OMI BrO: Implications for VSL Br_y & Tropospheric Bromine Loading

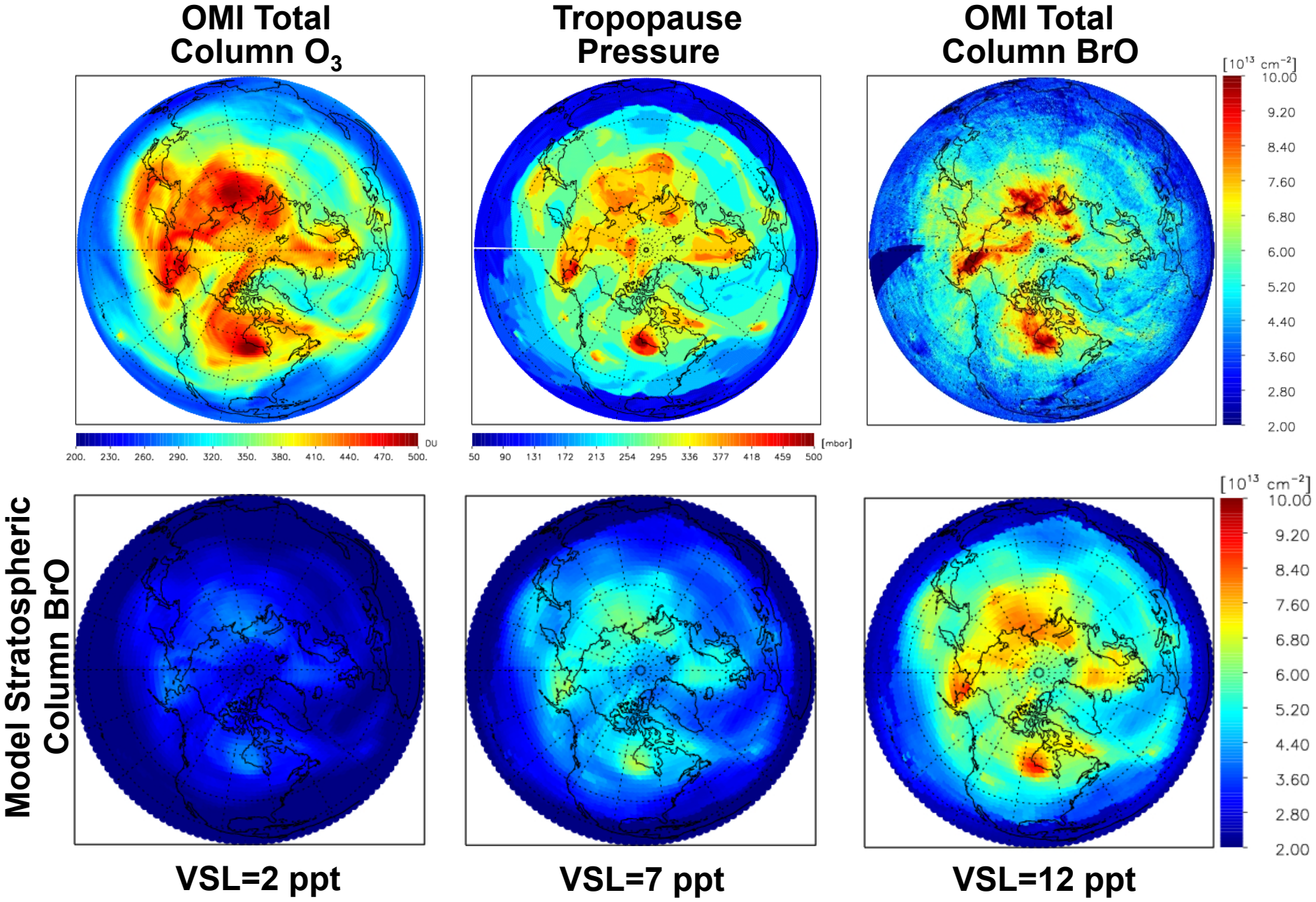
R. Salawitch, P. Wales, T. Canty, J. Nicely, D. Anderson, R. Suleiman, K. Chance, R. McPeters, P. K. Bhartia, T. Kurosu, G. Mount, E. Spinei, J. Herman, A. Cede, N. Abuhassan, W. Simpson, D. Donohue, B. Johnson, D. Kinnison, S. Tilmes, L. Pan, E. Atlas, S. Honomichl, V. Donets, S. Schauffler, R. Lueb, M. Navarro, D. Chen, G. Huey, D. Tanner, S. Hall, K. Ullmann, G. Wolfe, T. Hanisco, R. P. Fernandez, J.-F. Lamarque, A. Saiz-Lopez

Supply of Stratospheric Bromine by Very Short Lived Substances (VSLs)

- Important because without this source, models underestimate:
  - dO_3/dt in polar vortex (Frieler et al., 2006 … Oman & Douglass, 2014)
  - O_3 depletion after major volcanic eruptions (Salawitch et al., 2005 … Oman & Douglass, 2014)
- VSL halocarbons "tipping point" for response of surface UV radiation to geo-engineering of climate via stratospheric sulfate injection (Tilmes et al., 2012)
- Literal interpretation of satellite BrO has led to the inference of a global, ubiquitous, 1 to 2 ppt of tropospheric BrO which, if present, has important implications for the budget of tropospheric ozone and the oxidizing capacity of the troposphere (Ordóñez et al., 2012; Saiz-Lopez et al., 2012)

5 Apr 2008

Salawitch et al., 2010



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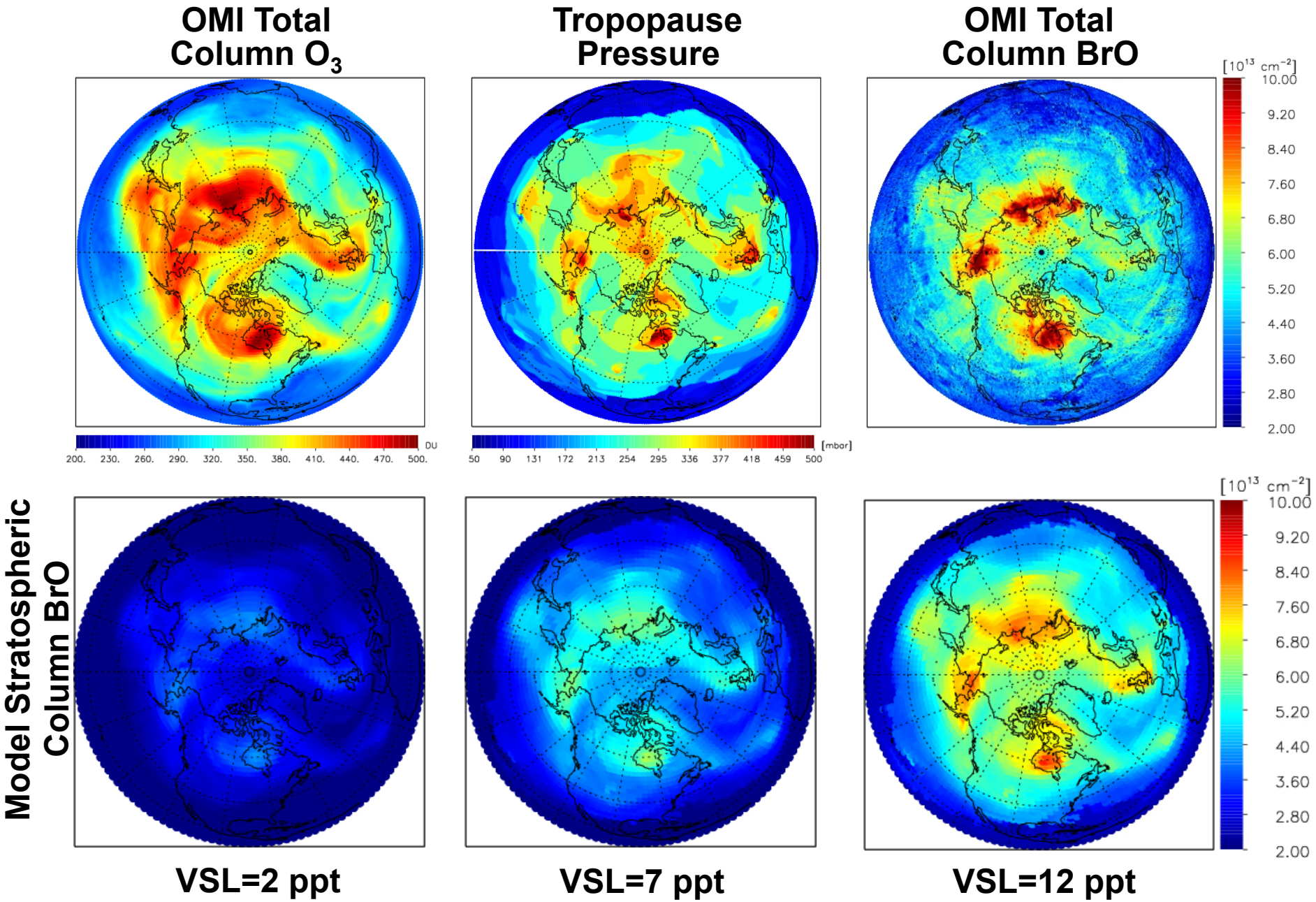

