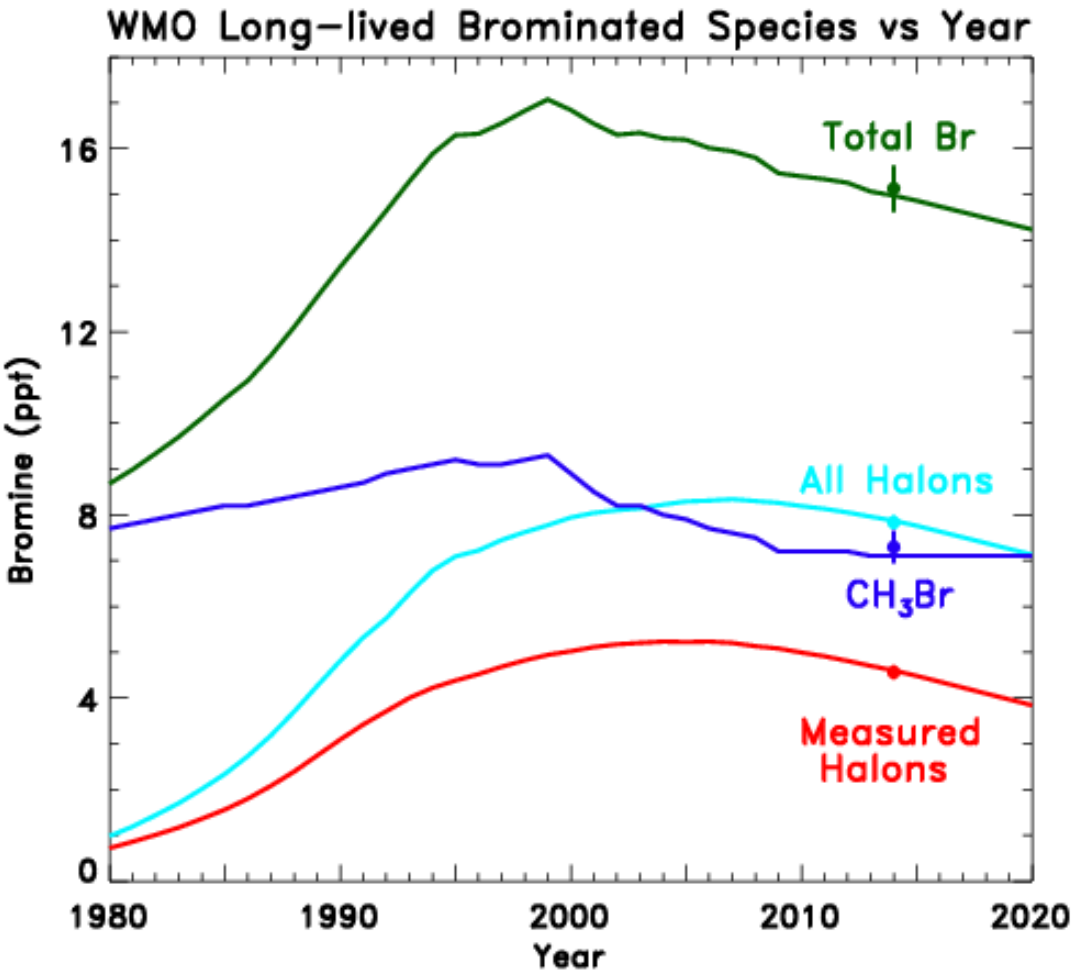
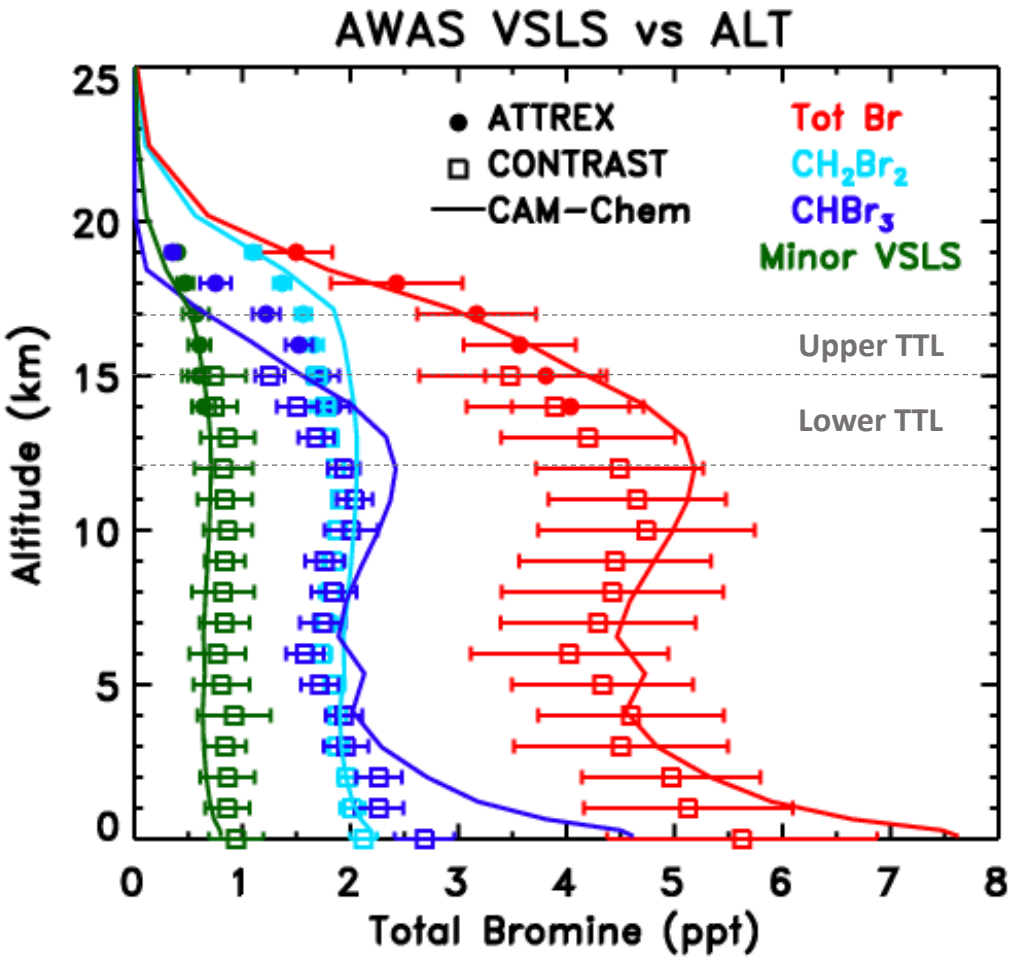


Figure 1-21, WMO/UNEP 2010

Lines: Table 5A-3, WMO/UNEP 2010
Points: CONTRAST Tropical Upper Trop, 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



VSLS: Very Short Lived Substance

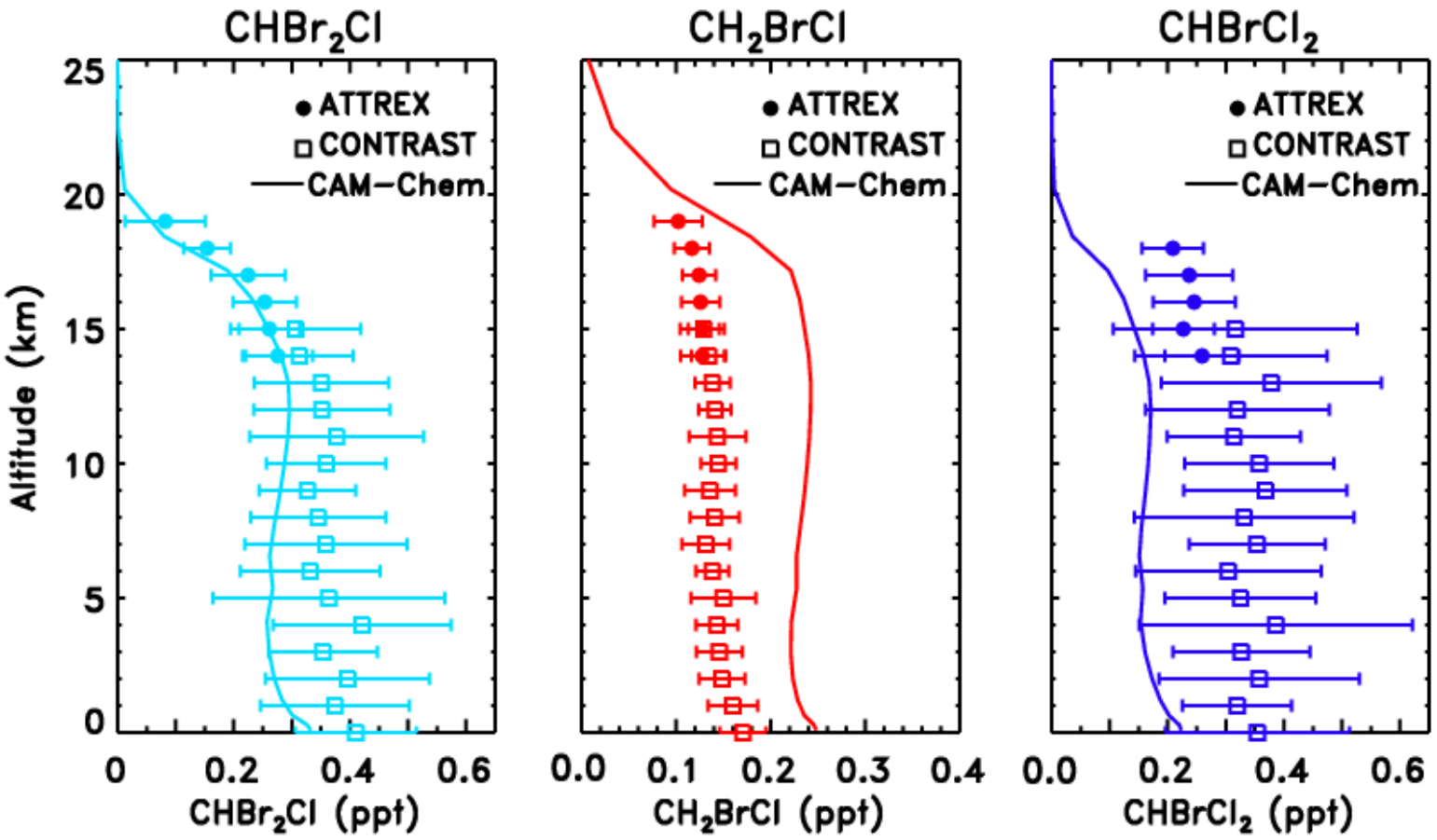


Measurements: AWAS

Model: Fernandez et al., ACPD, accepted, 2014 note: paper will not include CONTRAST data!

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

Closer look at minor VSLS

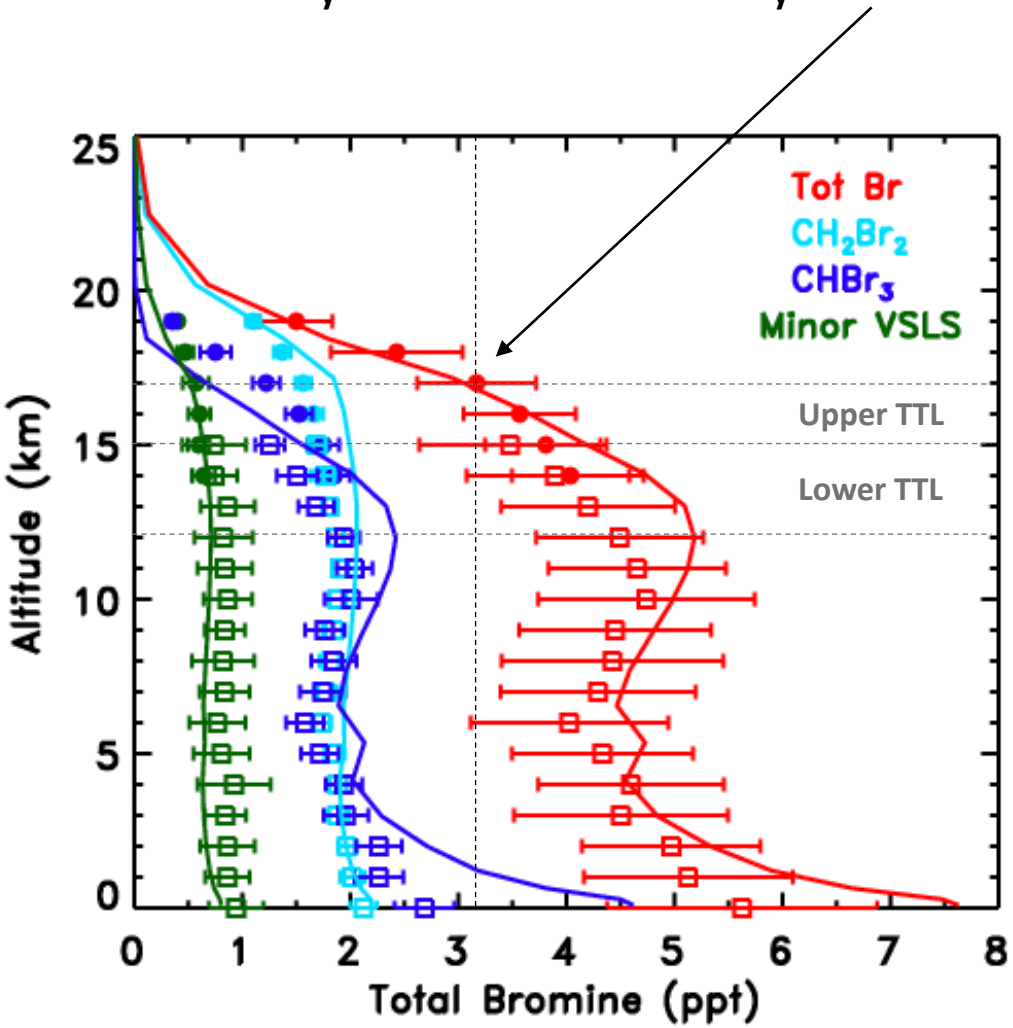


Measurements: AWAS

Model: Fernandez et al., ACPD, accepted, 2014

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 $Br_y^{VSLS\ SGI} \approx 3.2$ ppt



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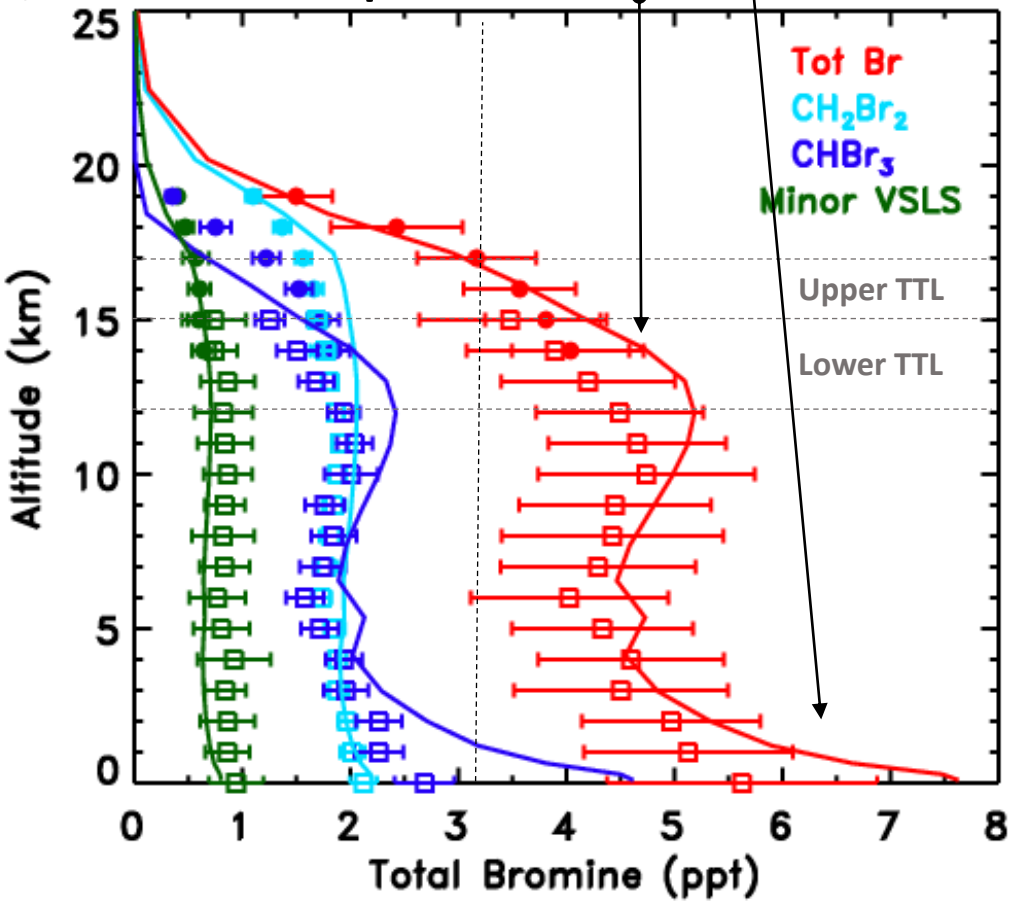
Product Gas Injection (PGI) depends on CBr_y near surface, lofting of bromine by saline aerosols, and het chem processes in TTL



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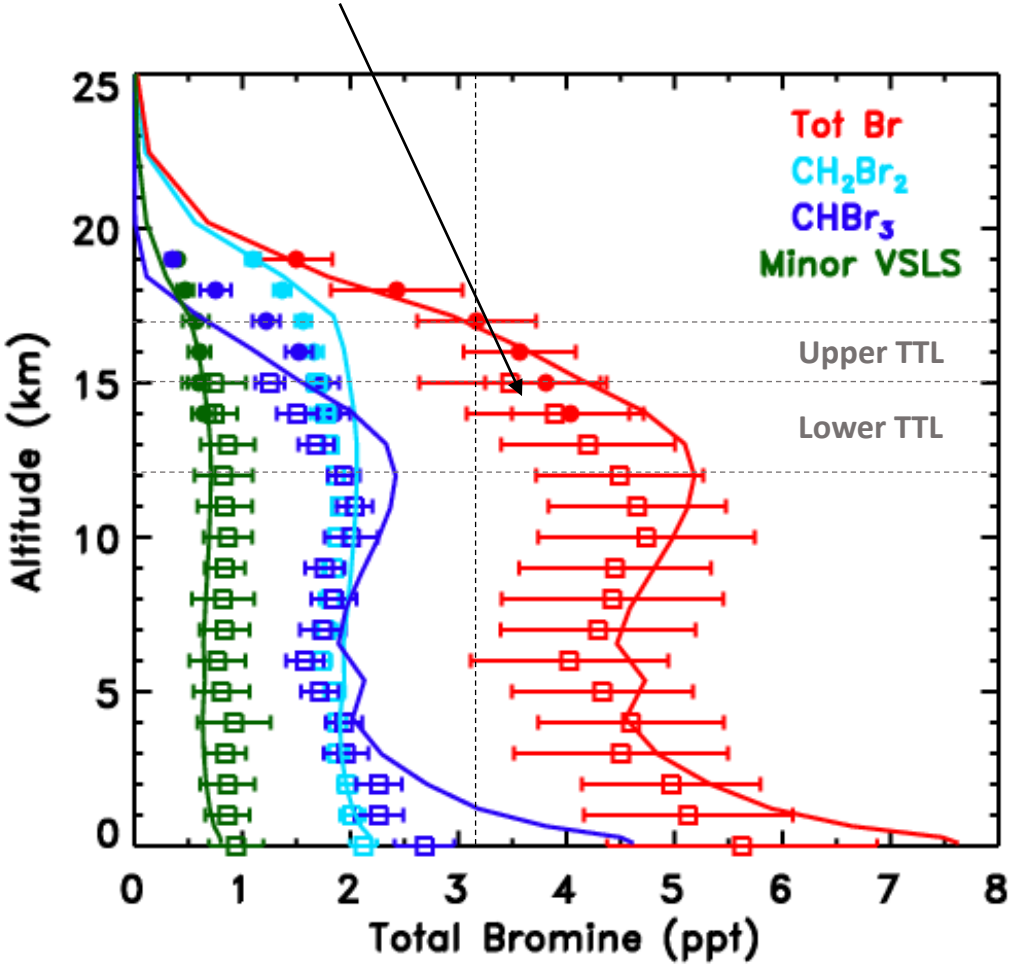
Geographically & seasonally distributed oceanic sources of VSLS as described in Ordonez et al. (2012)

Measurements of BrO in TTL were designed to constrain PGI



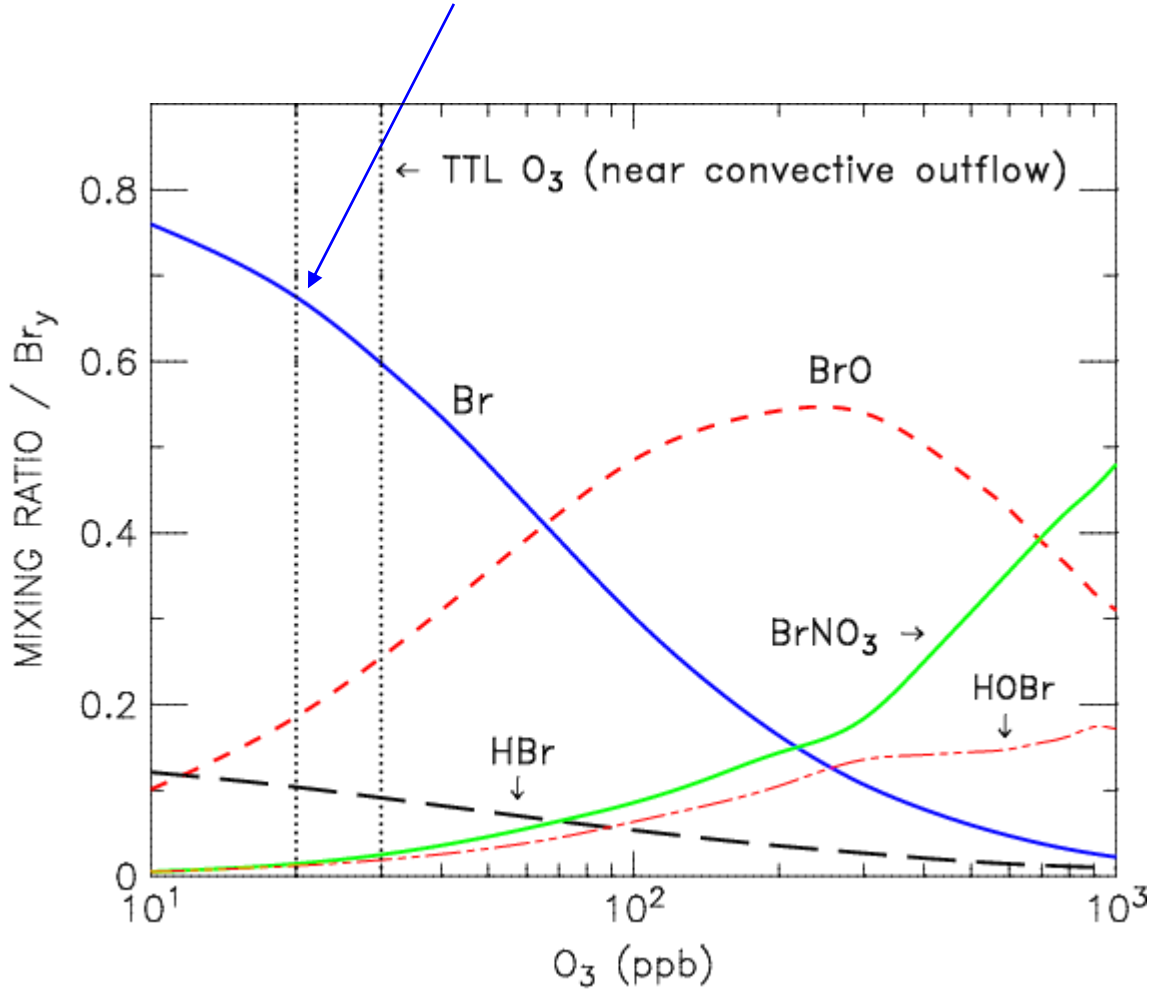
Measurements: AWAS

Model: Fernandez et al., ACPD, accepted, 2014

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

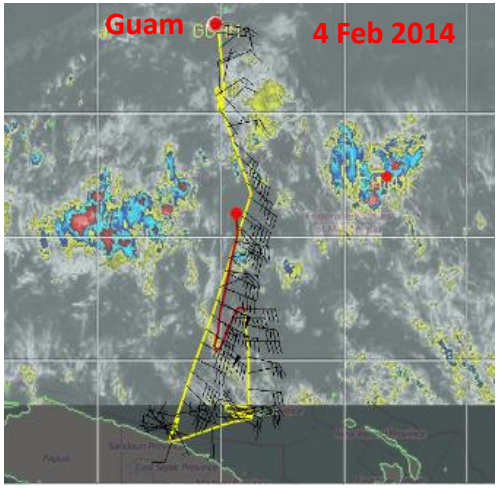
Measurements of BrO in TTL were designed to constrain PGI

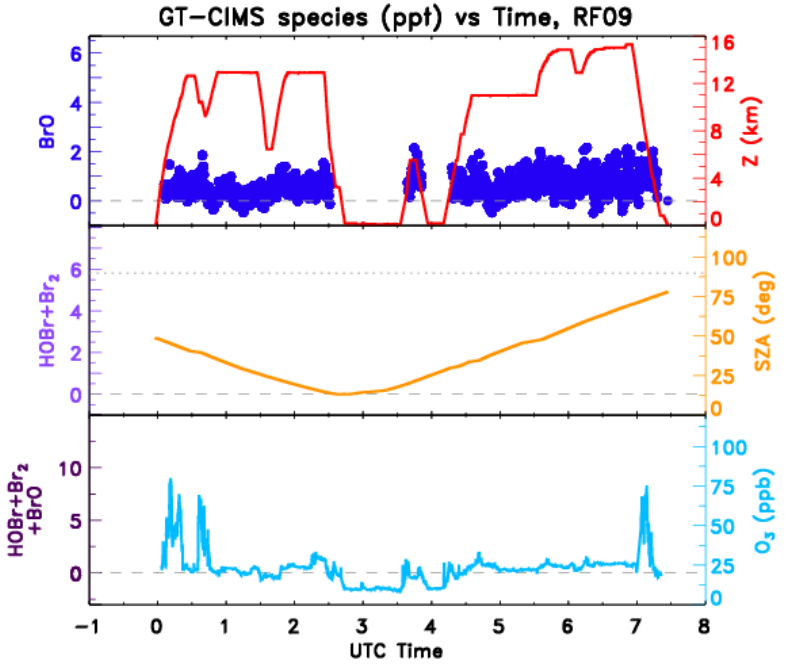
But theory indicates most of the product gas, if present in the gas phase, will be in the form of atomic-Br



Fernandez et al., ACPD, accepted, 2014

RF09: Convective Outflow and Equator Crossing





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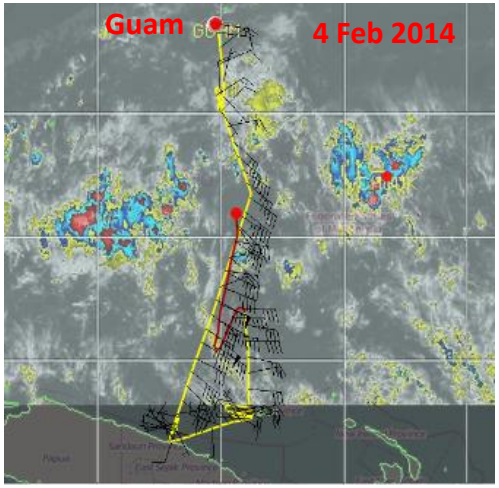
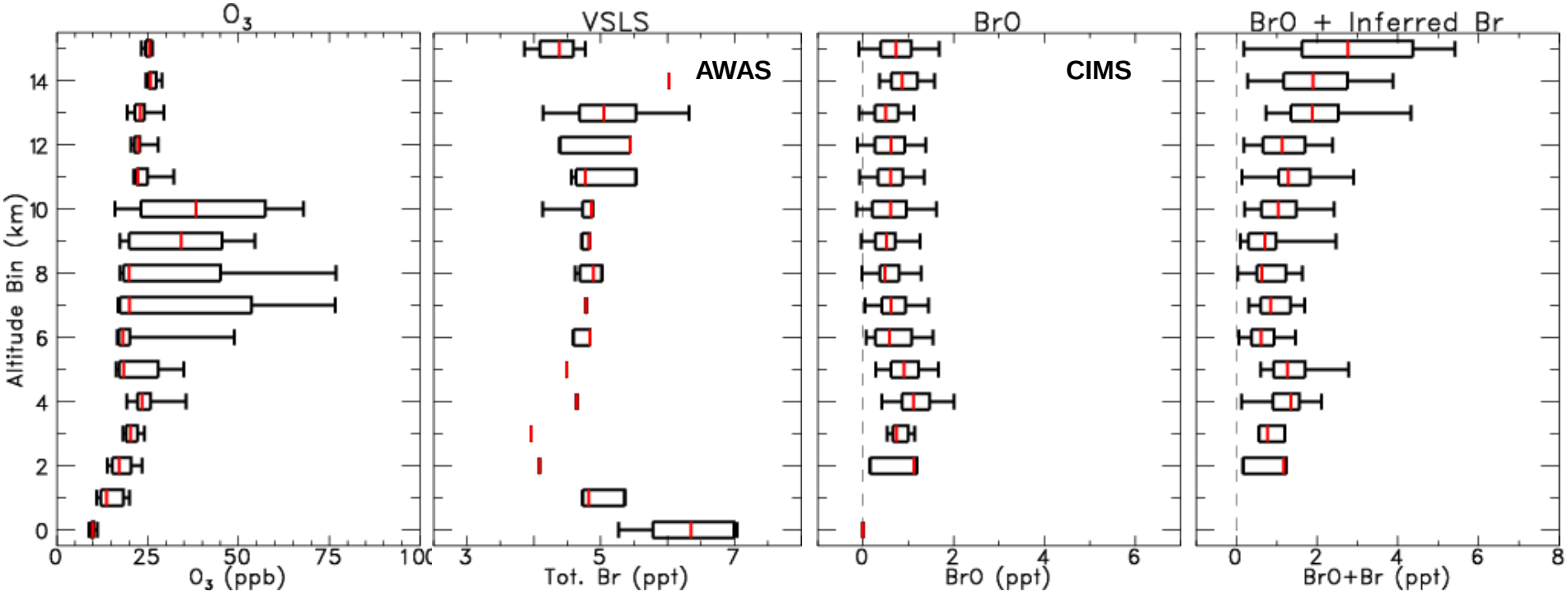
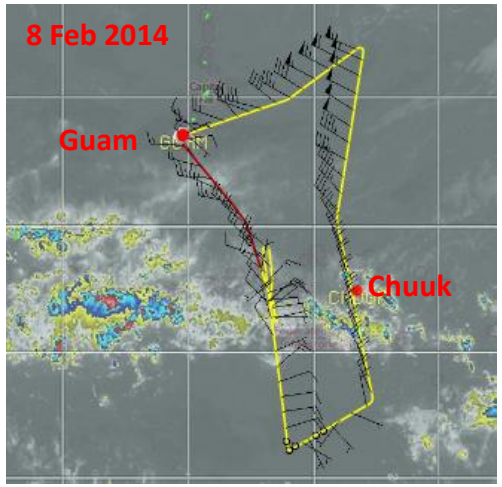
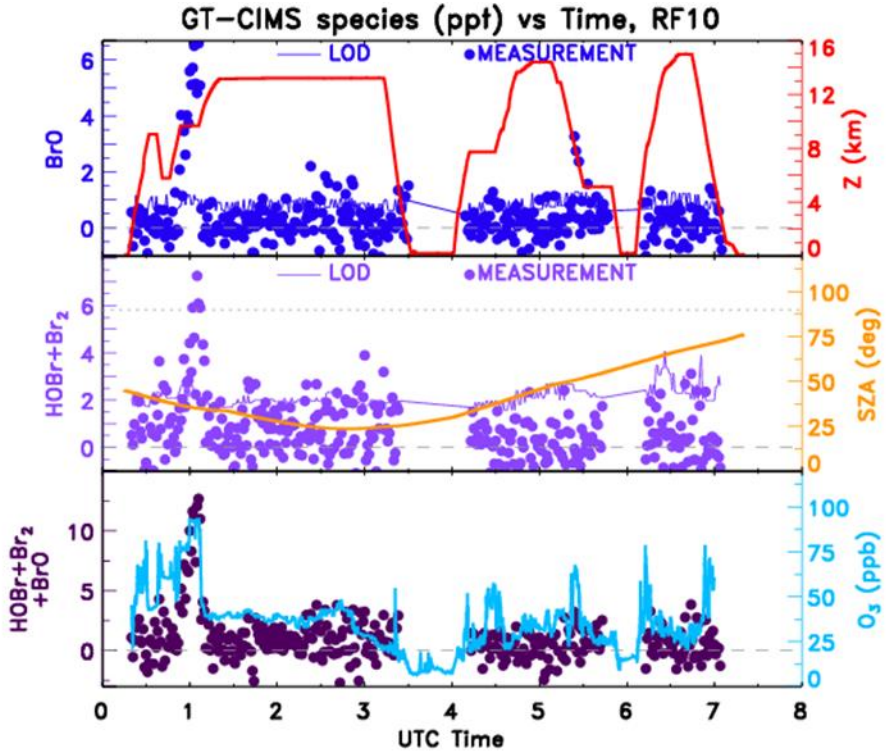




RF10: Subtropical Jet Pollution and ITCZ Survey





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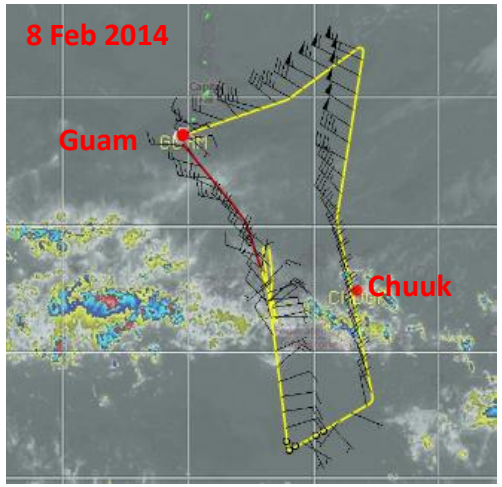

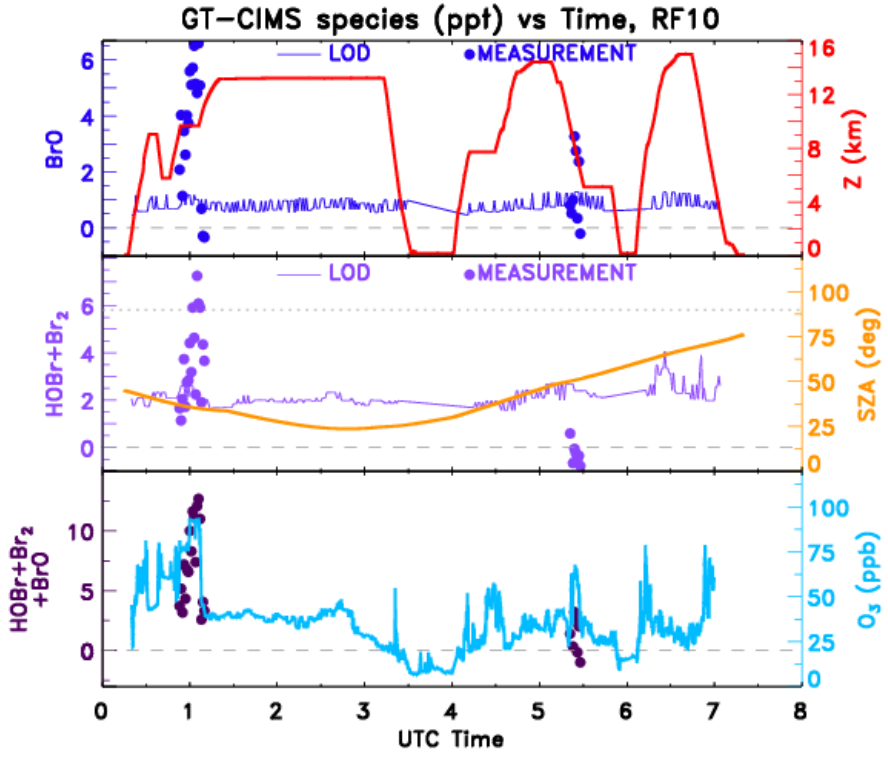

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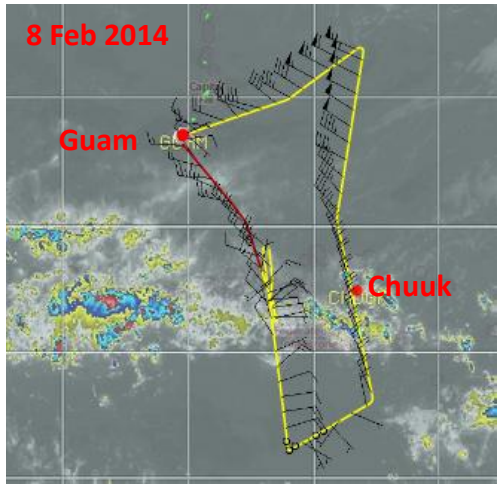
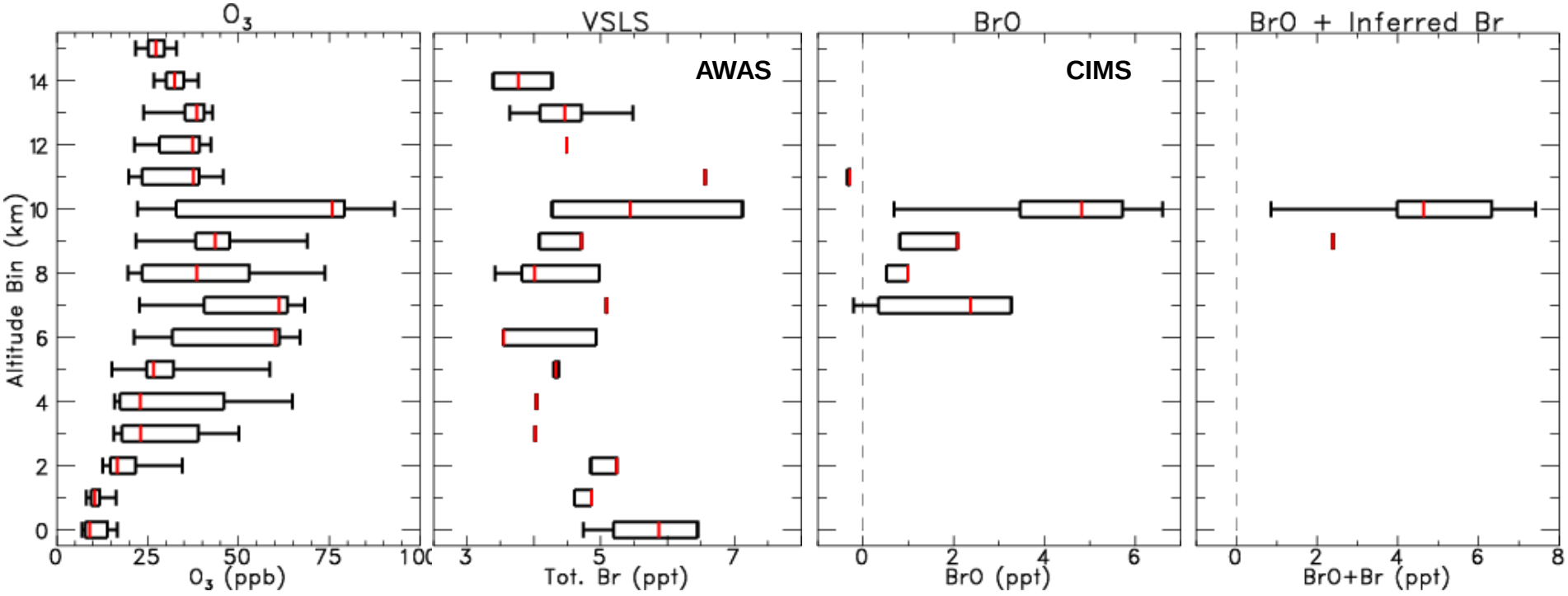
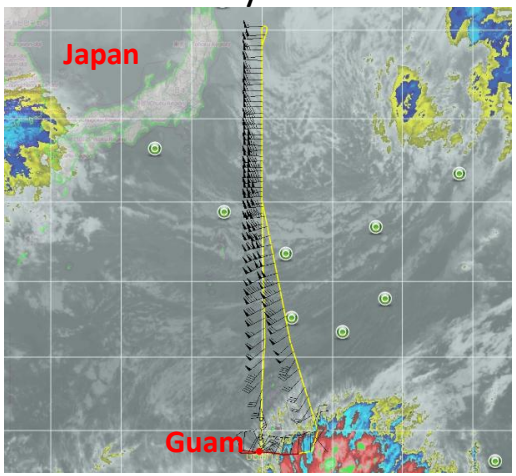