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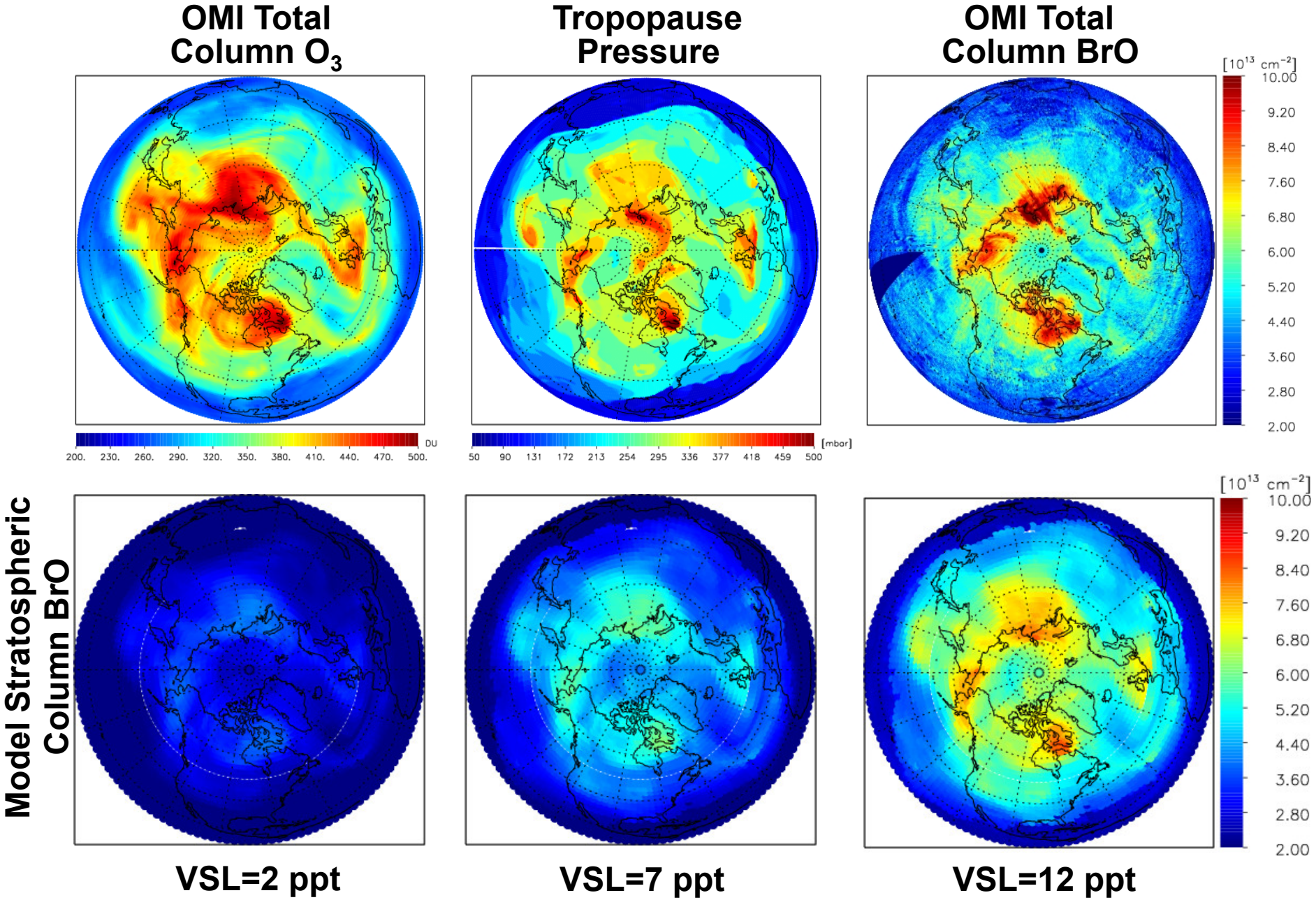

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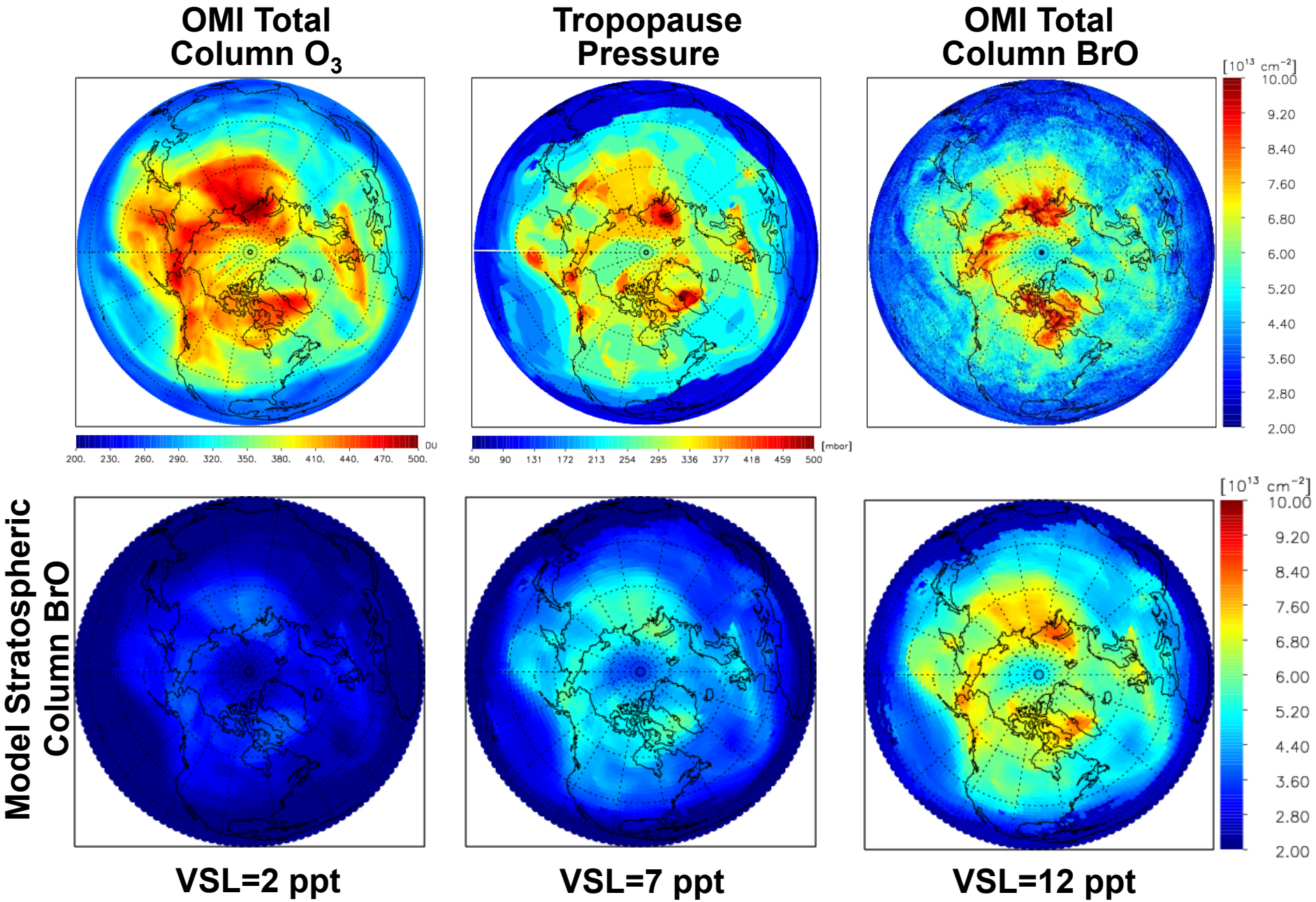