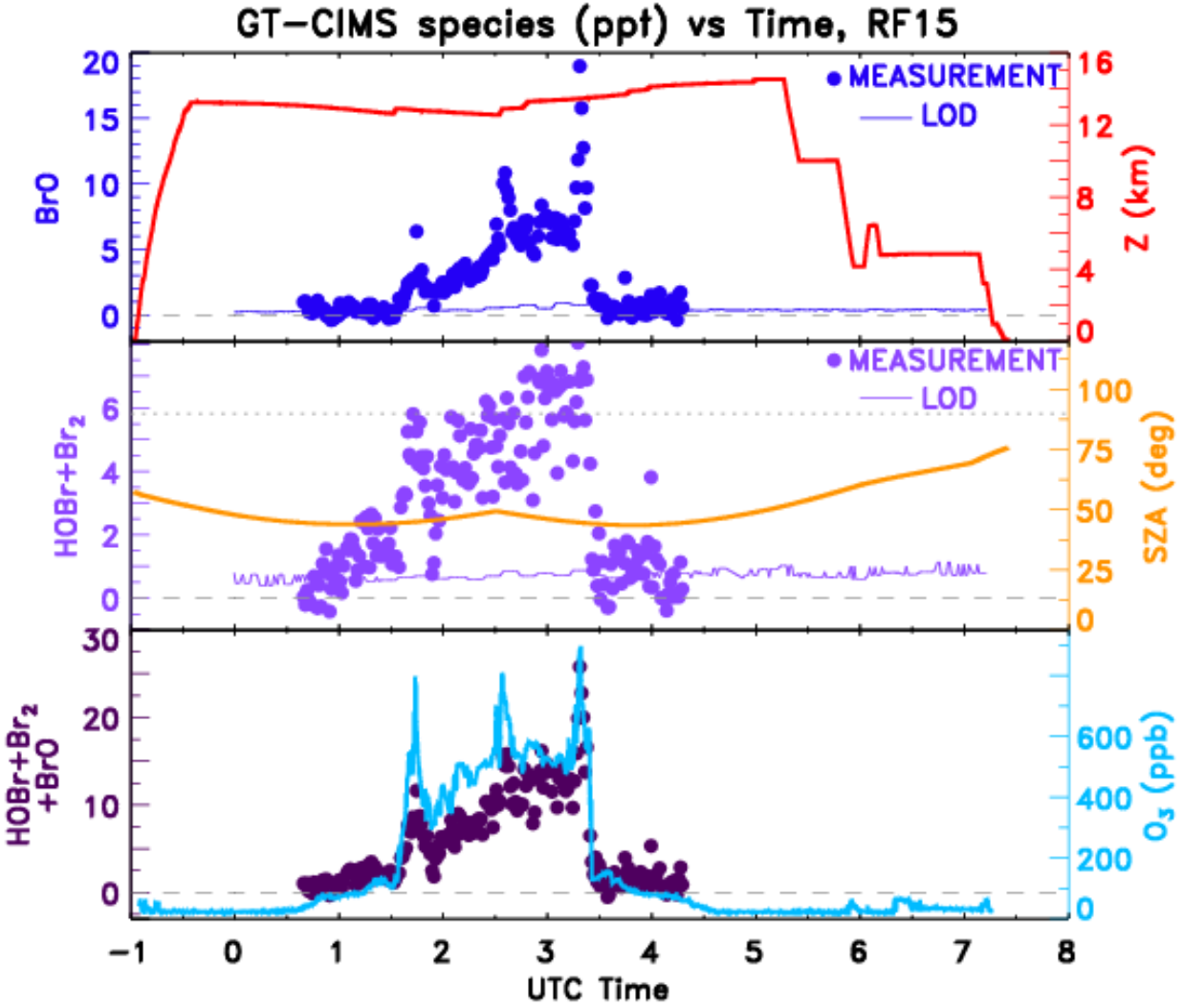
EQ



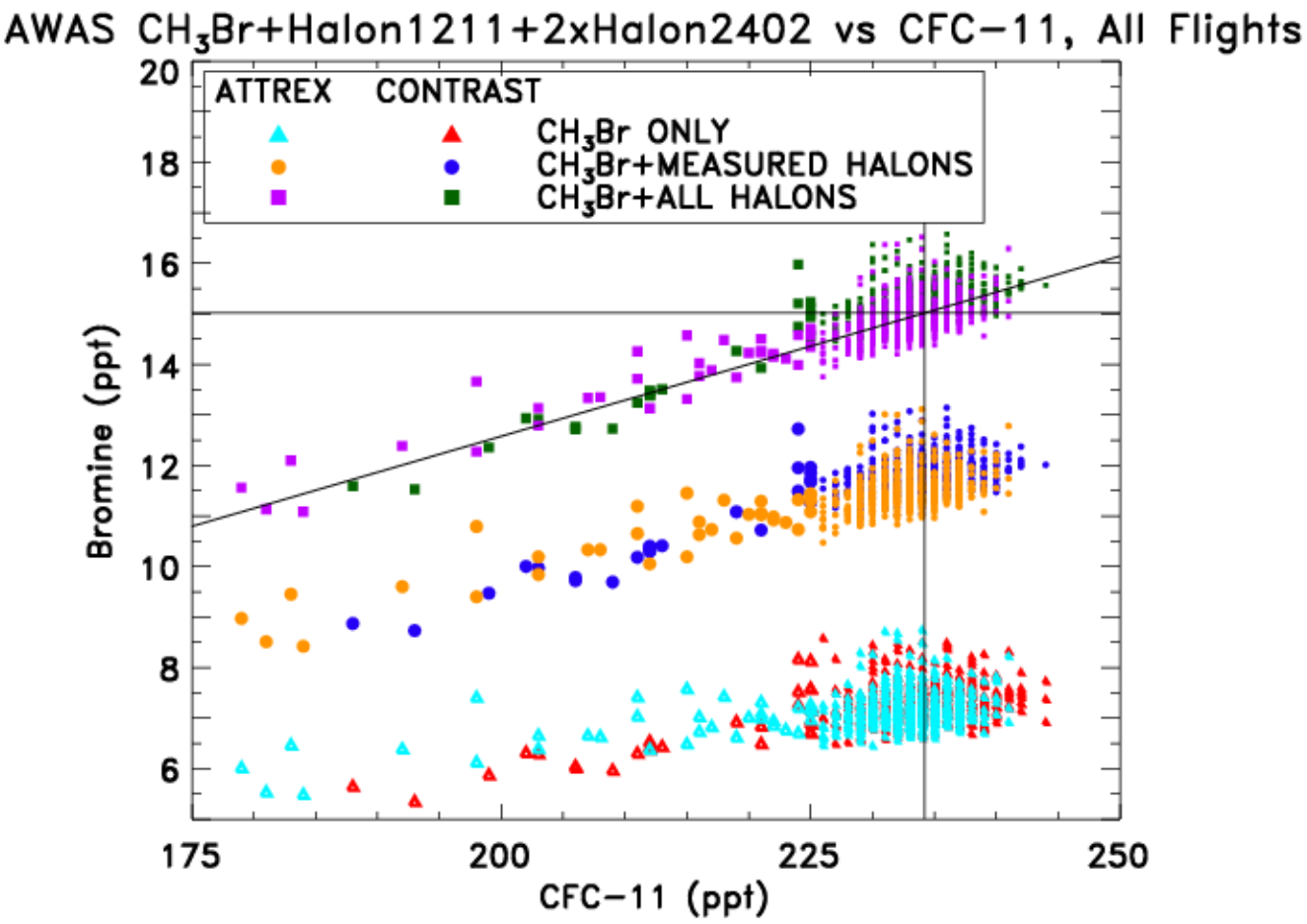
RF15: 25 Feb 2014

Northern Survey: reached 385 K





All ATTREX & CONTRAST flights



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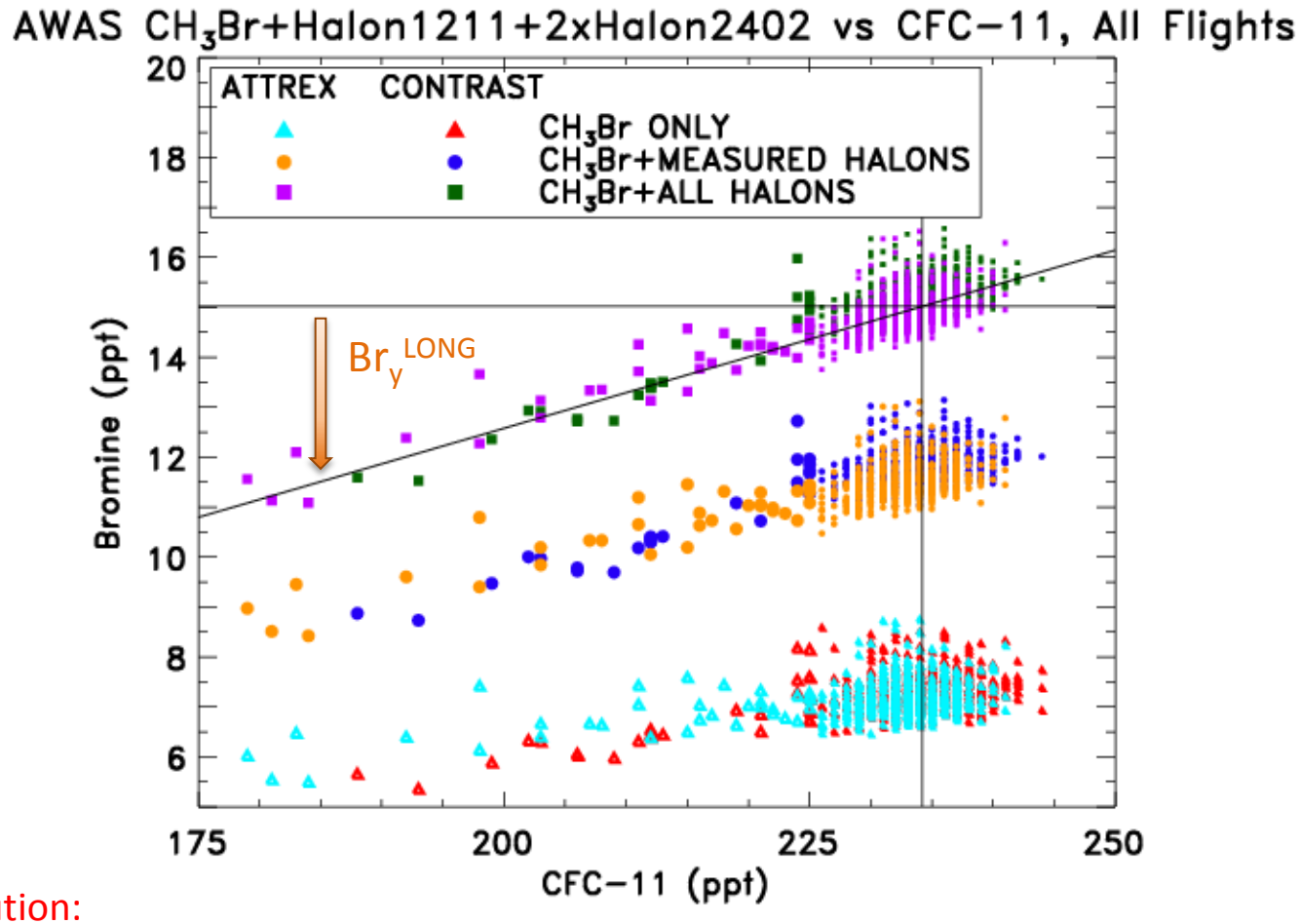
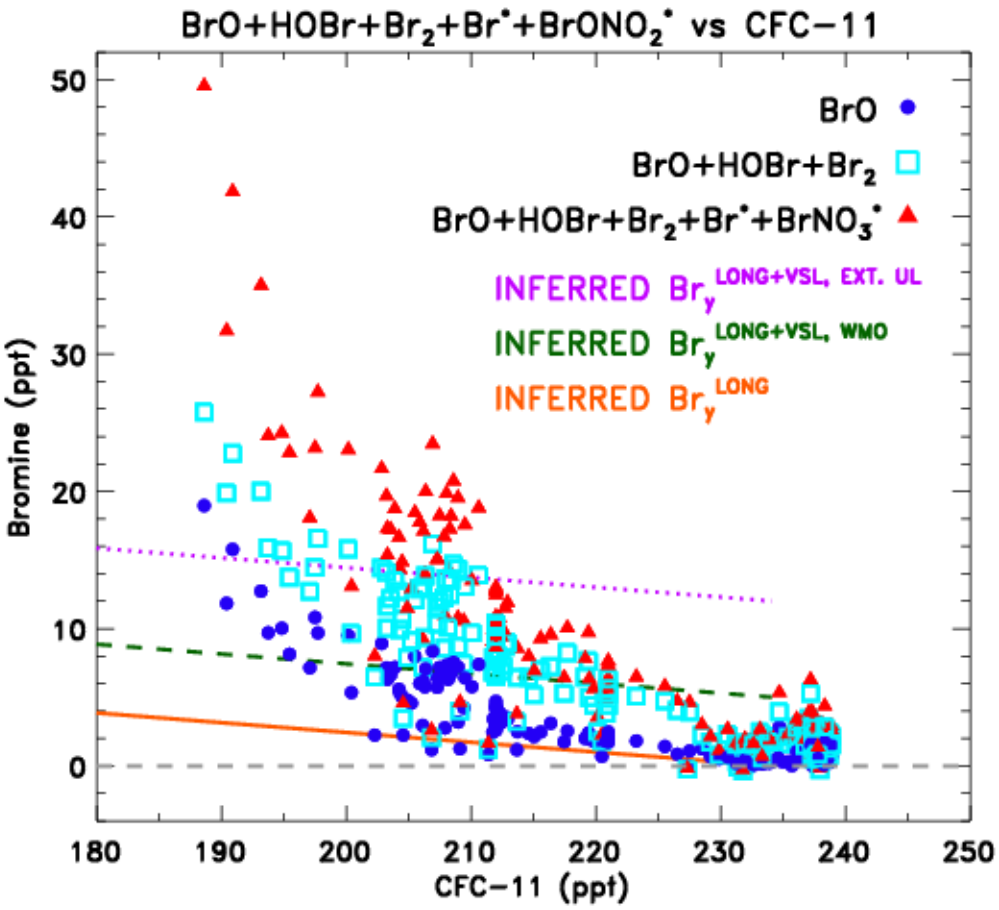


VSLS Contribution:

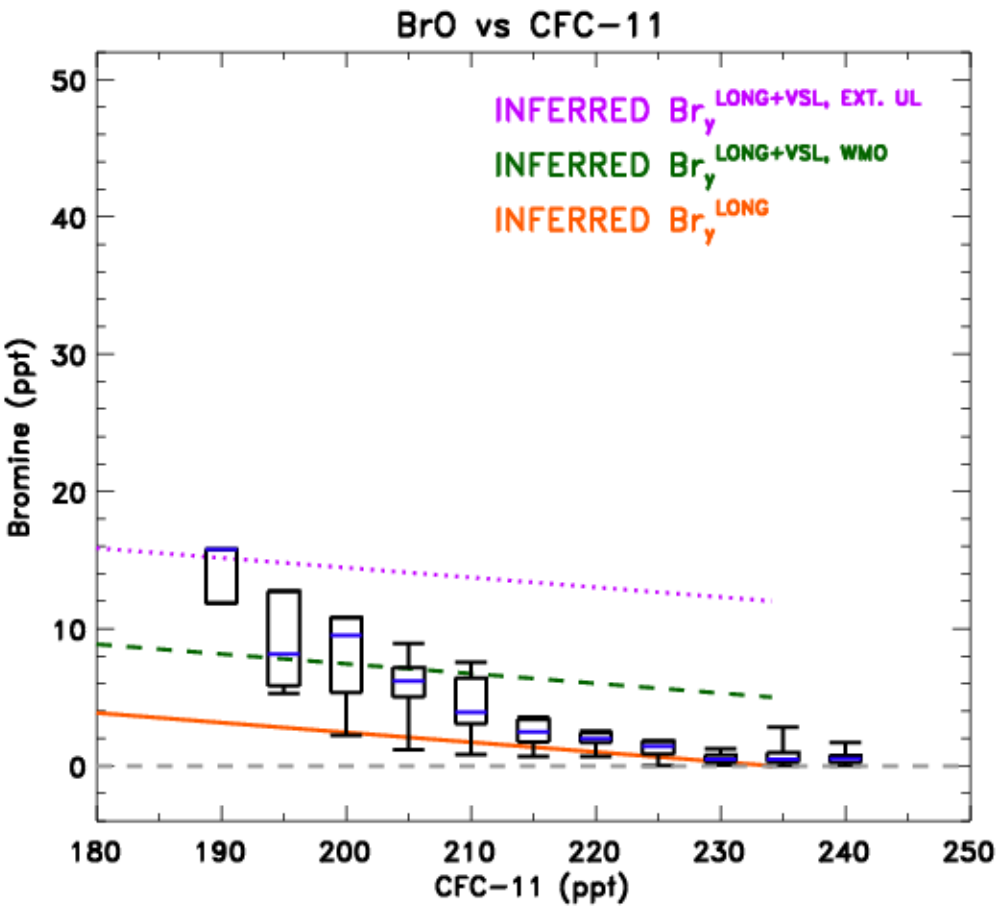
- $CHBr_3$ + CH_2Br_2 contribute another ~2.7 ppt to Br_y for RF 15
- Analysis in backup
- Uncertainty challenging to calculated due to considerable variability in tropical upper trop

RF15


BrO+HOBr+Br2+Br*+BrONO2* vs CFC−11
BrO
BrO+HOBr+Br2
BrO+HOBr+Br2+Br*+BrNO3*
INFERRED Bry LONG+VSL, EXT. UL
INFERRED Bry LONG+VSL, WMO
INFERRED Bry LONG
Bromine (ppt)
CFC−11 (ppt)
0
10
20
30
40
50
180
190
200
210
220
230
240
250

RF15

EXT. UL:
Extreme Upper Limit, from Salawitch et al. (2010)



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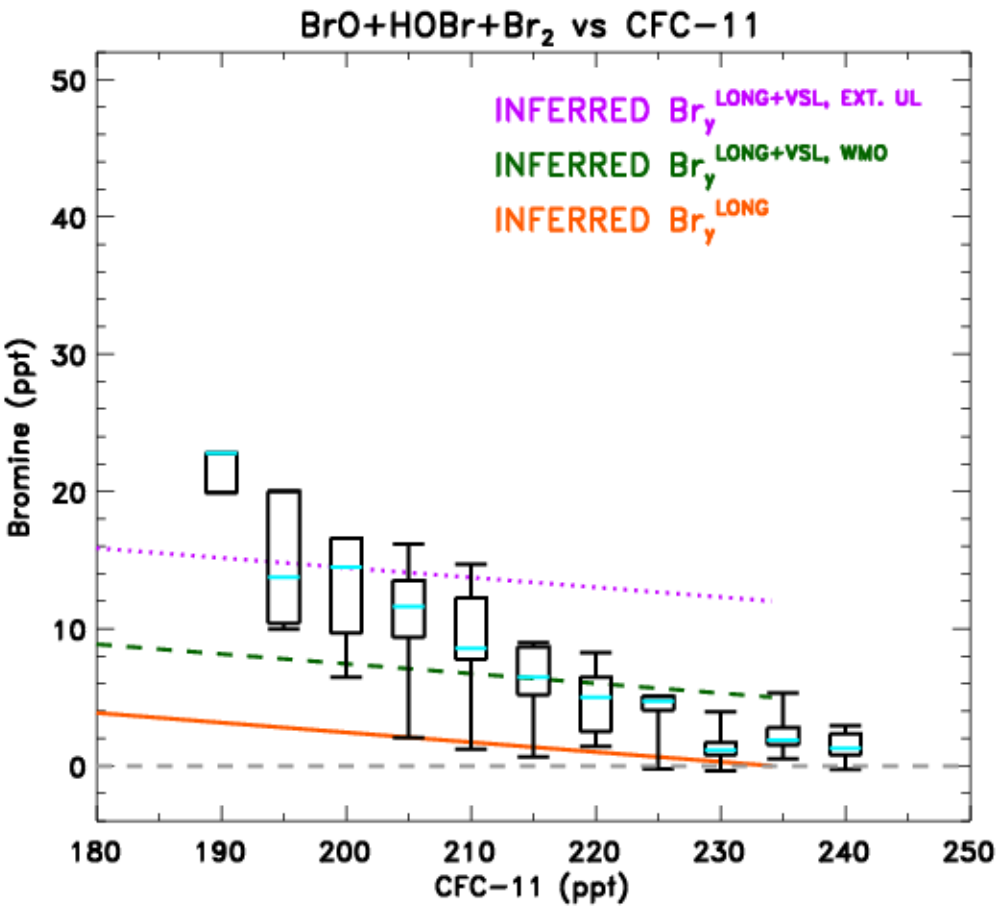

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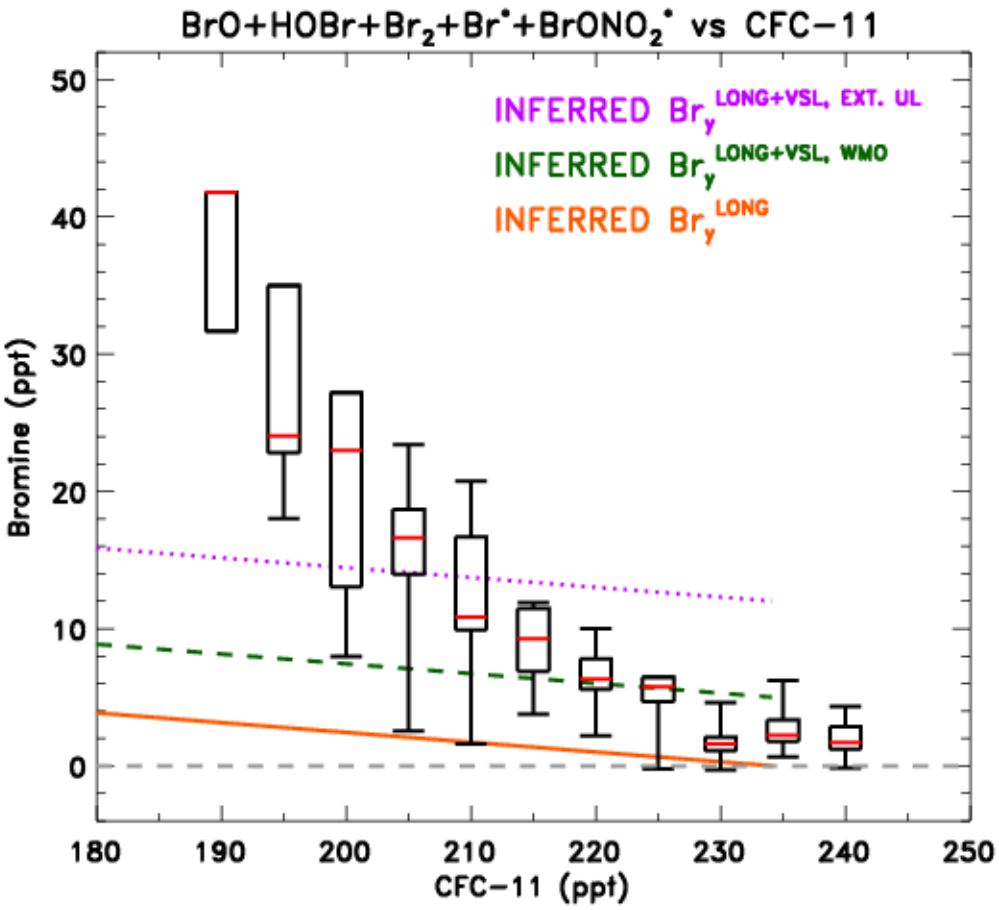

Concluding Remarks

$Br_y^{SGI\ VSLS}$ & $Br_y^{CH3Br\ \&\ Halons}$ will be well quantified by ATTREX/CONTRAST

$Br_y^{PGI\ VSLS/others}$ challenge to quantify because low O_3 environment of TTL titrates BrO+Br towards Br, leading to ambient BrO near CIMS Limit of Detection even if considerable levels of inorganic bromine are present in TTL

High CIMS BrO in lowermost stratosphere, RF15, where BrO+Br is driven back to BrO by high O_3, suggestive of quite high Br_y^{PGI}

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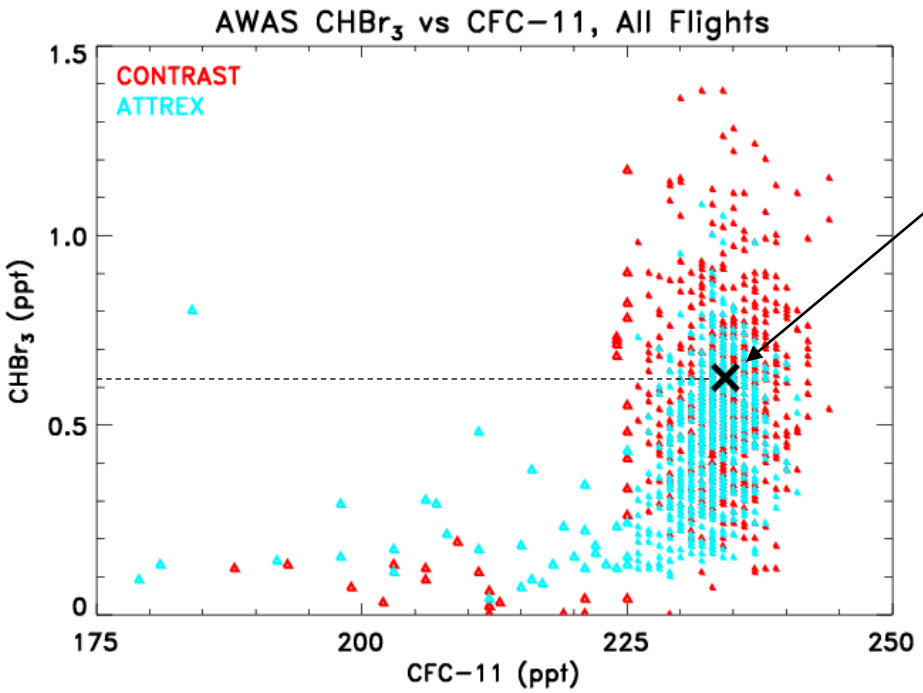
It was a sincere pleasure to:

a) co-lead CONTRAST and fly on the GV (HIAPER)
b) collaborate with ATTREX & CAST teams

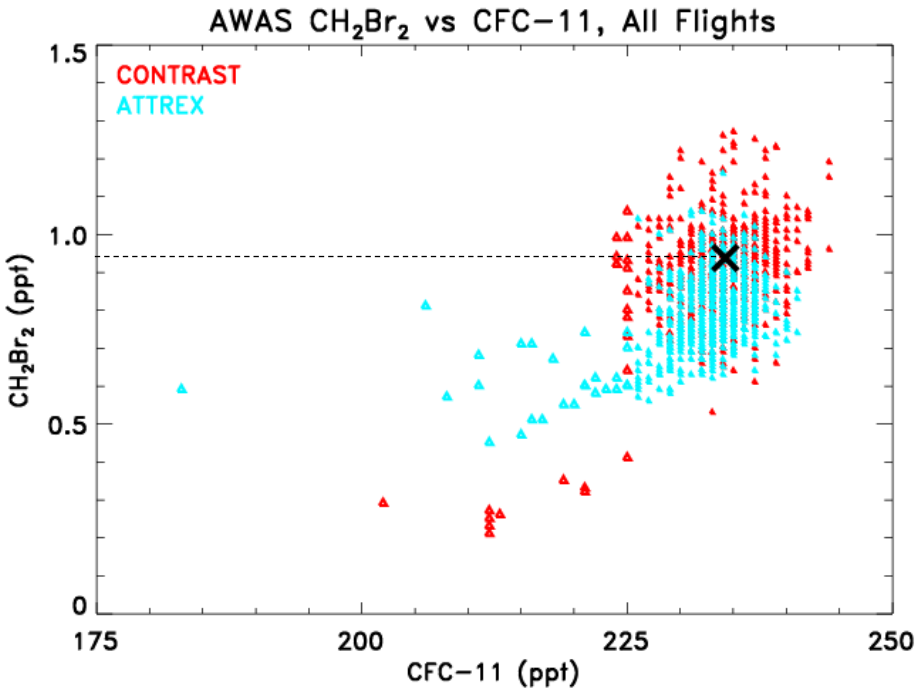
Looking forward to the science that will emerge !

Backup Slides To Follow

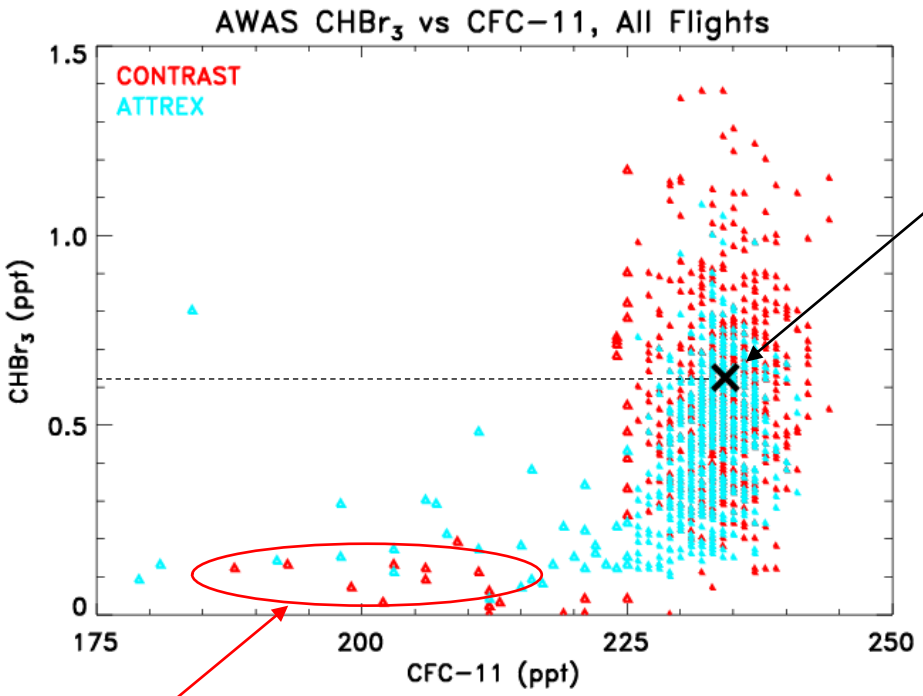
All ATTREX & CONTRAST flights



×：Upper Tropical Troposphere mean value, CONTRAST

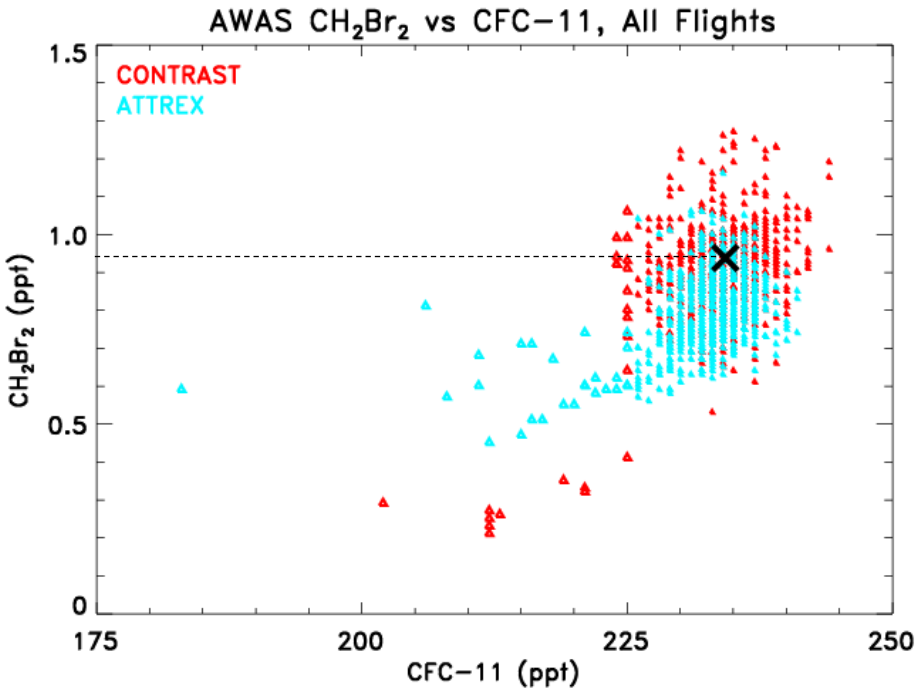


All ATTREX & CONTRAST flights



×：Upper Tropical Troposphere mean value, CONTRAST

These points collected RF15



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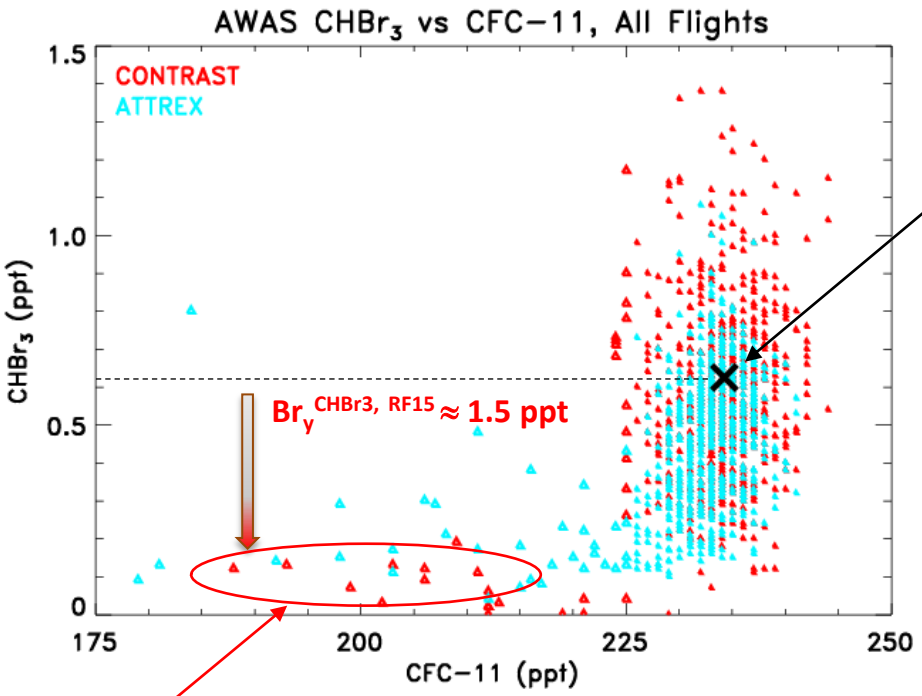

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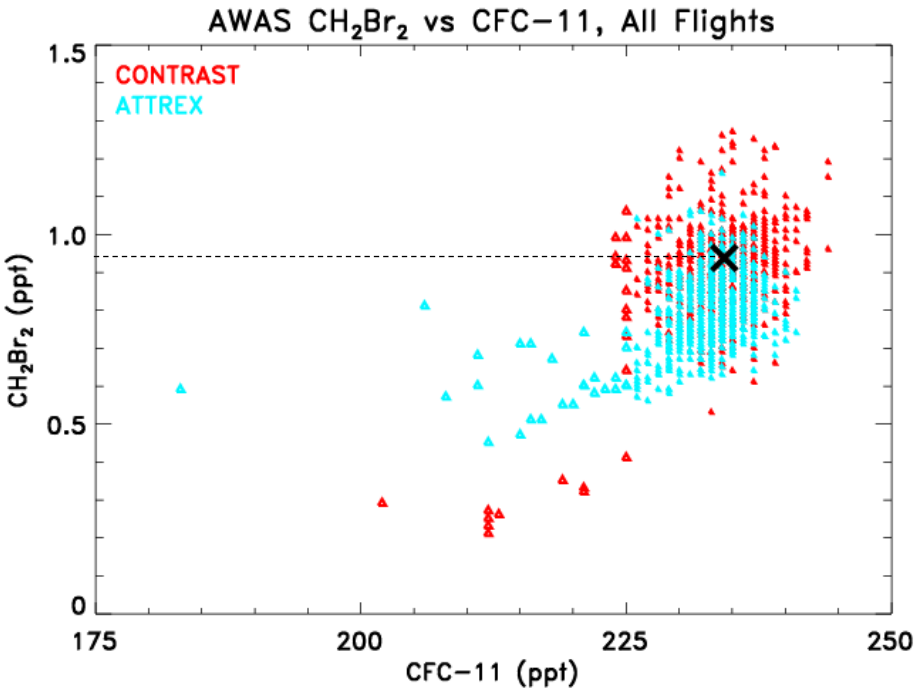