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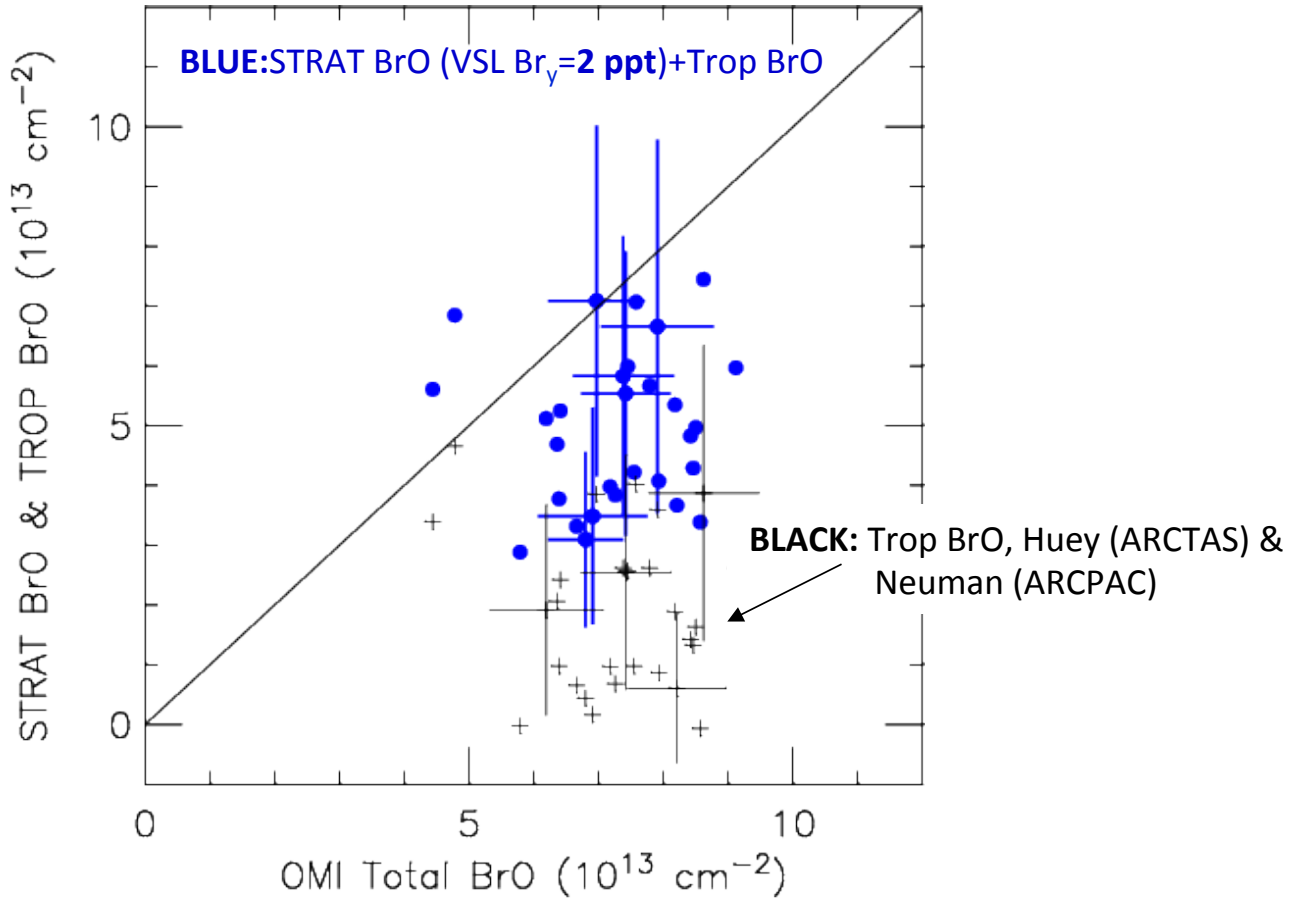
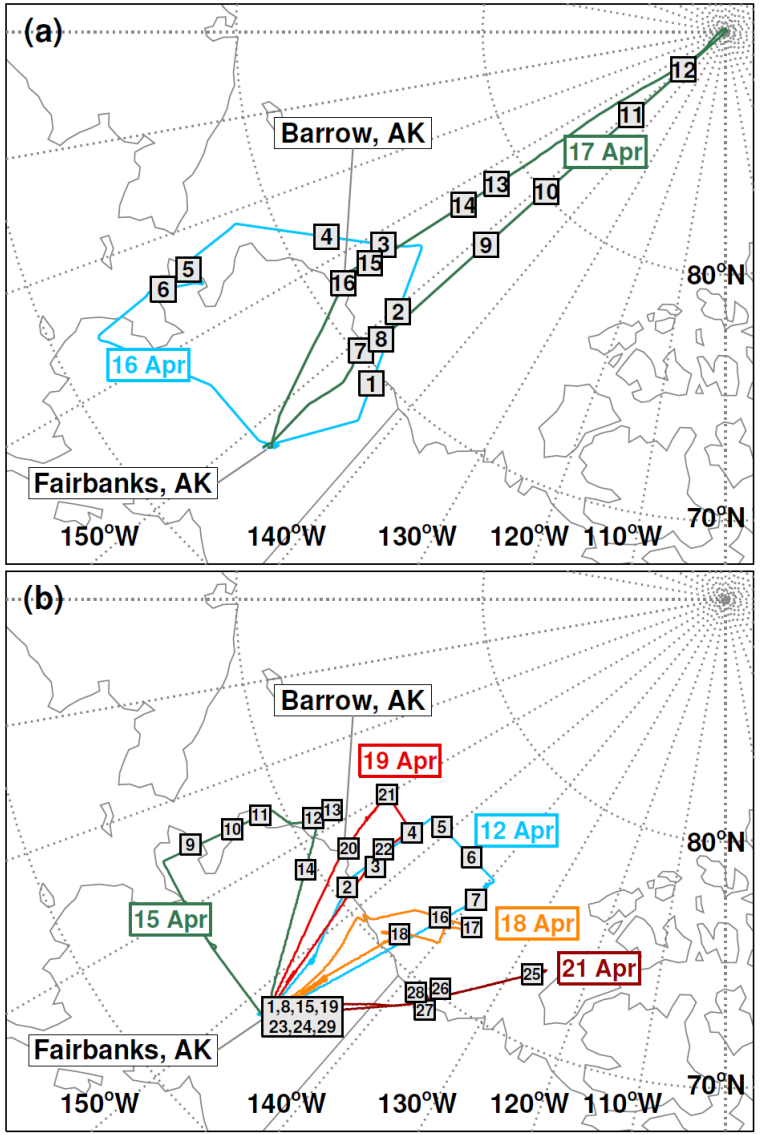
$$\frac{\text{STRAT BrO (model, fn of VSL } Br_y\text{) + Trop BrO (Aircraft Data)}}{\text{OMI Total Column BrO}}$$

Trop BrO based on 29 profiles conducted during ARCTAS & ARCPAC





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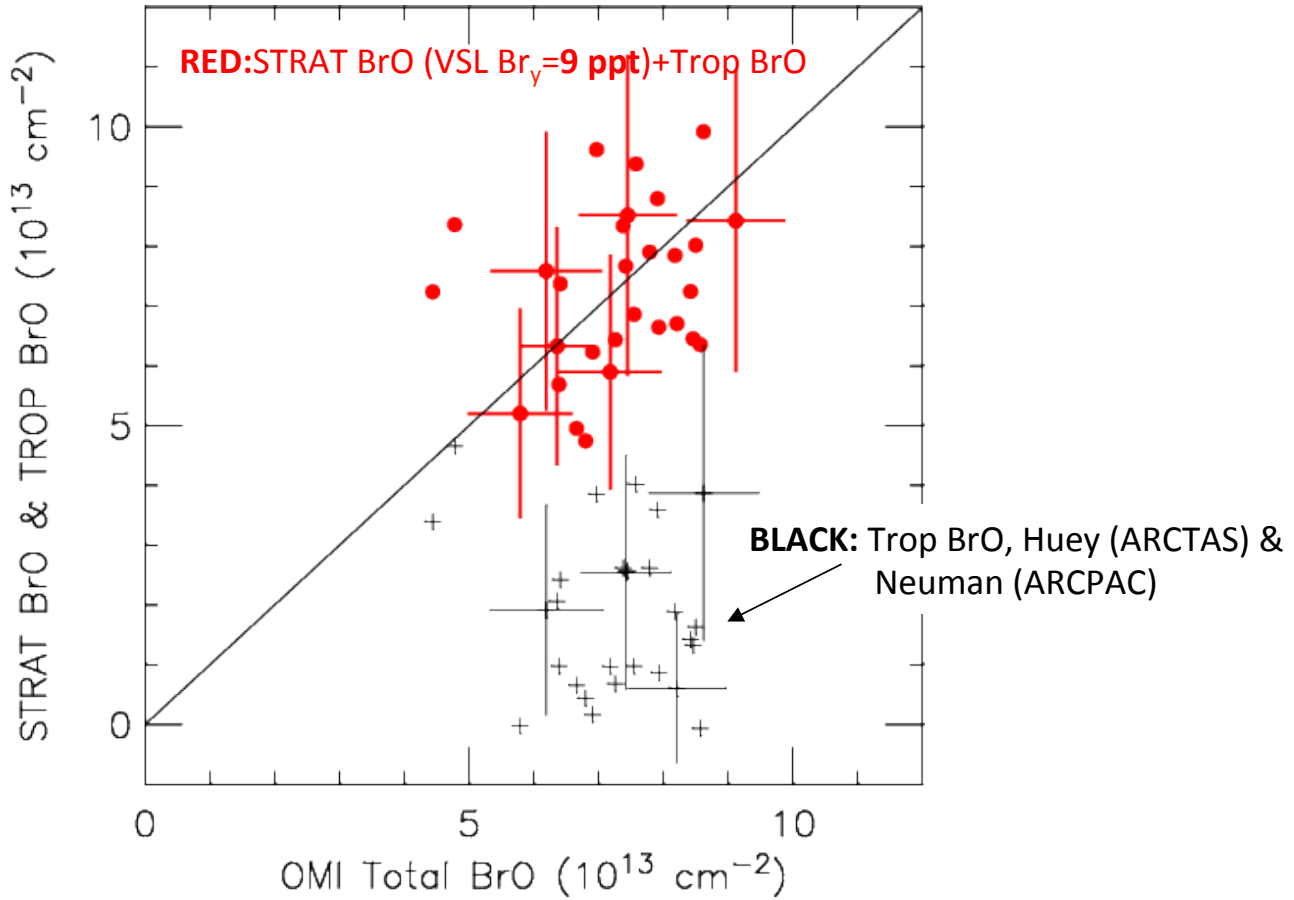