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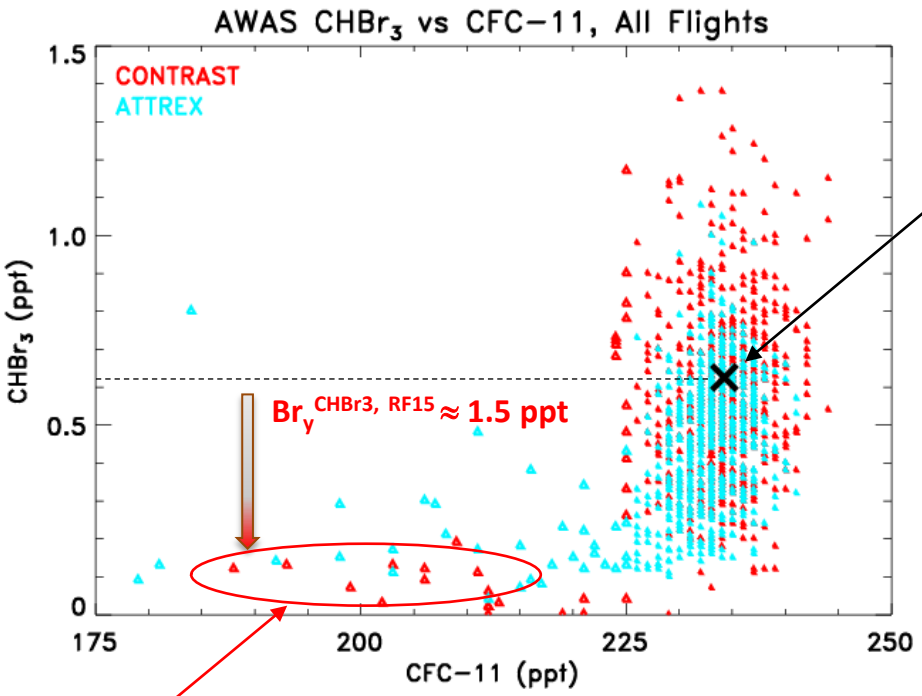

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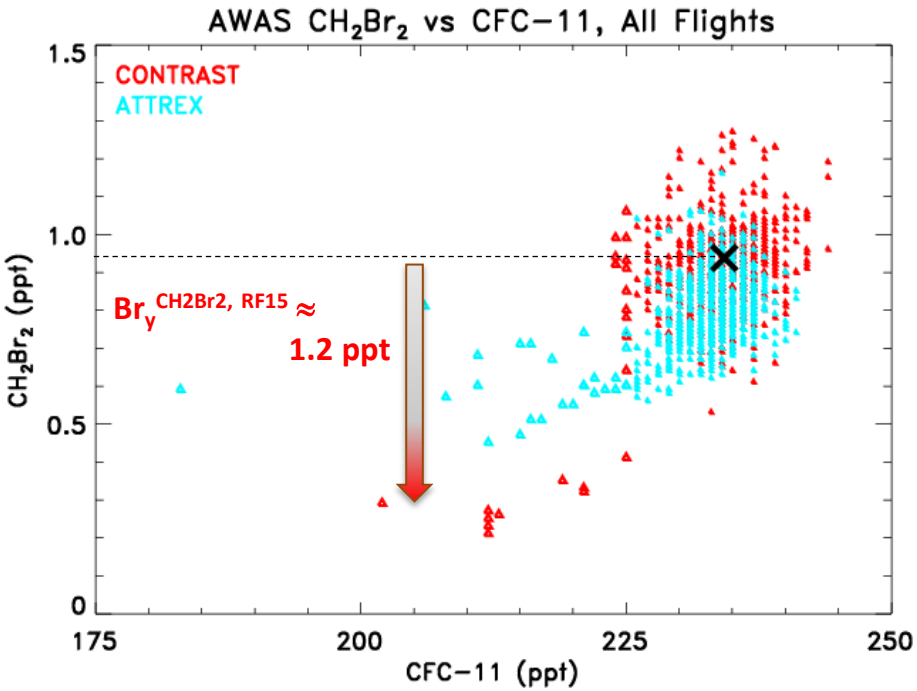

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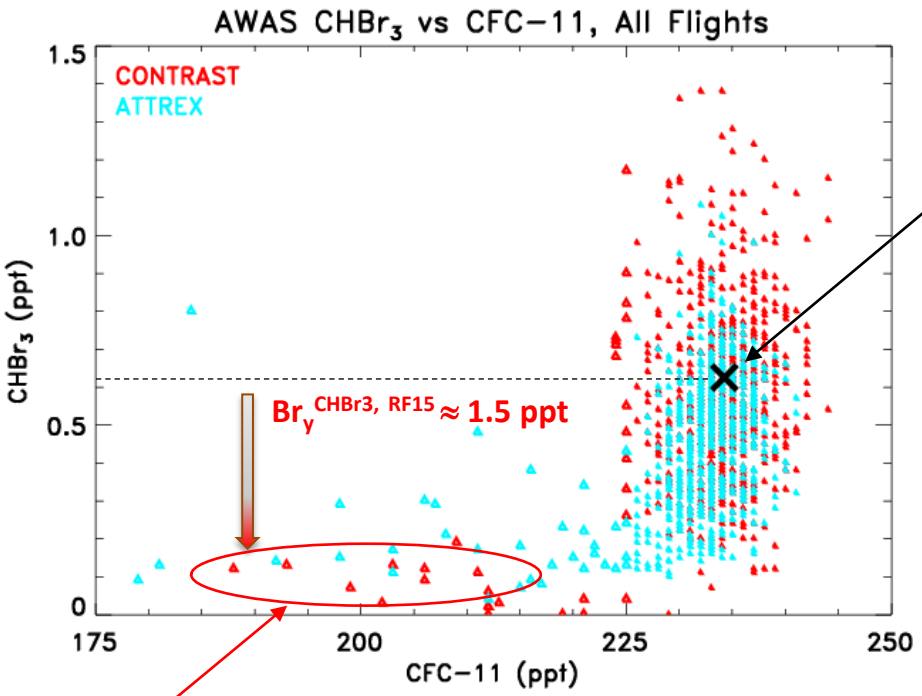

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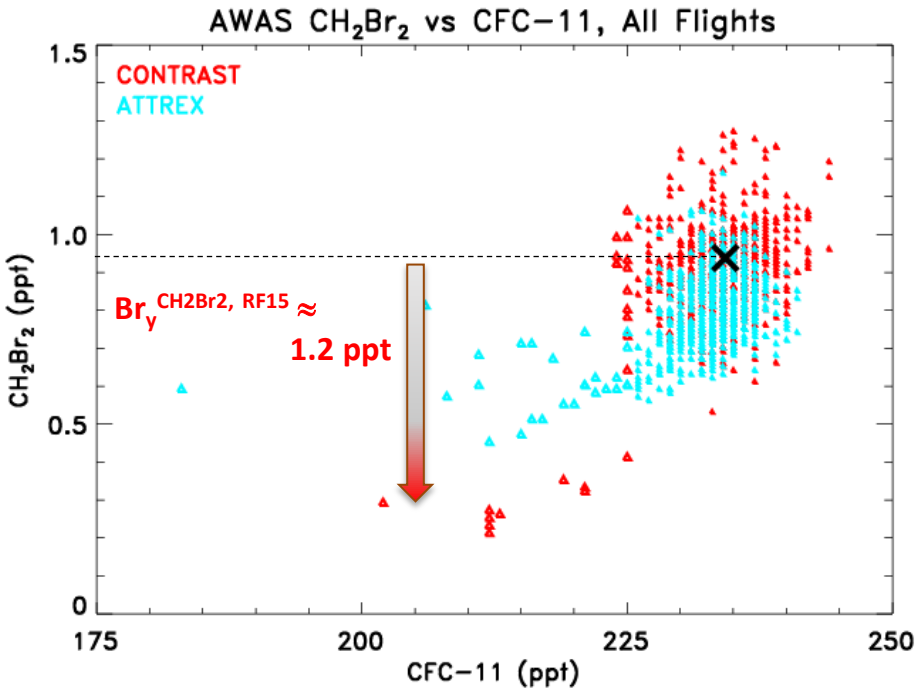

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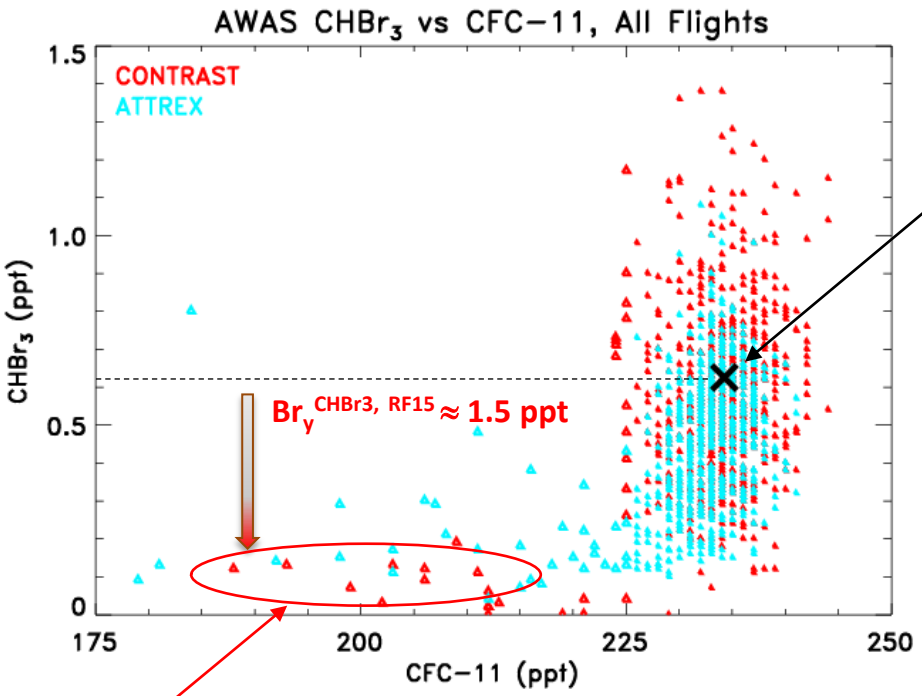
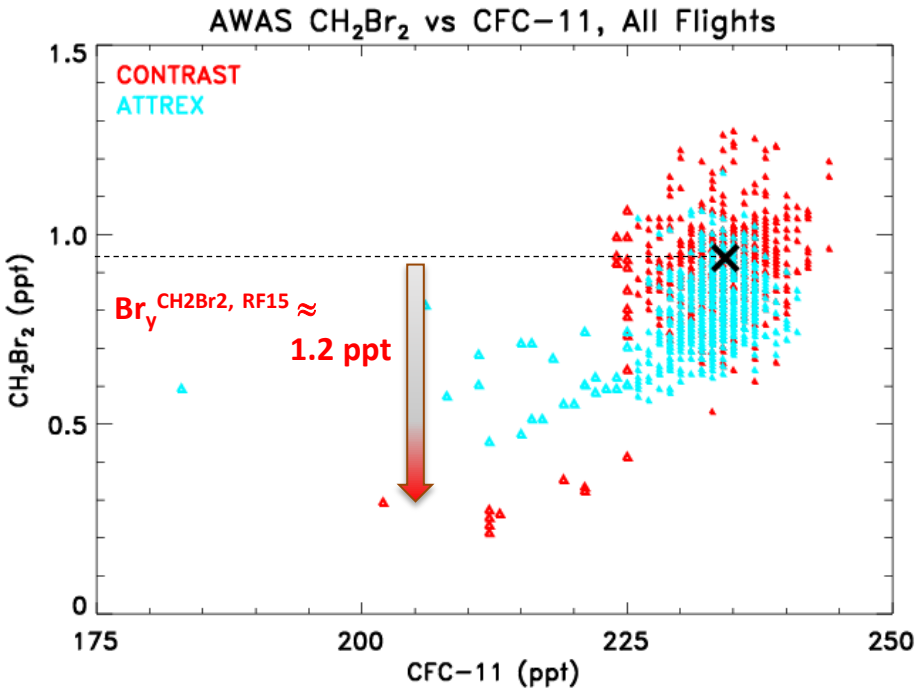


×：Upper Tropical Troposphere mean value, CONTRAST

$Br_y^{CHBr3,\ RF15} \approx 1.5$ ppt

These points collected RF15



$Br_y^{CH2Br2,\ RF15} \approx$ 1.2 ppt

$Br_y^{CHBr3+CH2Br2,\ RF15} \approx 2.7$ ppt

Backup Slide #1

$BrONO_2$ formation:

$BrO + NO_2 + M \Rightarrow k$

$BrONO_2$ loss:

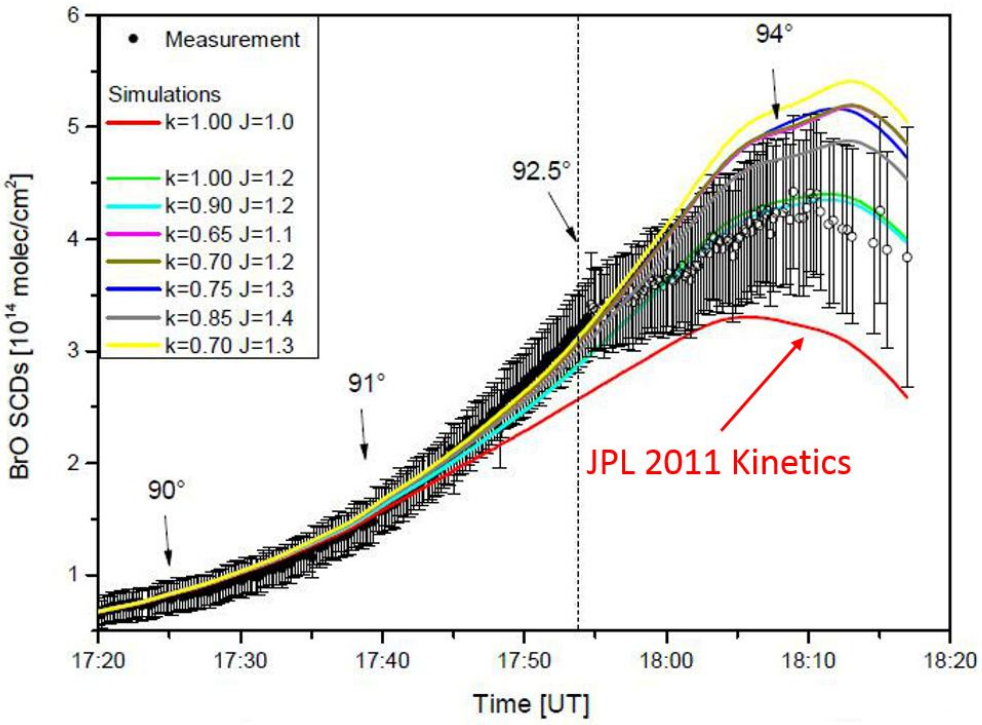
$BrONO_2 + h\nu \Rightarrow J$

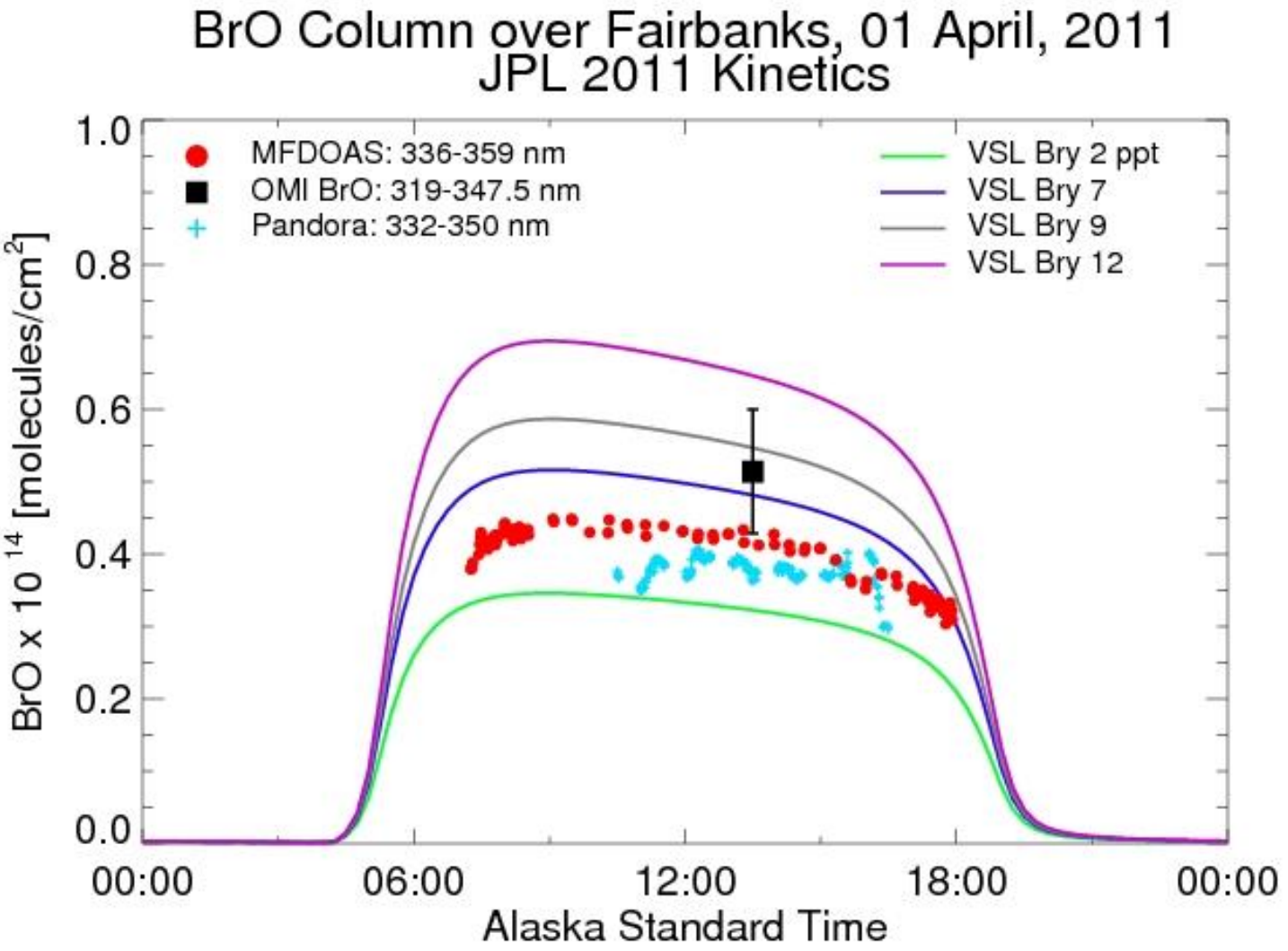
Kreycy et al. (2013) proposed k & J are misrepresented in JPL (2011) and that the ratio **J / k should rise by 27%**

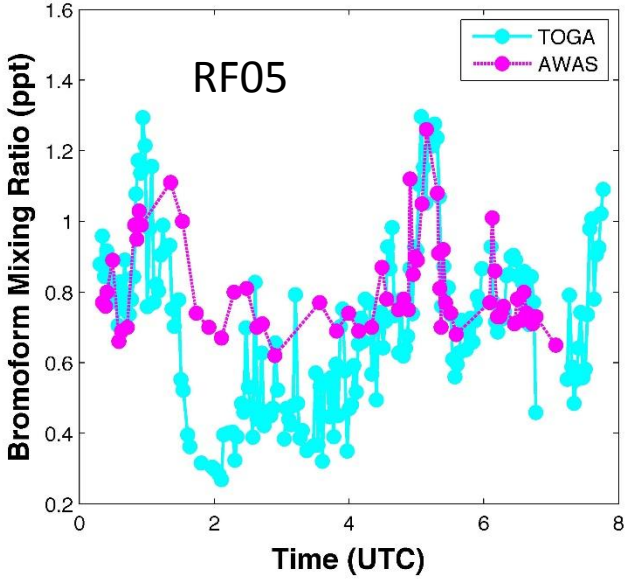
This suggestion ***could*** be consistent with laboratory measurements of:

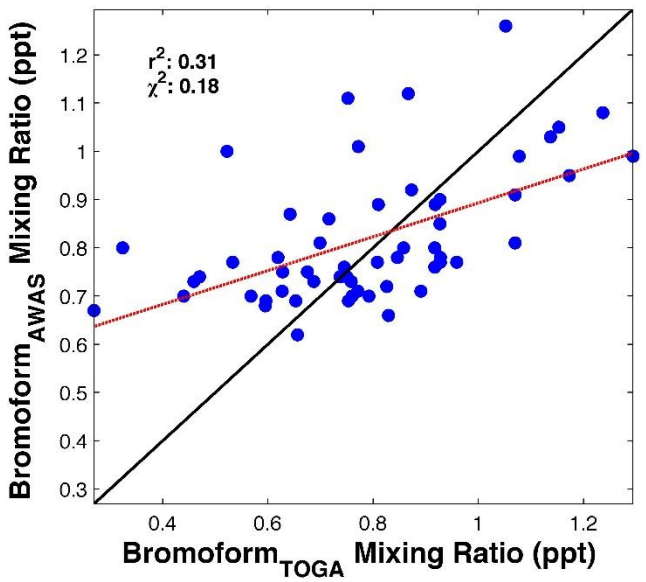
$BrONO_2$ formation rate constant

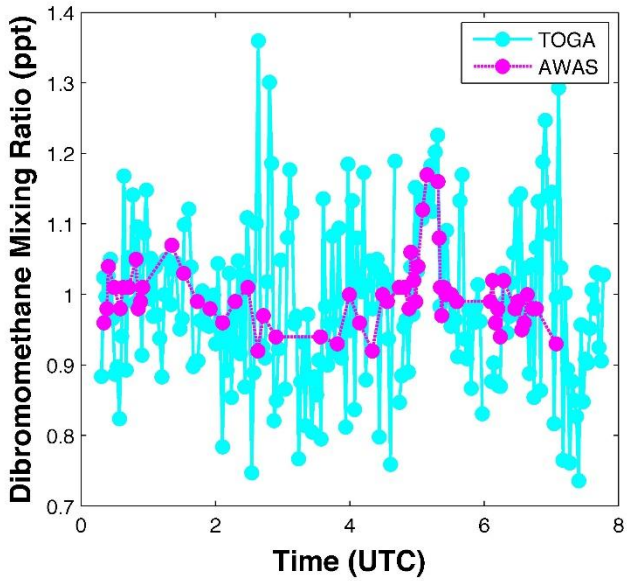
$BrONO_2$ cross section

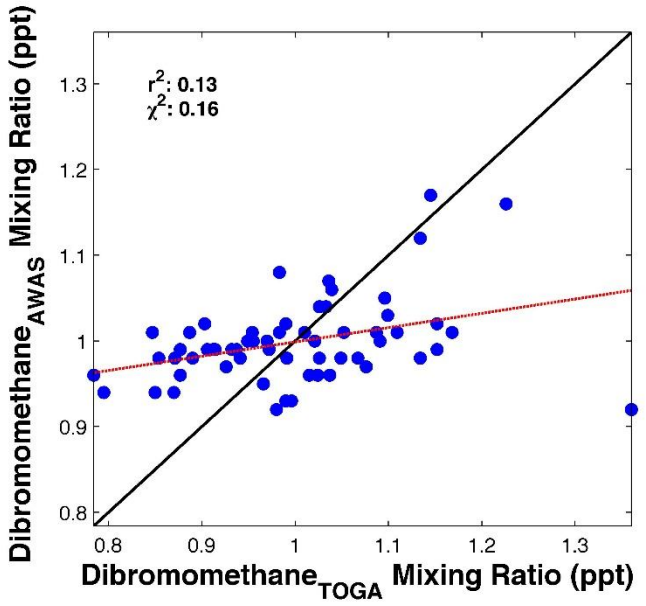


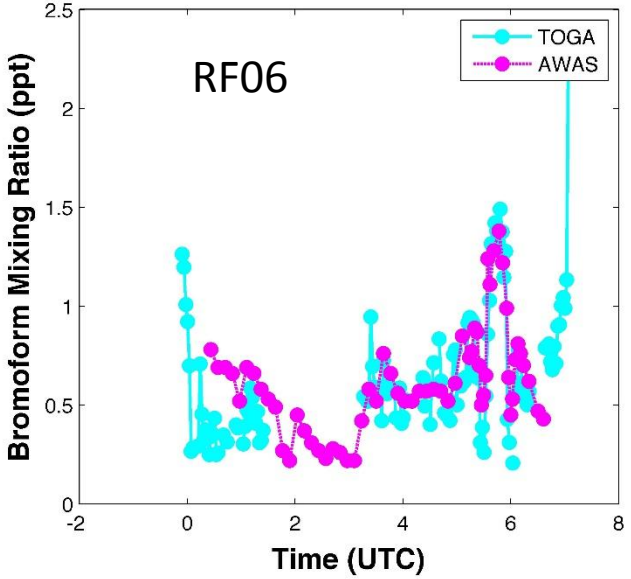

BrO Column over Fairbanks, 01 April, 2011
JPL 2011 Kinetics
MFDOAS: 336-359 nm
OMI BrO: 319-347.5 nm
Pandora: 332-350 nm
VSL Bry 2 ppt
VSL Bry 7
VSL Bry 9
VSL Bry 12
BrO x 10 14 [molecules/cm2]
1.0
0.8
0.6
0.4
0.2
0.0
00:00
06:00
12:00
18:00
00:00
Alaska Standard Time

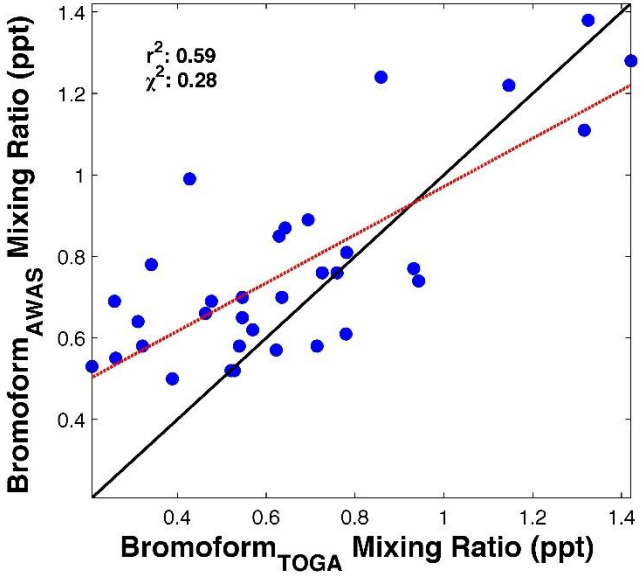

RF05
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

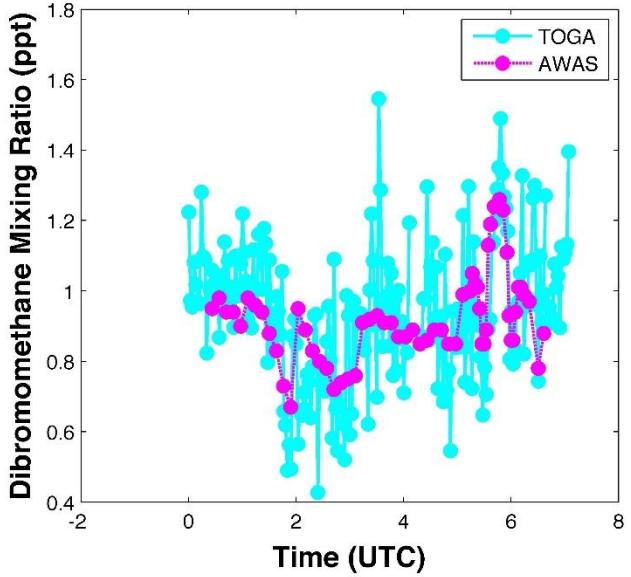

r²: 0.31
χ²: 0.18
Bromoform_AWAS Mixing Ratio (ppt)
Bromoform_TOGA Mixing Ratio (ppt)

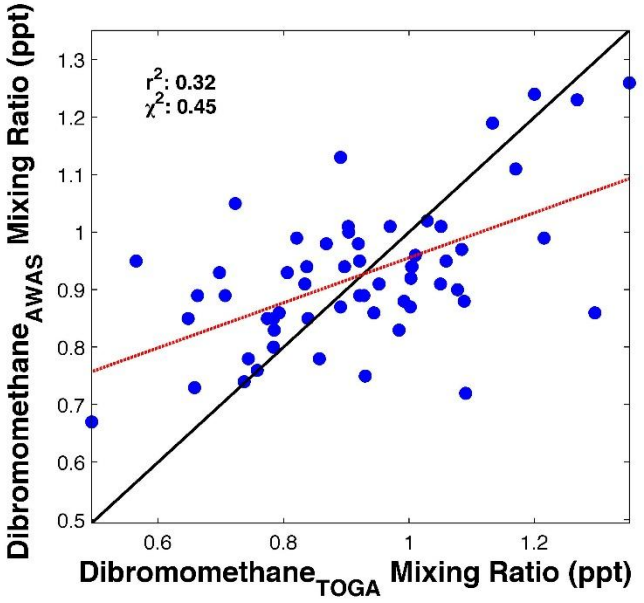

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

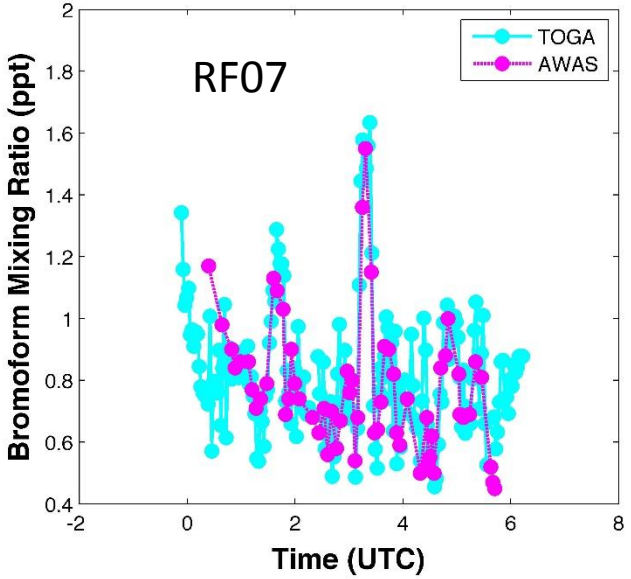

r²: 0.13
χ²: 0.16
Dibromomethane_AWAS Mixing Ratio (ppt)
Dibromomethane_TOGA Mixing Ratio (ppt)

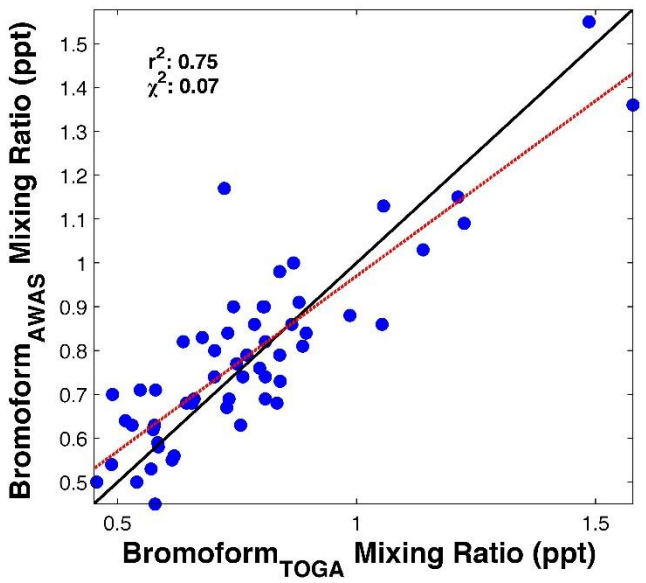

RF06
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

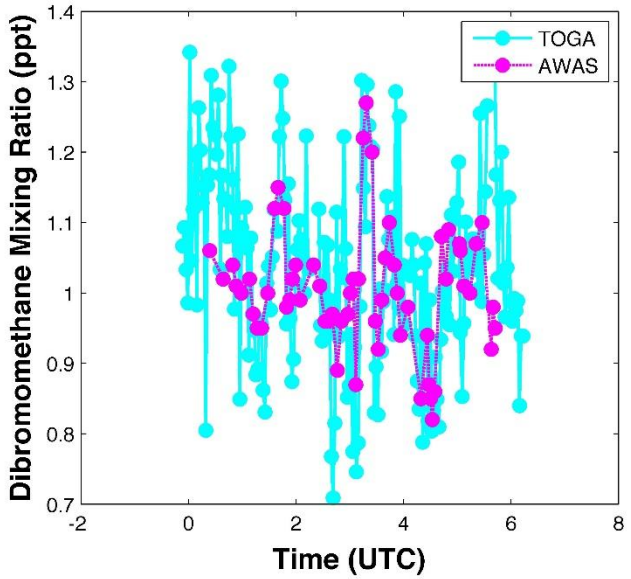

r²: 0.59
χ²: 0.28
Bromoform_AWAS Mixing Ratio (ppt)
Bromoform_TOGA Mixing Ratio (ppt)

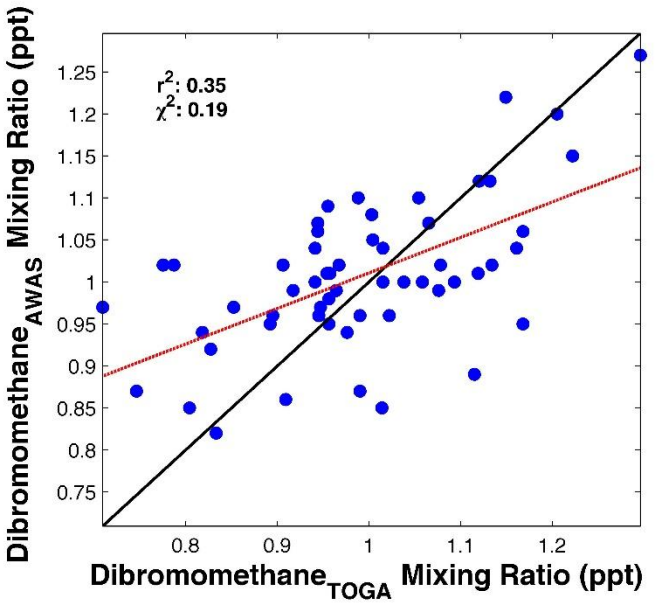

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

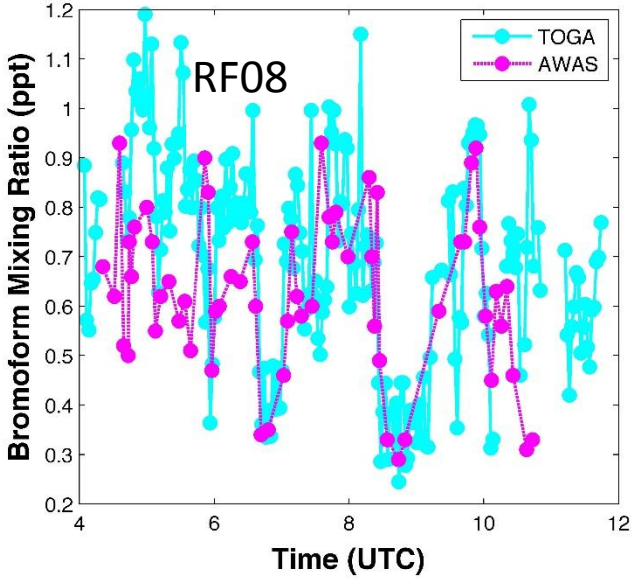

r²: 0.32
χ²: 0.45
Dibromomethane_AWAS Mixing Ratio (ppt)
Dibromomethane_TOGA Mixing Ratio (ppt)

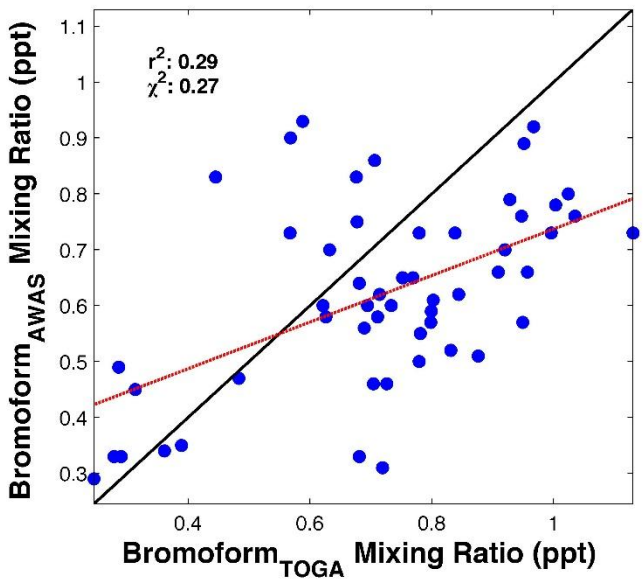

RF07
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

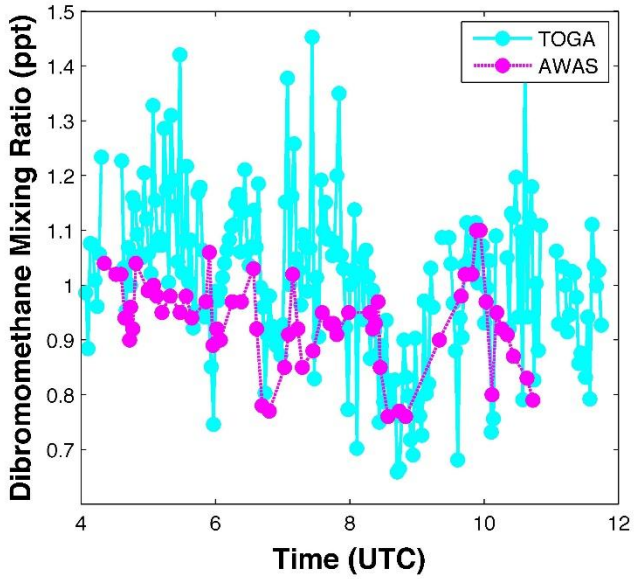

r2: 0.75
χ2: 0.07
Bromoform AWAS Mixing Ratio (ppt)
Bromoform TOGA Mixing Ratio (ppt)