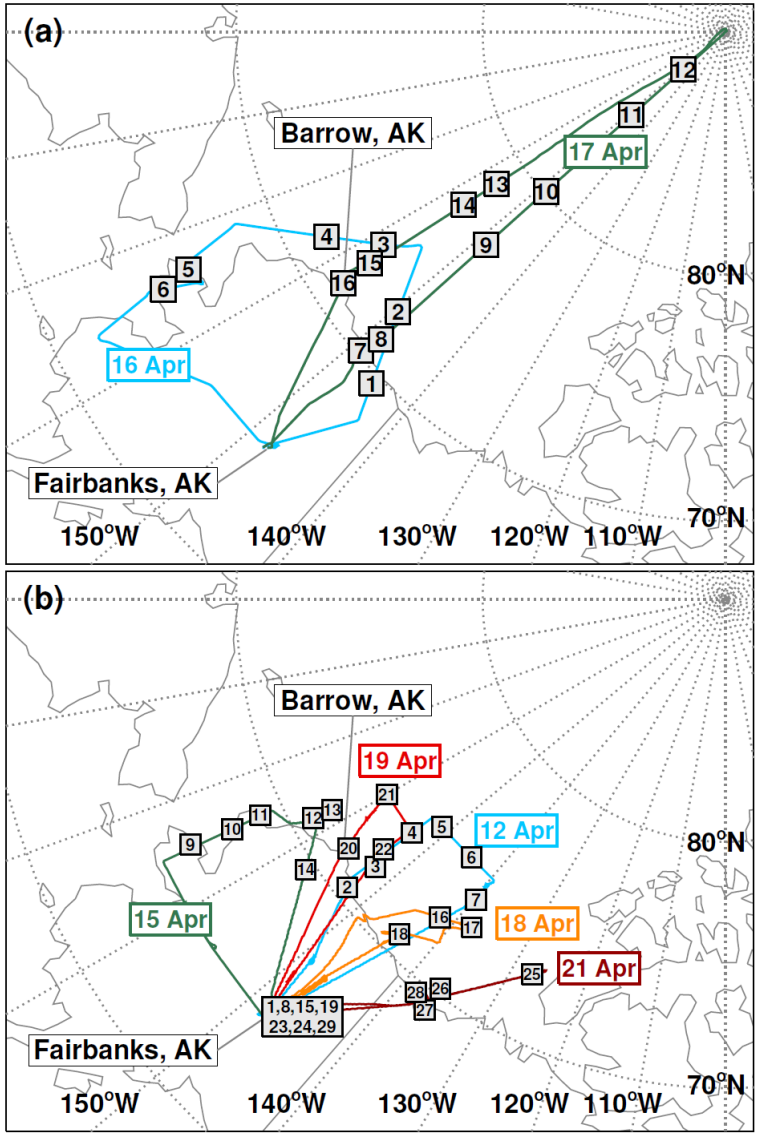

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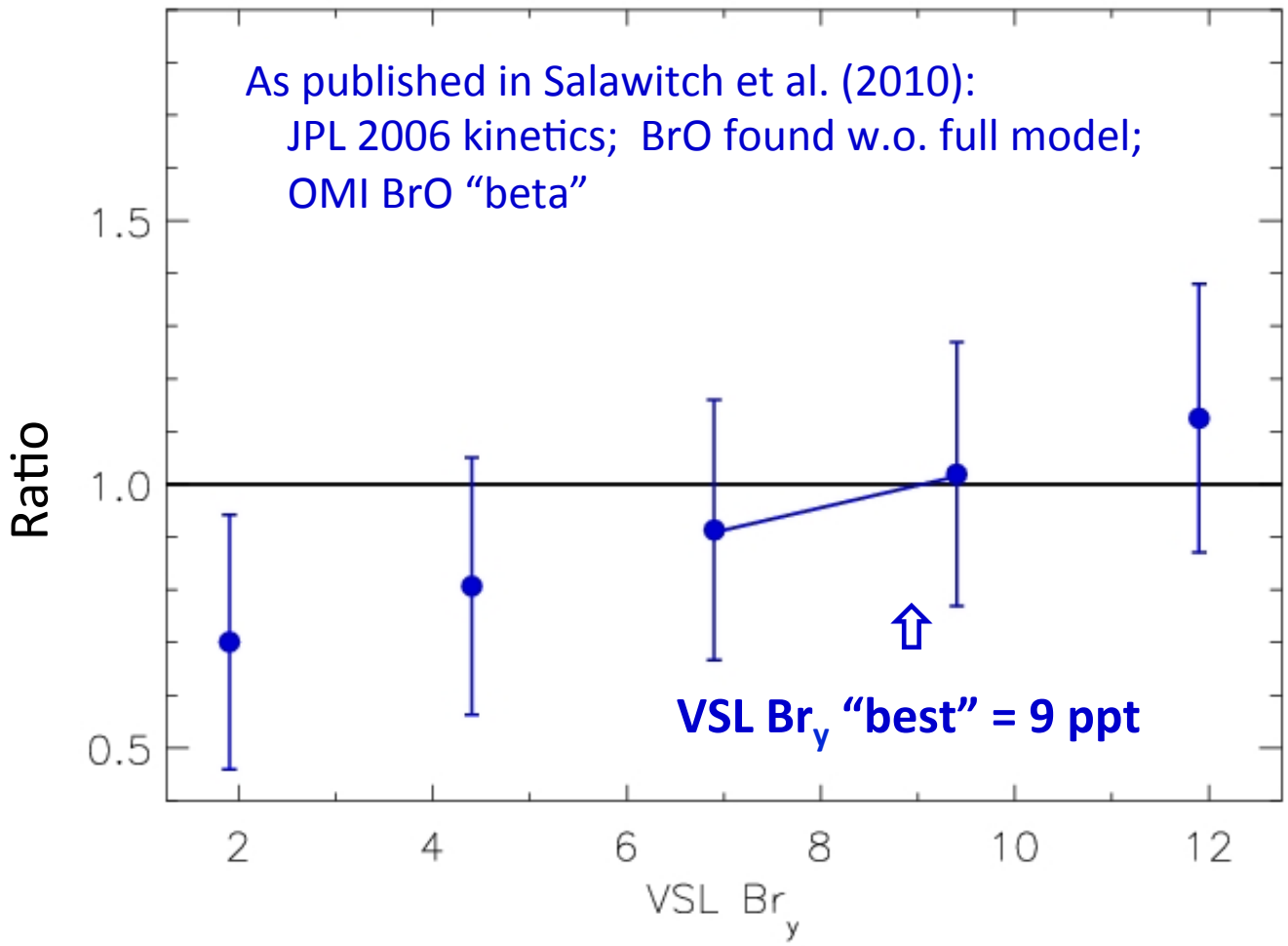

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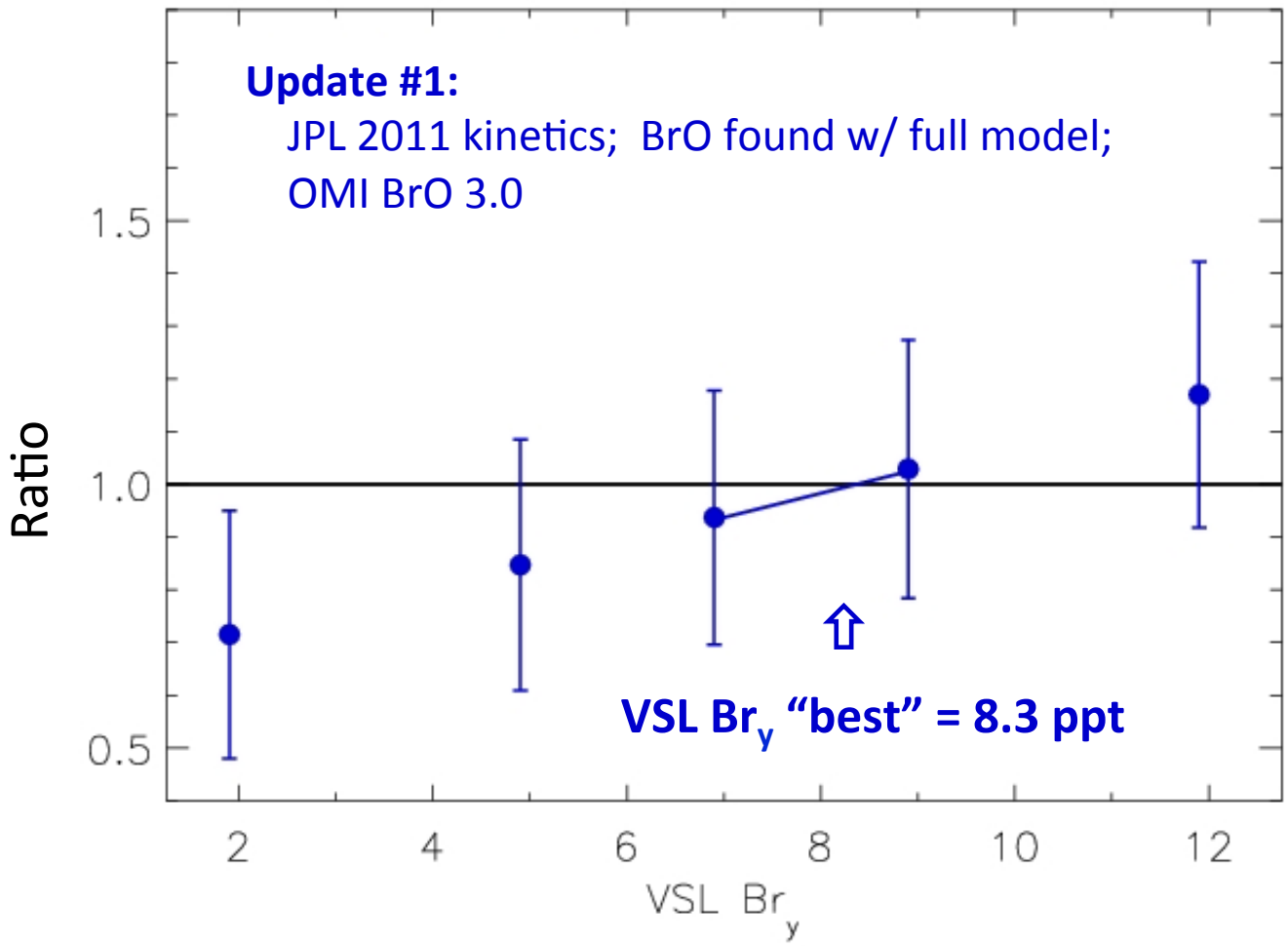
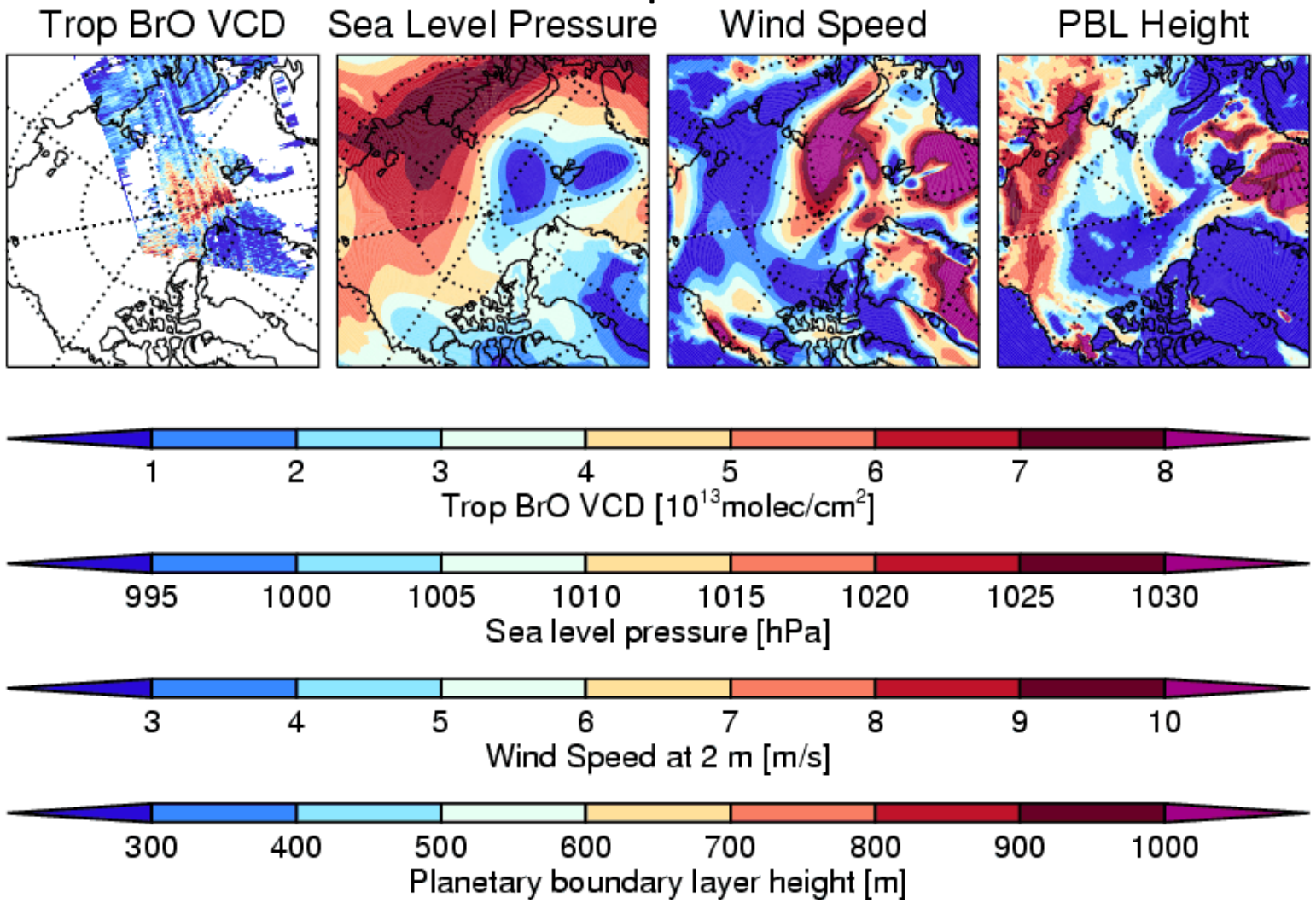


Supply of Stratospheric Bromine by Very Short Lived Substances (VSLs)

- Proper interpretation of "bromine explosion" contingent on ability to accurately distinguish stratospheric and tropospheric contribution to total column BrO (Choi et al., 2012; Liao et al., 2012)

16 April 2008



Choi et al., 2012

OMI BrO Validation Campaign

Fairbanks, Alaska, 24 March to 9 April 2011

BrO Instruments

- WSU MFDOAS – direct sun , zenith (Mount, Spinei)
- GSFC PANDORA – direct sun, zenith (Herman)
- U Alaska mini MAXDOAS – zenith (Simpson, Donohue)

All instrument teams retrieve BrO, O_3, NO_2, OClO, and HCHO

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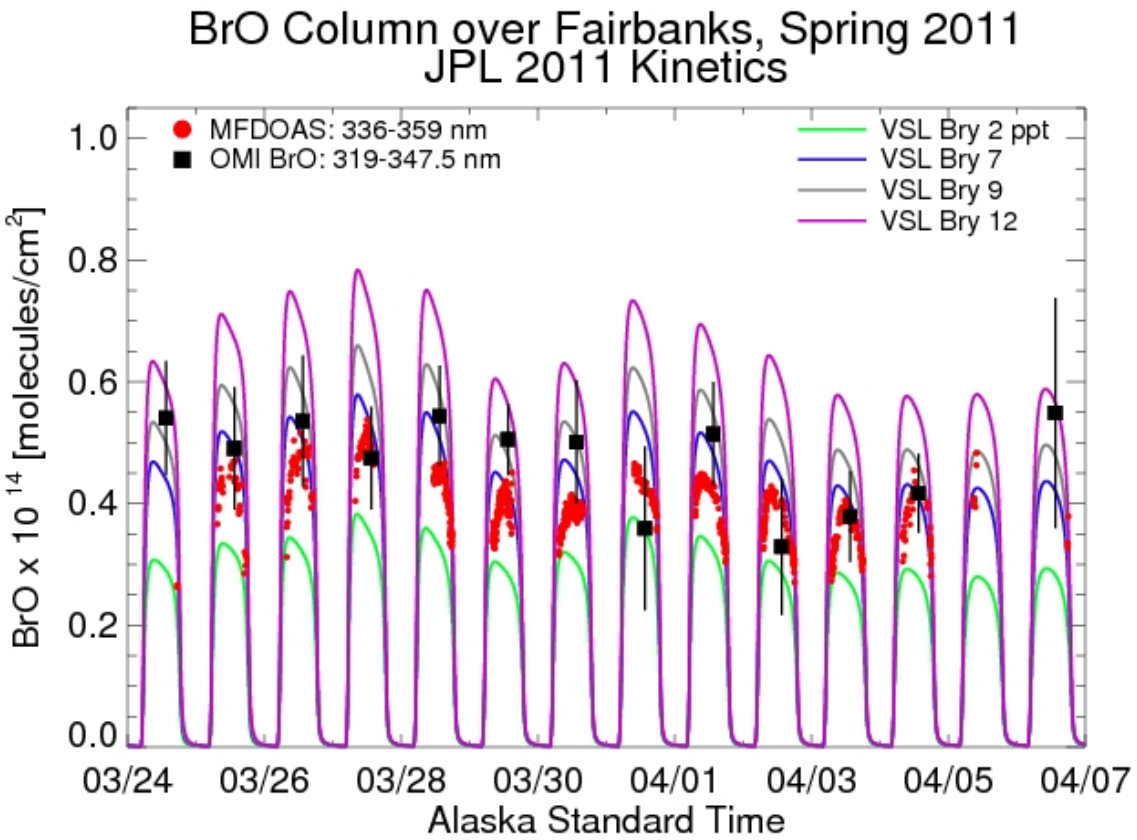