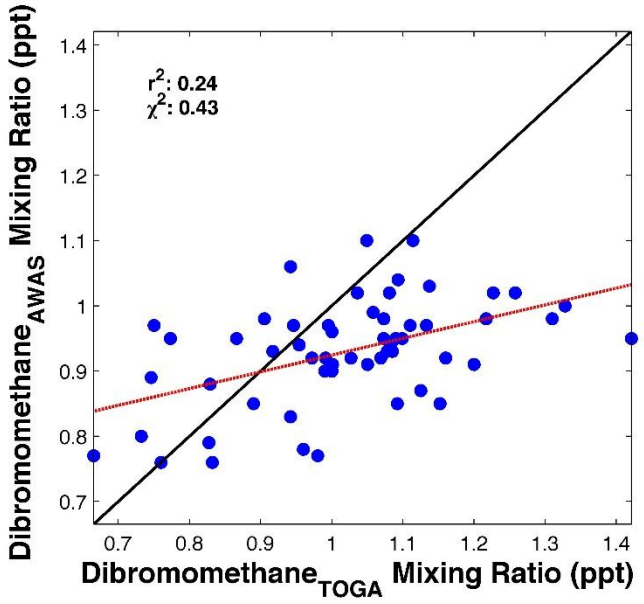

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

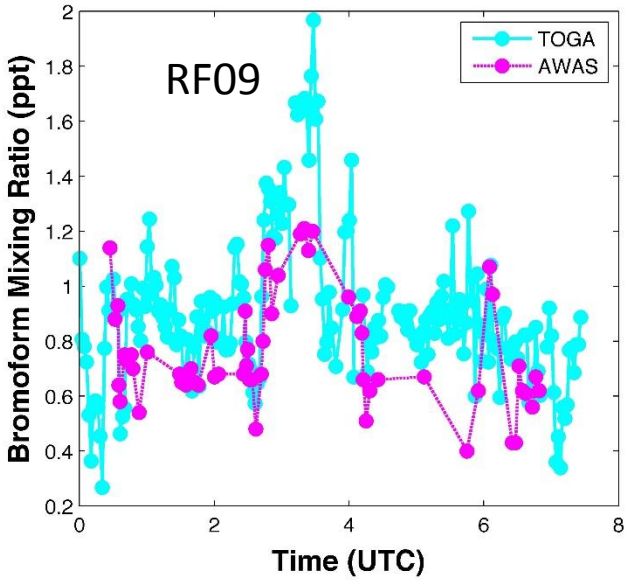

r2: 0.35
χ2: 0.19
Dibromomethane AWAS Mixing Ratio (ppt)
Dibromomethane TOGA Mixing Ratio (ppt)

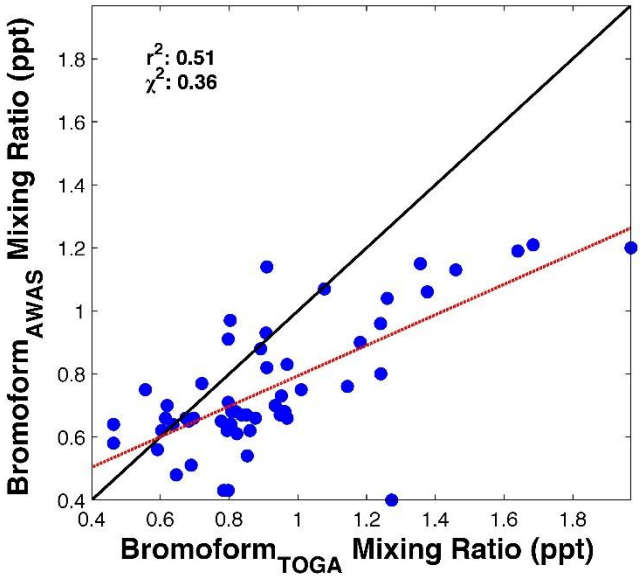

RF08
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

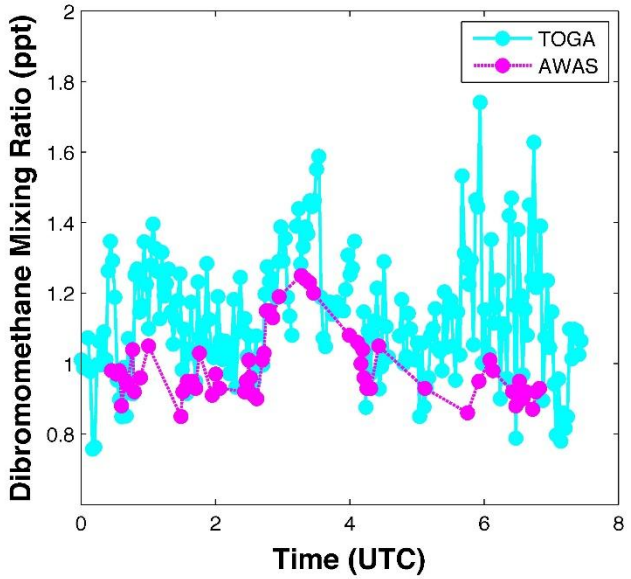

r2: 0.29
χ2: 0.27
BromoformAWAS Mixing Ratio (ppt)
BromoformTOGA Mixing Ratio (ppt)

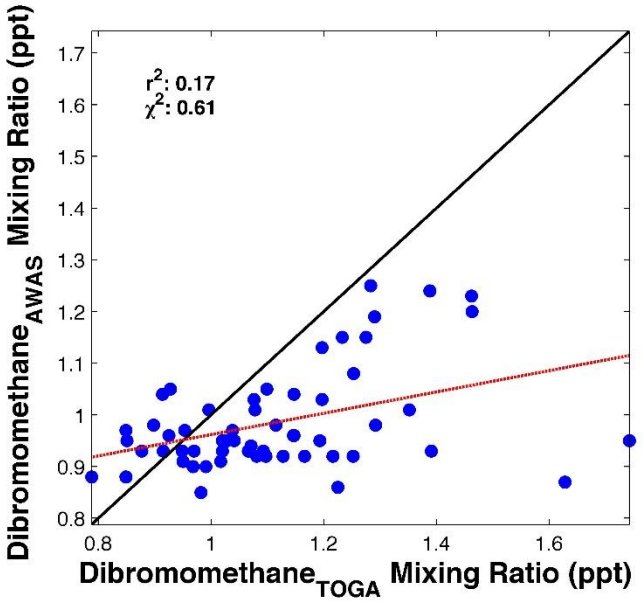

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

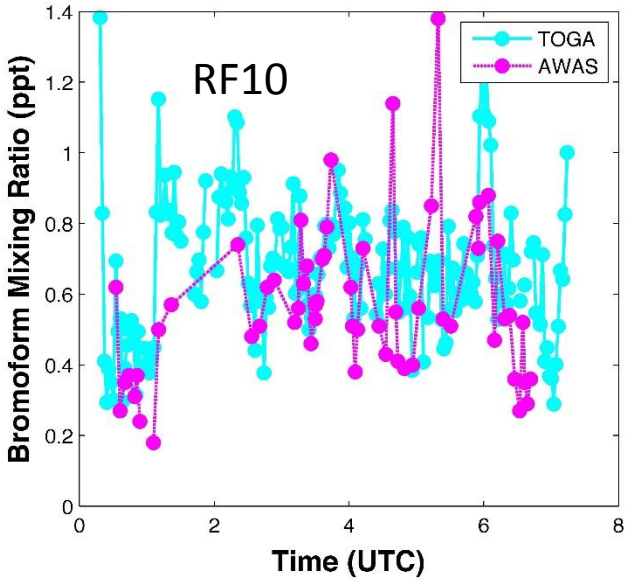

r2: 0.24
χ2: 0.43
DibromomethaneAWAS Mixing Ratio (ppt)
DibromomethaneTOGA Mixing Ratio (ppt)

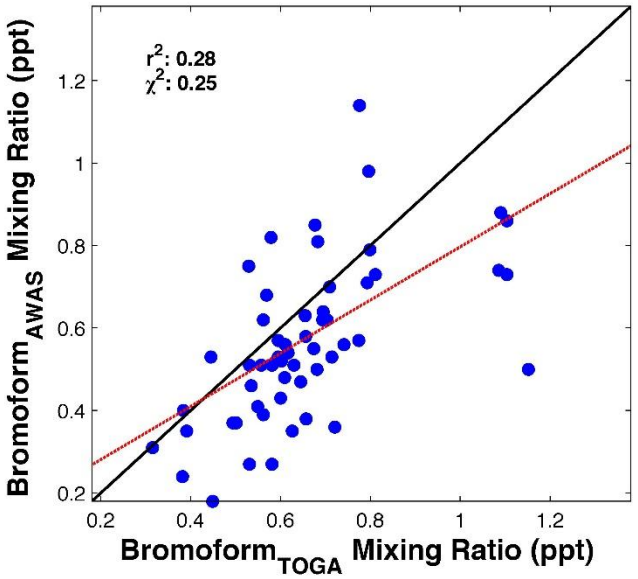

RF09
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

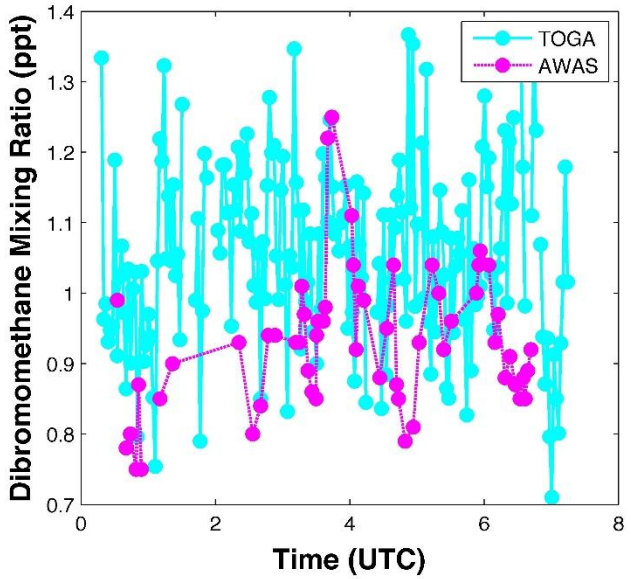

r²: 0.51
χ²: 0.36
Bromoform_AWAS Mixing Ratio (ppt)
Bromoform_TOGA Mixing Ratio (ppt)

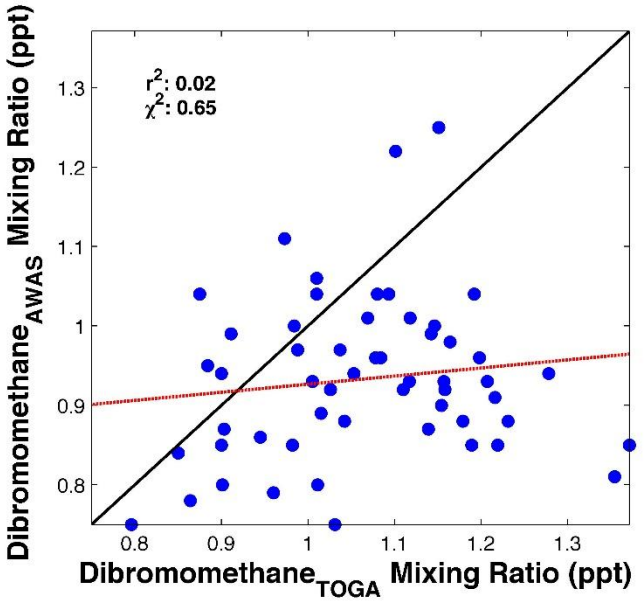

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

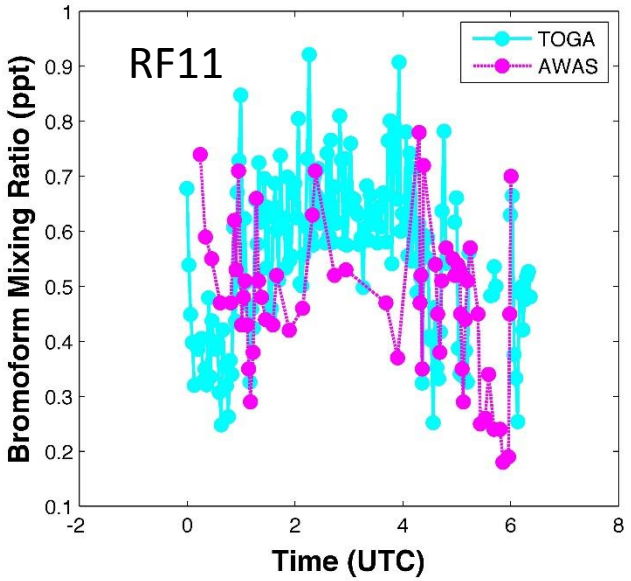

r²: 0.17
χ²: 0.61
Dibromomethane_AWAS Mixing Ratio (ppt)
Dibromomethane_TOGA Mixing Ratio (ppt)

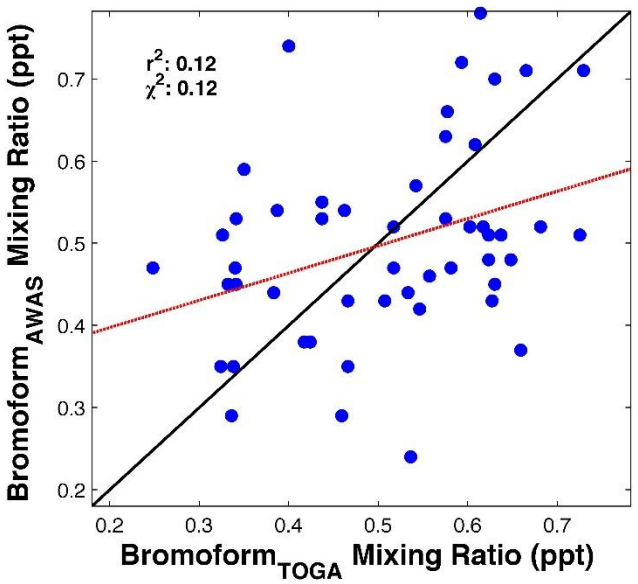

RF10
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

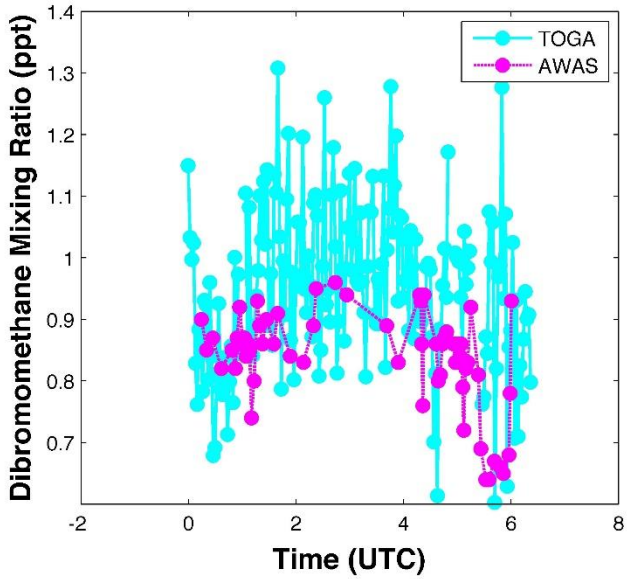

r²: 0.28
χ²: 0.25
Bromoform_AWAS Mixing Ratio (ppt)
Bromoform_TOGA Mixing Ratio (ppt)

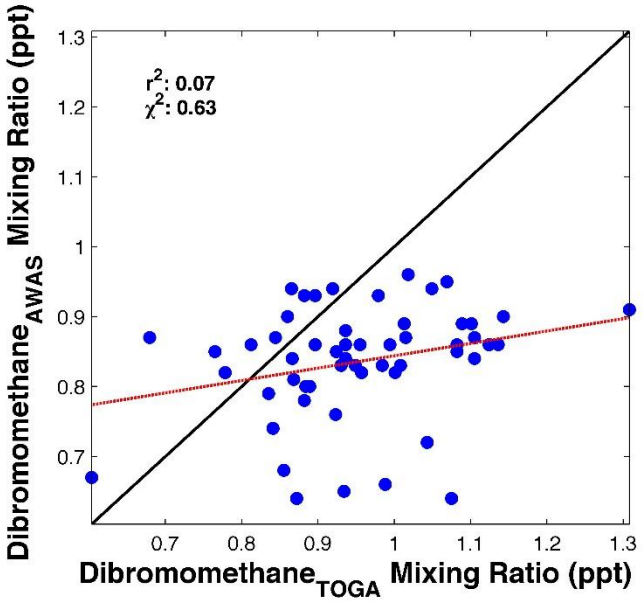

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

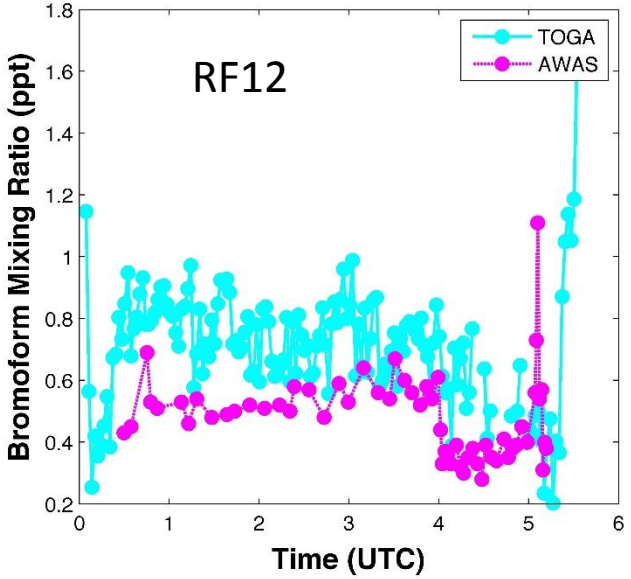

r²: 0.02
χ²: 0.65
Dibromomethane_AWAS Mixing Ratio (ppt)
Dibromomethane_TOGA Mixing Ratio (ppt)