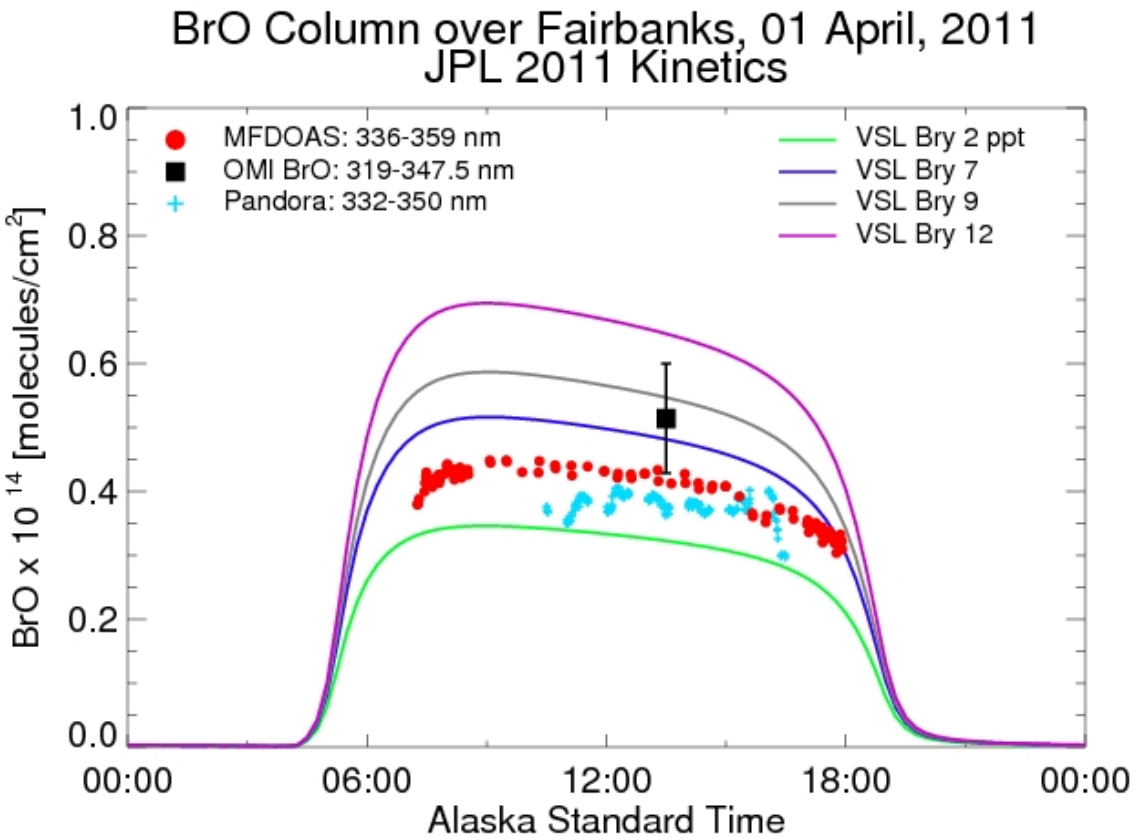

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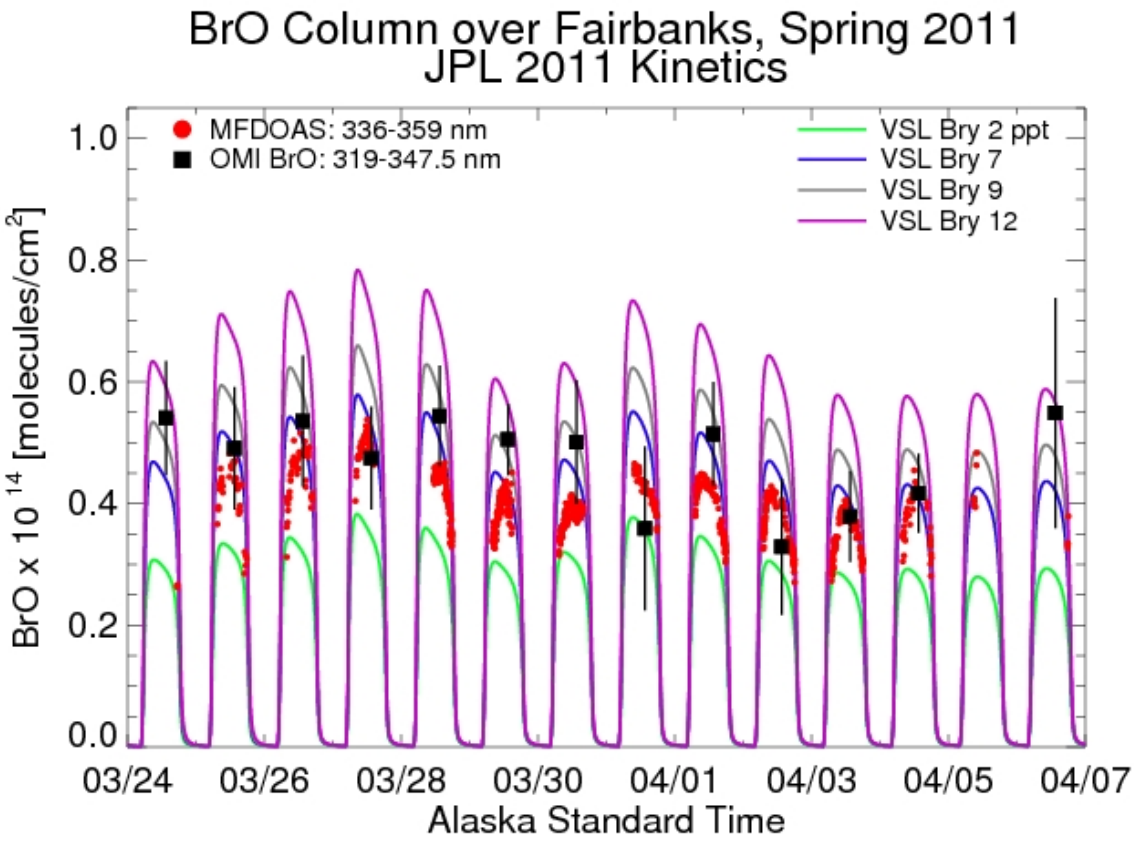
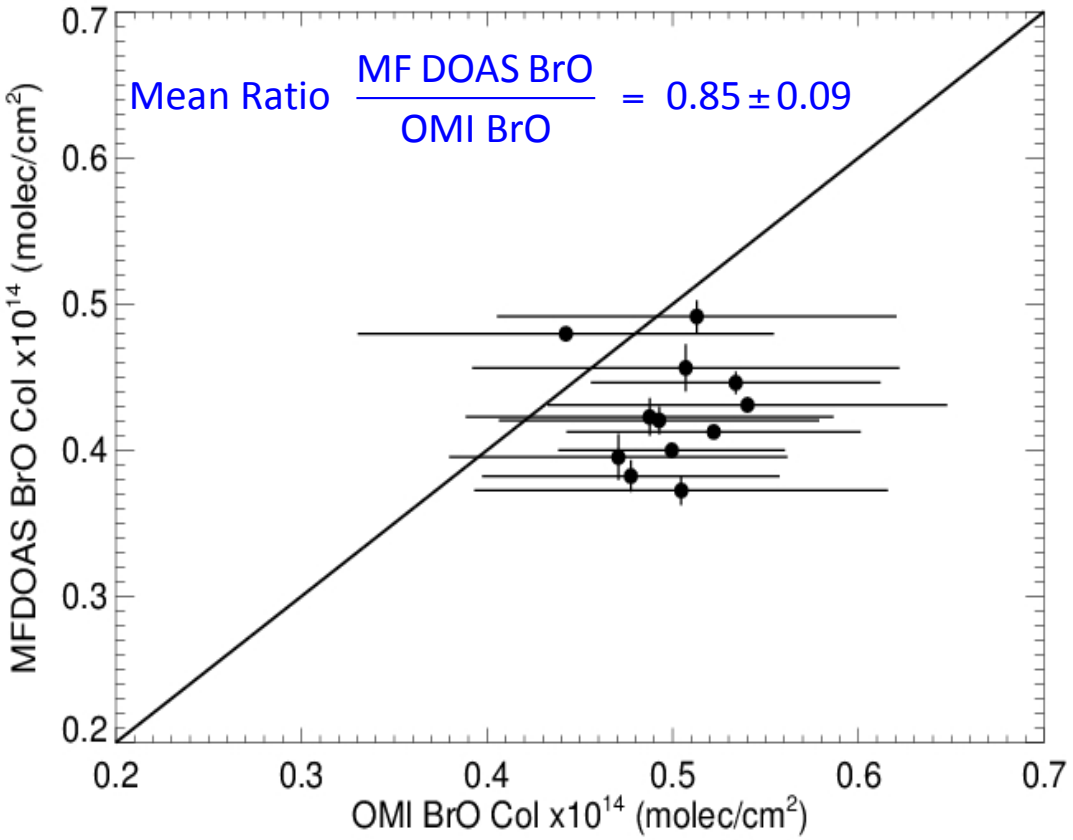




Bromine Nitrate ($BrONO_2$) Kinetics

$BrONO_2$ formation:

$BrO + NO_2 + M \Rightarrow k$

$BrONO_2$ loss:

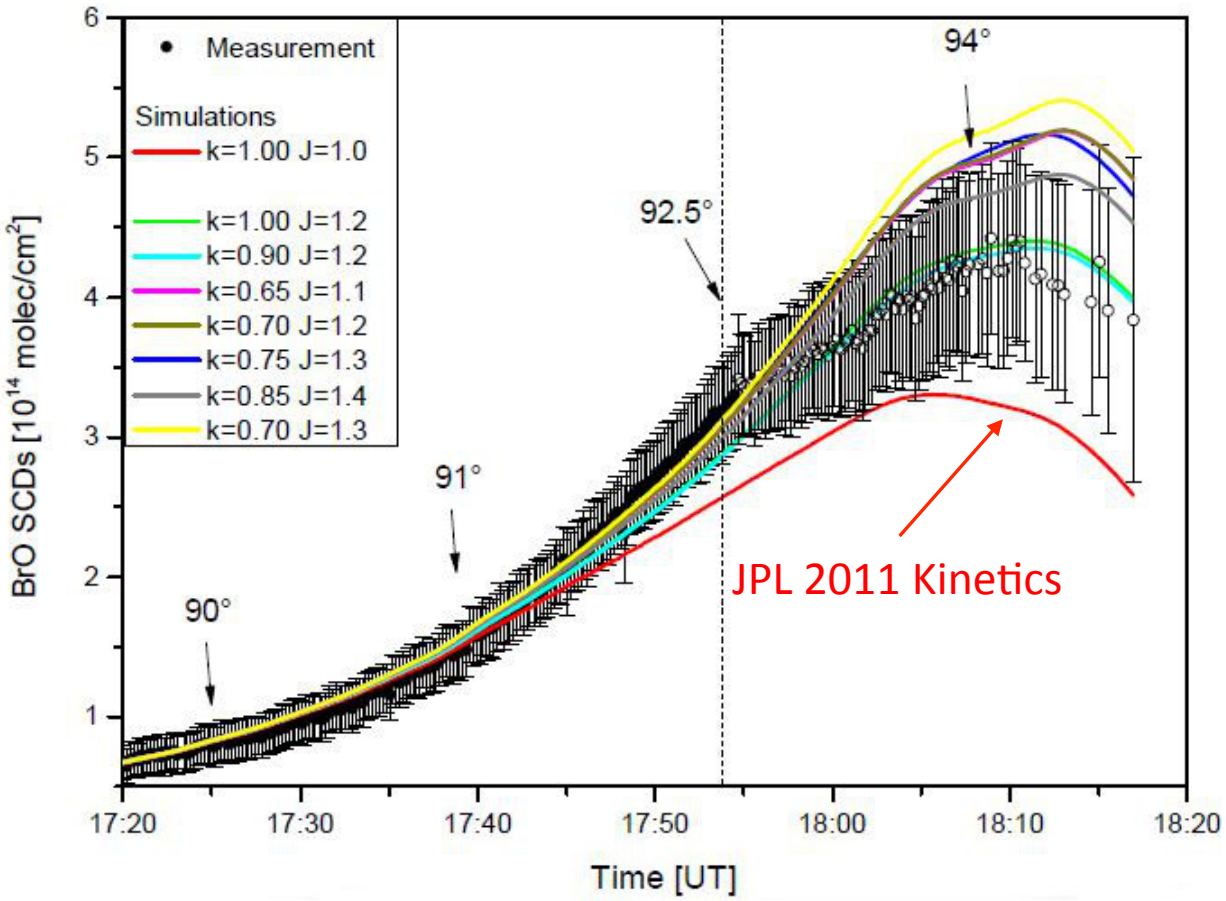
$BrONO_2 + h\nu \Rightarrow J$

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



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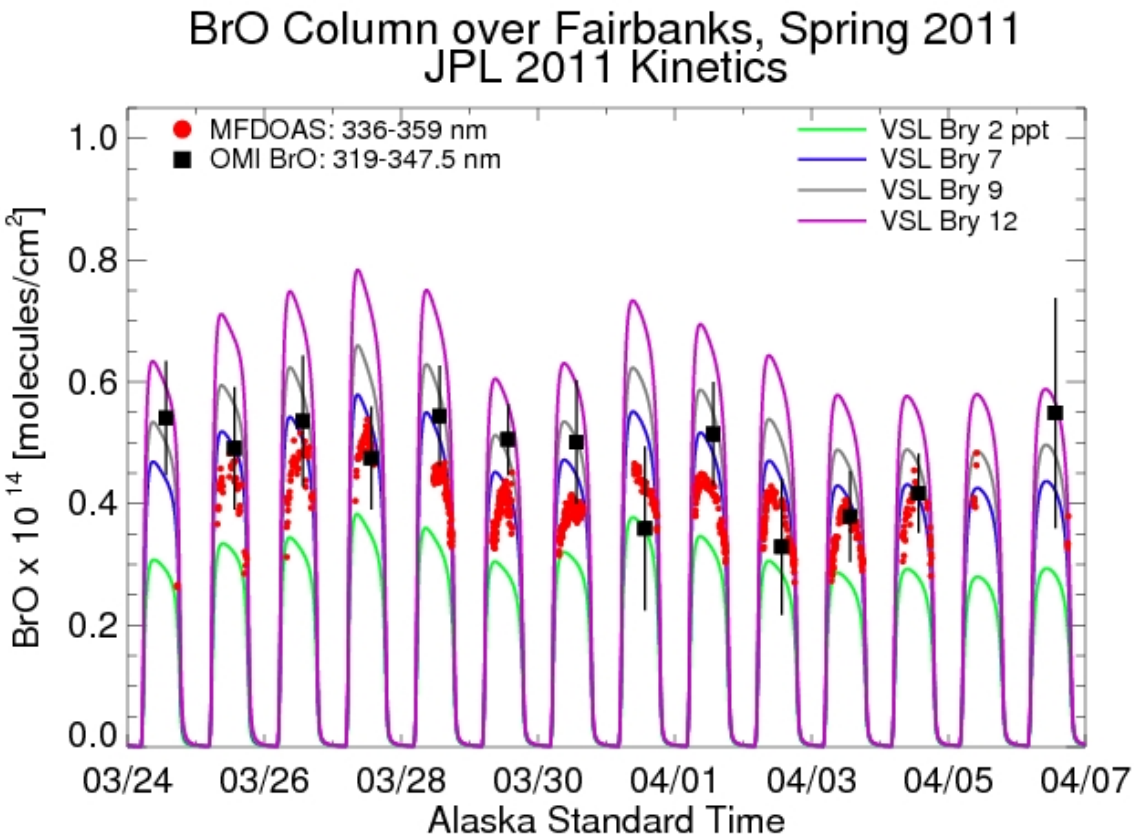

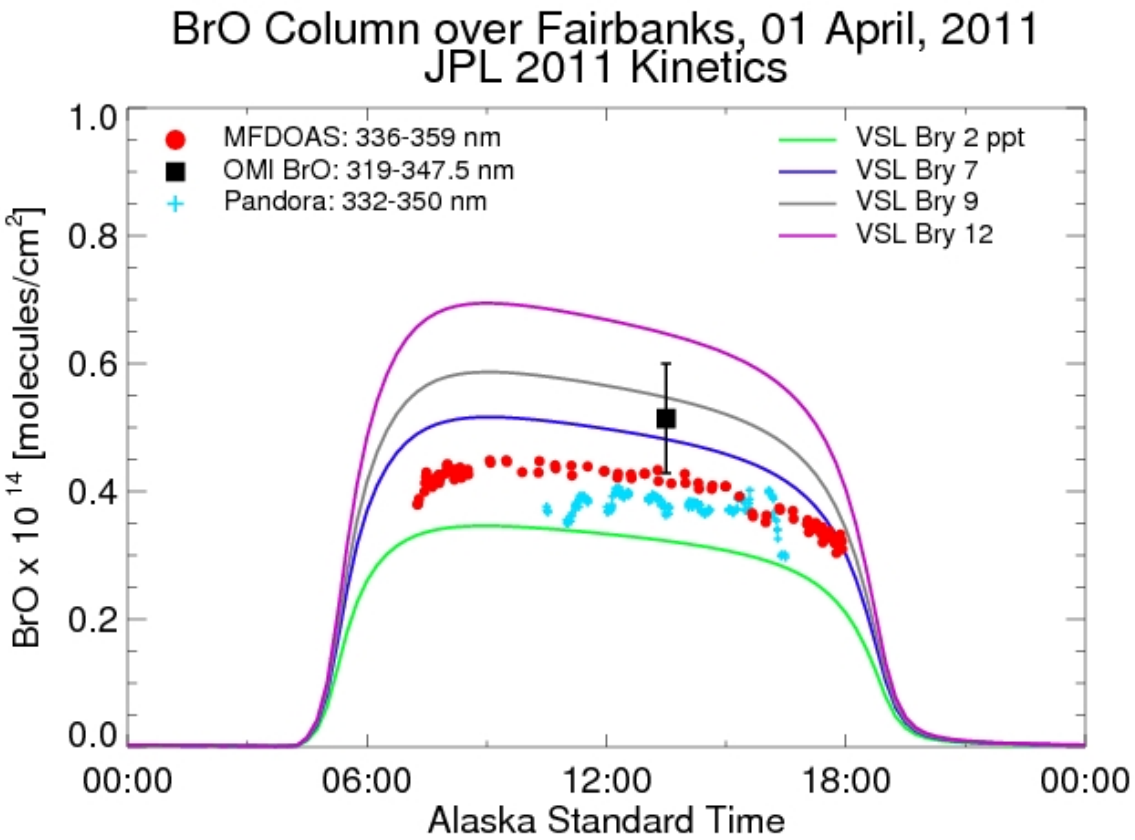

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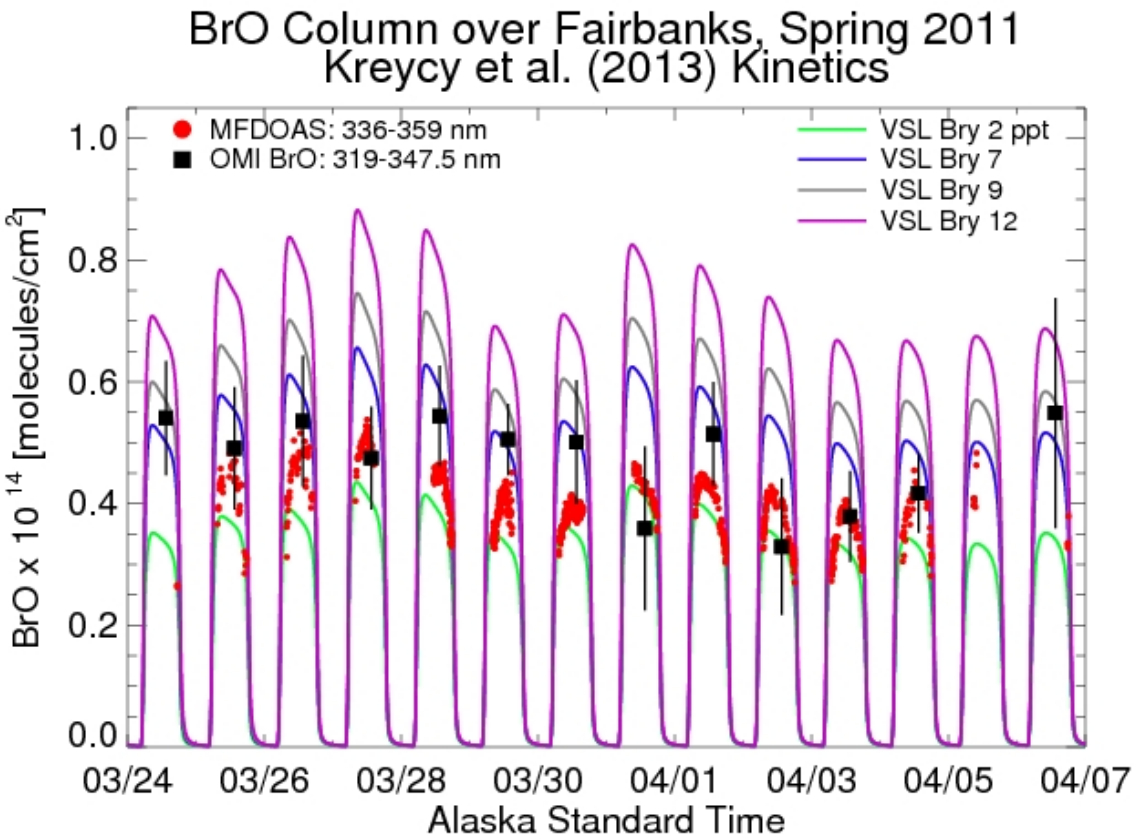