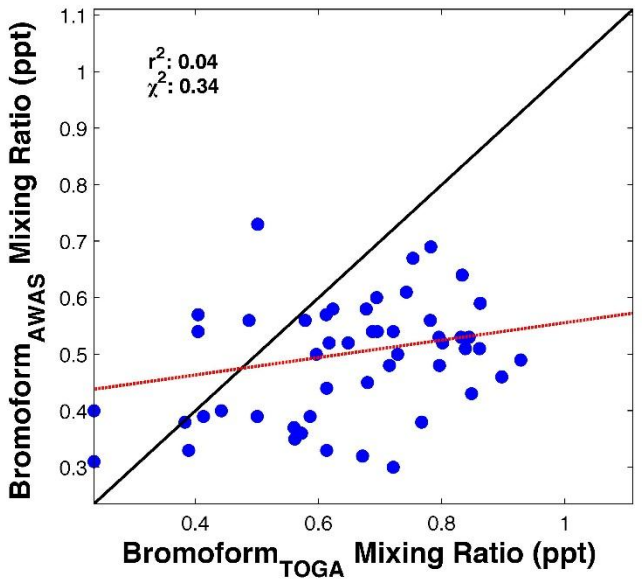

RF11
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

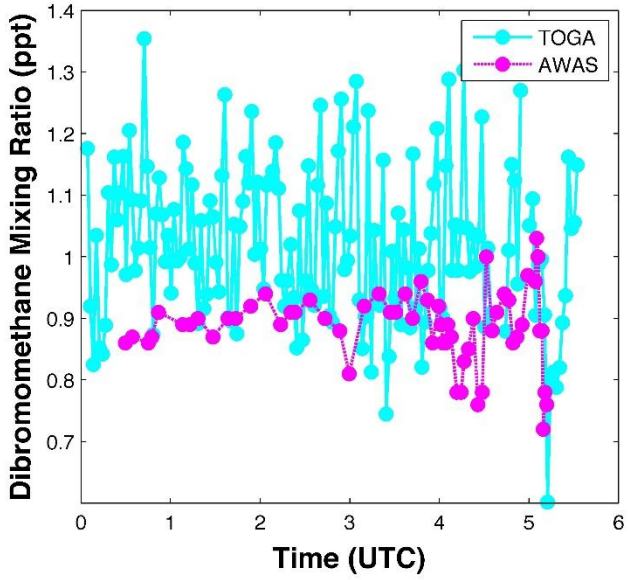

r²: 0.12
χ²: 0.12
Bromoform_AWAS Mixing Ratio (ppt)
Bromoform_TOGA Mixing Ratio (ppt)

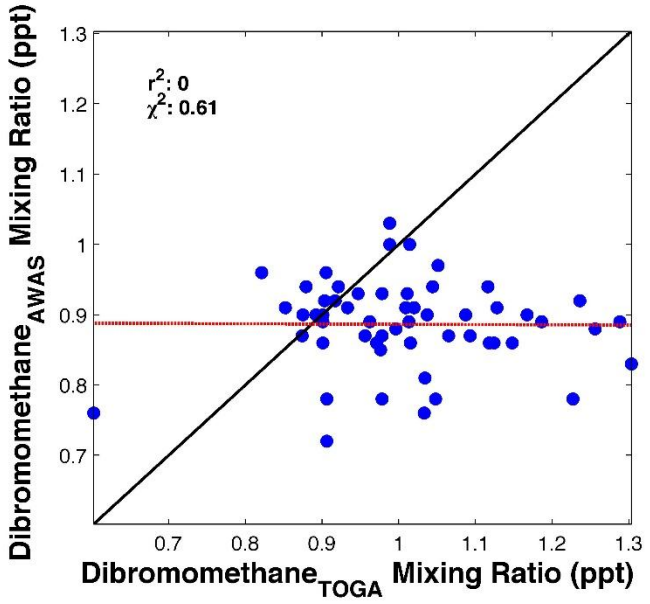

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

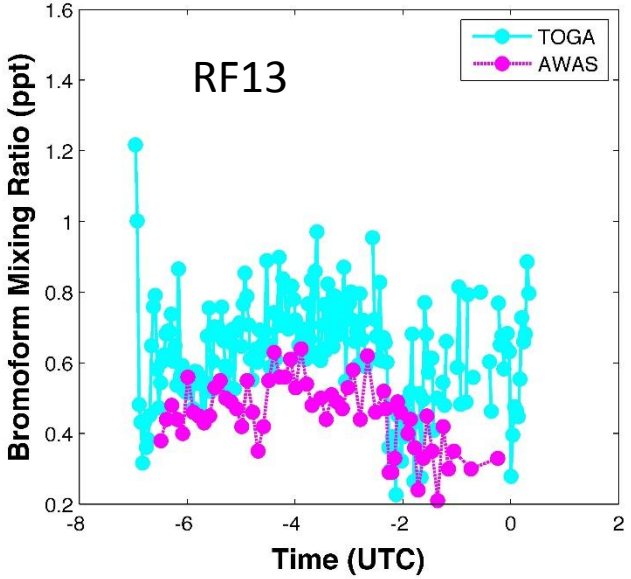

r²: 0.07
χ²: 0.63
Dibromomethane_AWAS Mixing Ratio (ppt)
Dibromomethane_TOGA Mixing Ratio (ppt)

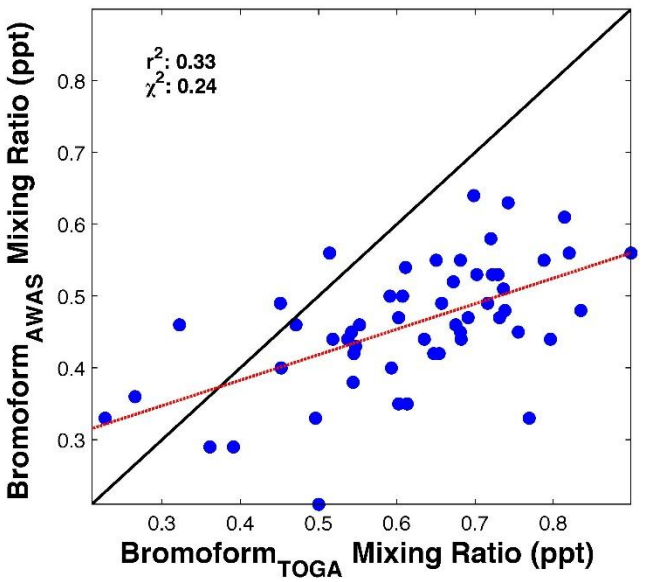

RF12
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

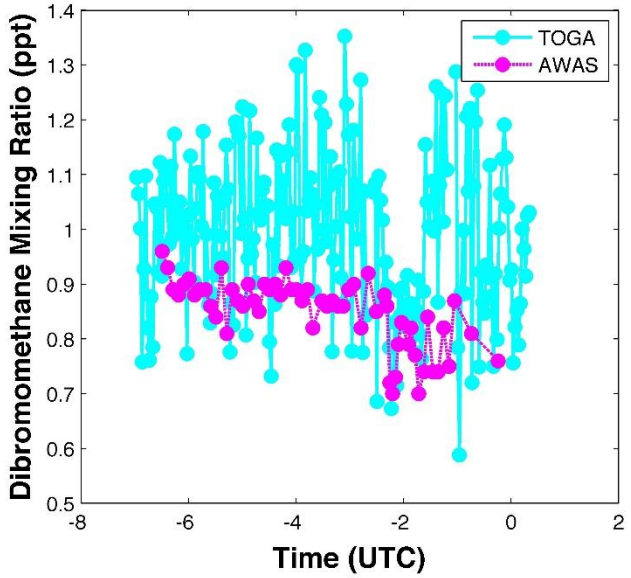

r2: 0.04
χ2: 0.34
Bromoform AWAS Mixing Ratio (ppt)
Bromoform TOGA Mixing Ratio (ppt)

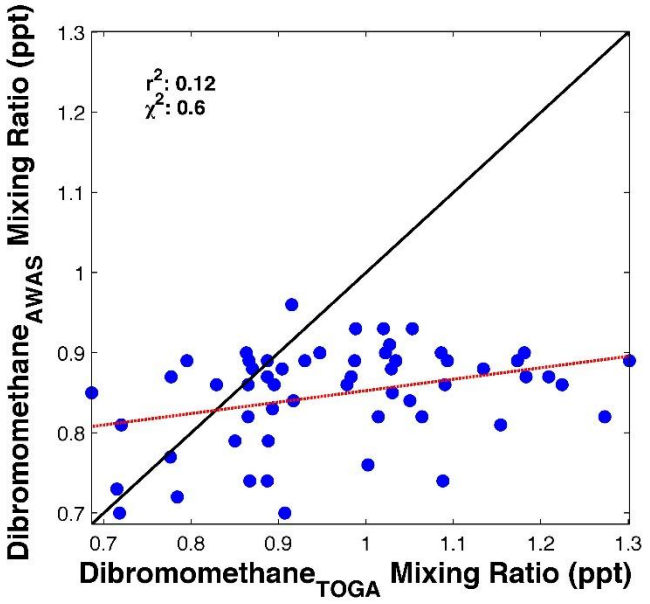

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

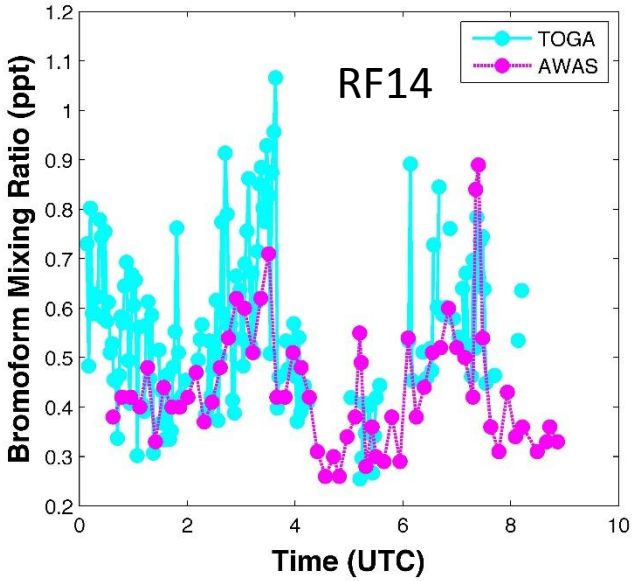

r2: 0
χ2: 0.61
Dibromomethane AWAS Mixing Ratio (ppt)
Dibromomethane TOGA Mixing Ratio (ppt)

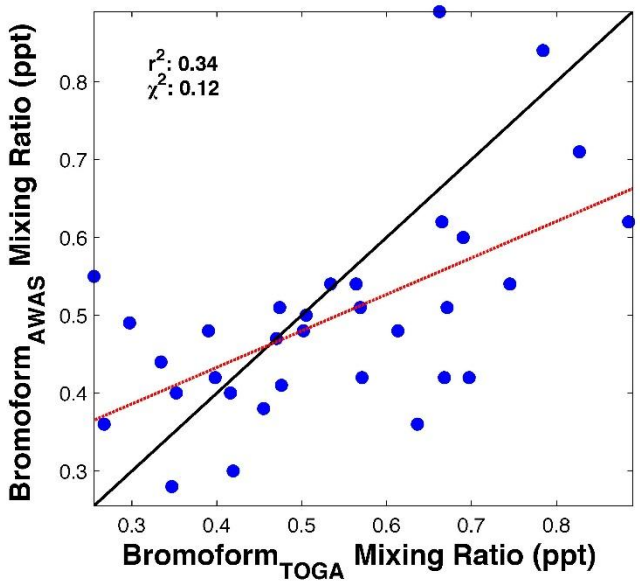

RF13
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

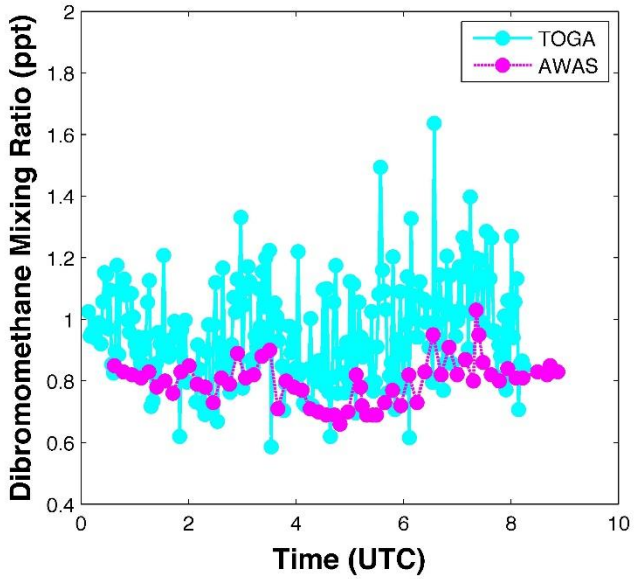

r2: 0.33
χ2: 0.24
BromoformAWAS Mixing Ratio (ppt)
BromoformTOGA Mixing Ratio (ppt)

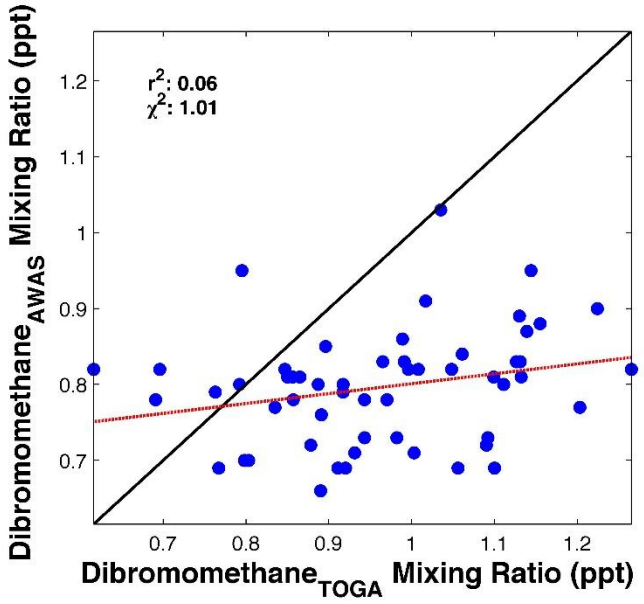

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)

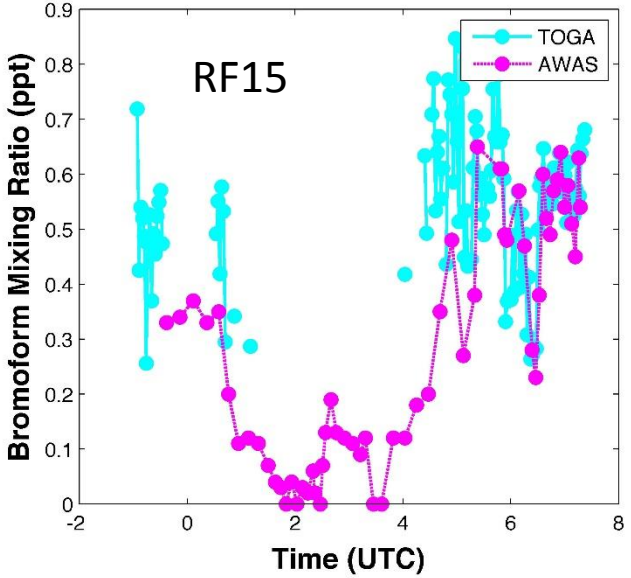

r2: 0.12
χ2: 0.6
DibromomethaneAWAS Mixing Ratio (ppt)
DibromomethaneTOGA Mixing Ratio (ppt)

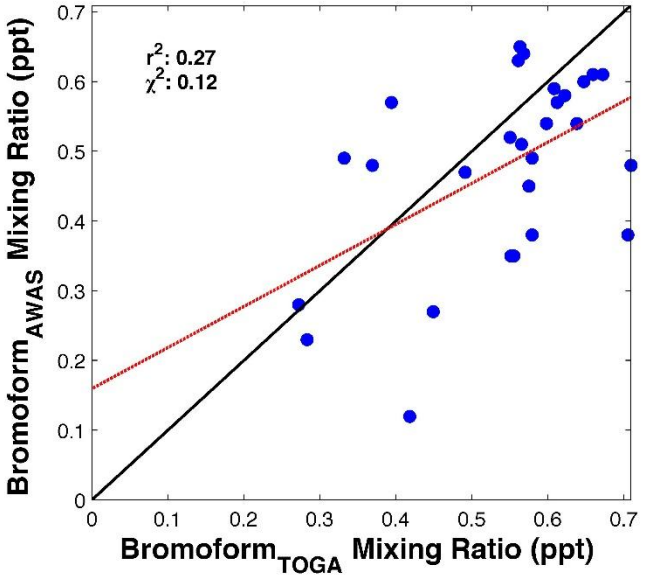

RF14
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)

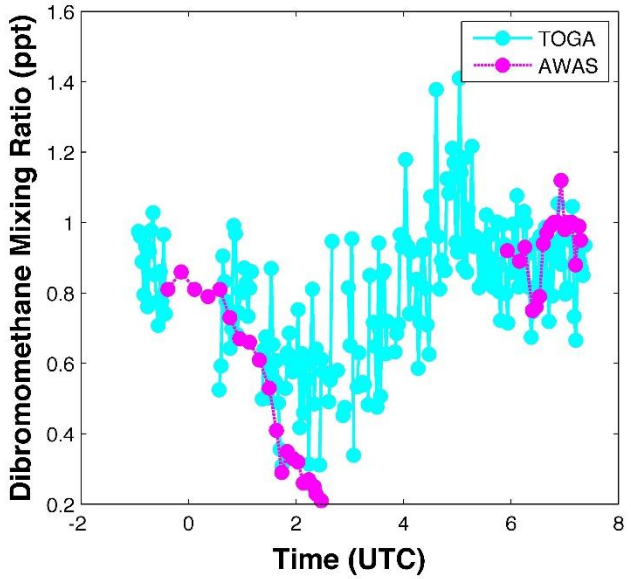

r2: 0.34
χ2: 0.12
BromoformAWAS Mixing Ratio (ppt)
BromoformTOGA Mixing Ratio (ppt)

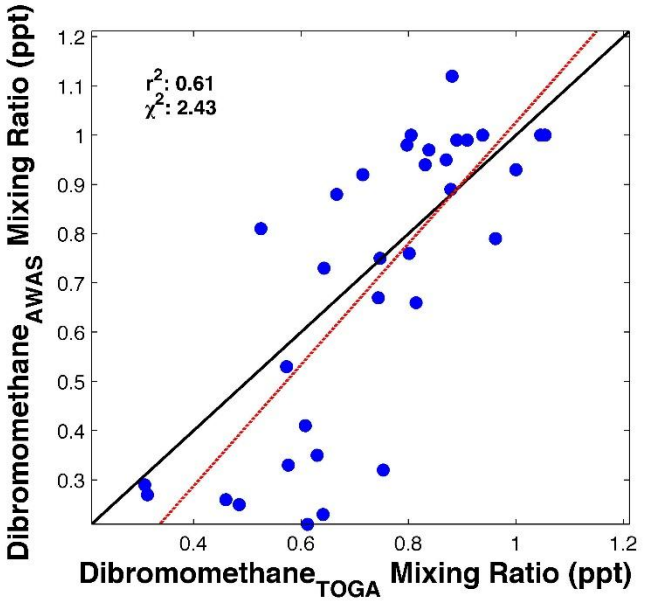

TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)


r2: 0.06
χ2: 1.01
DibromomethaneAWAS Mixing Ratio (ppt)
DibromomethaneTOGA Mixing Ratio (ppt)


RF15
TOGA
AWAS
Bromoform Mixing Ratio (ppt)
Time (UTC)


r²: 0.27
χ²: 0.12
Bromoform_AWAS Mixing Ratio (ppt)
Bromoform_TOGA Mixing Ratio (ppt)


TOGA
AWAS
Dibromomethane Mixing Ratio (ppt)
Time (UTC)


r²: 0.61
χ²: 2.43
Dibromomethane_AWAS Mixing Ratio (ppt)
Dibromomethane_TOGA Mixing Ratio (ppt)