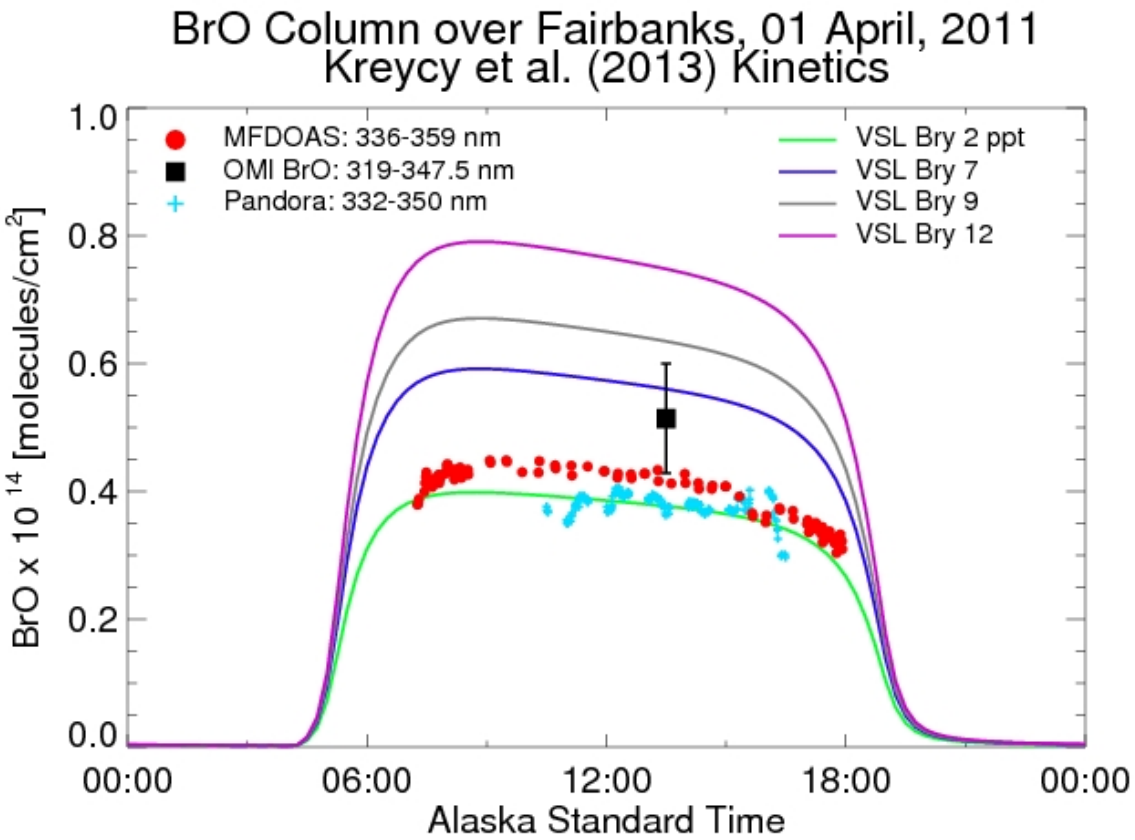

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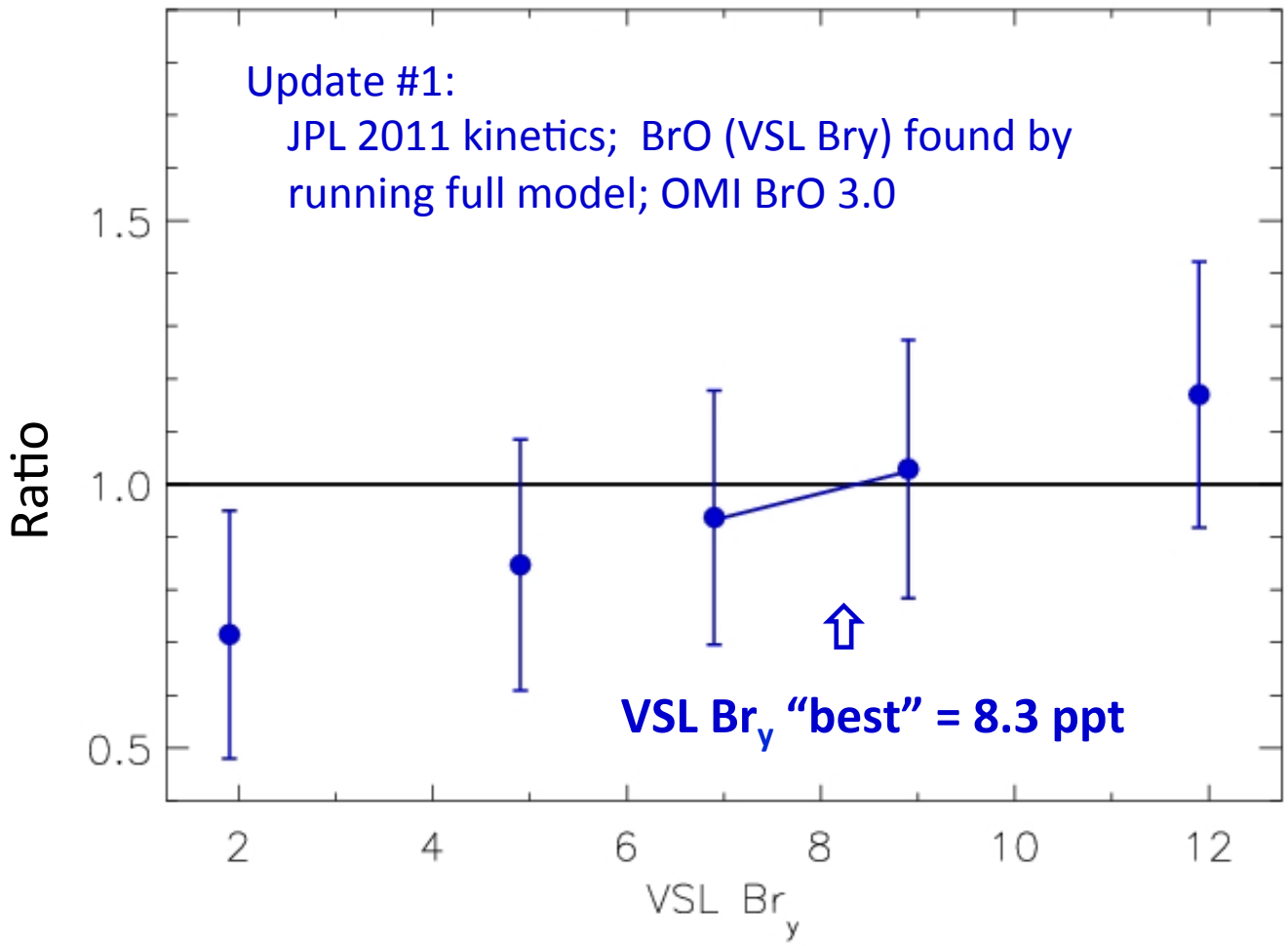

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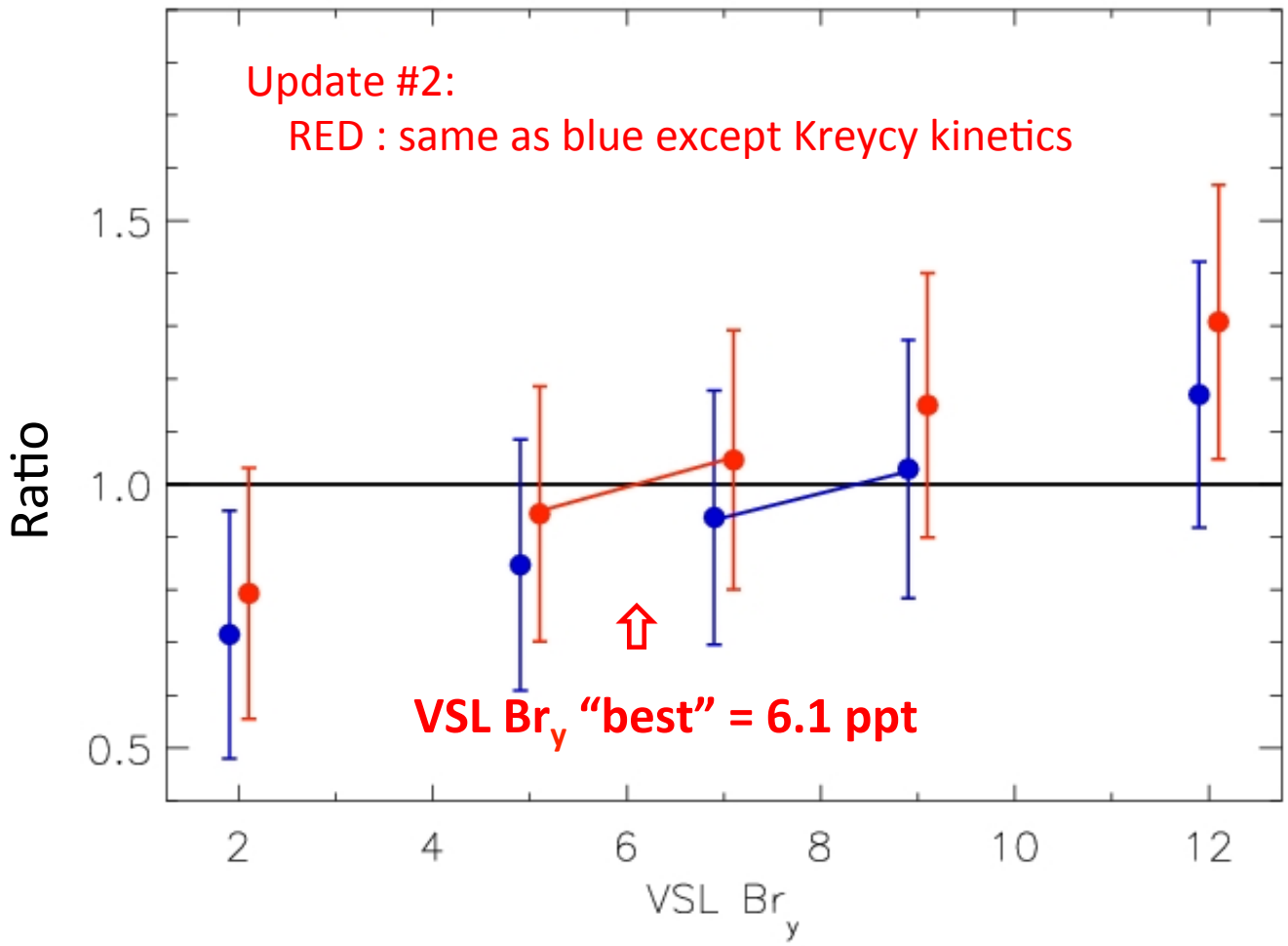

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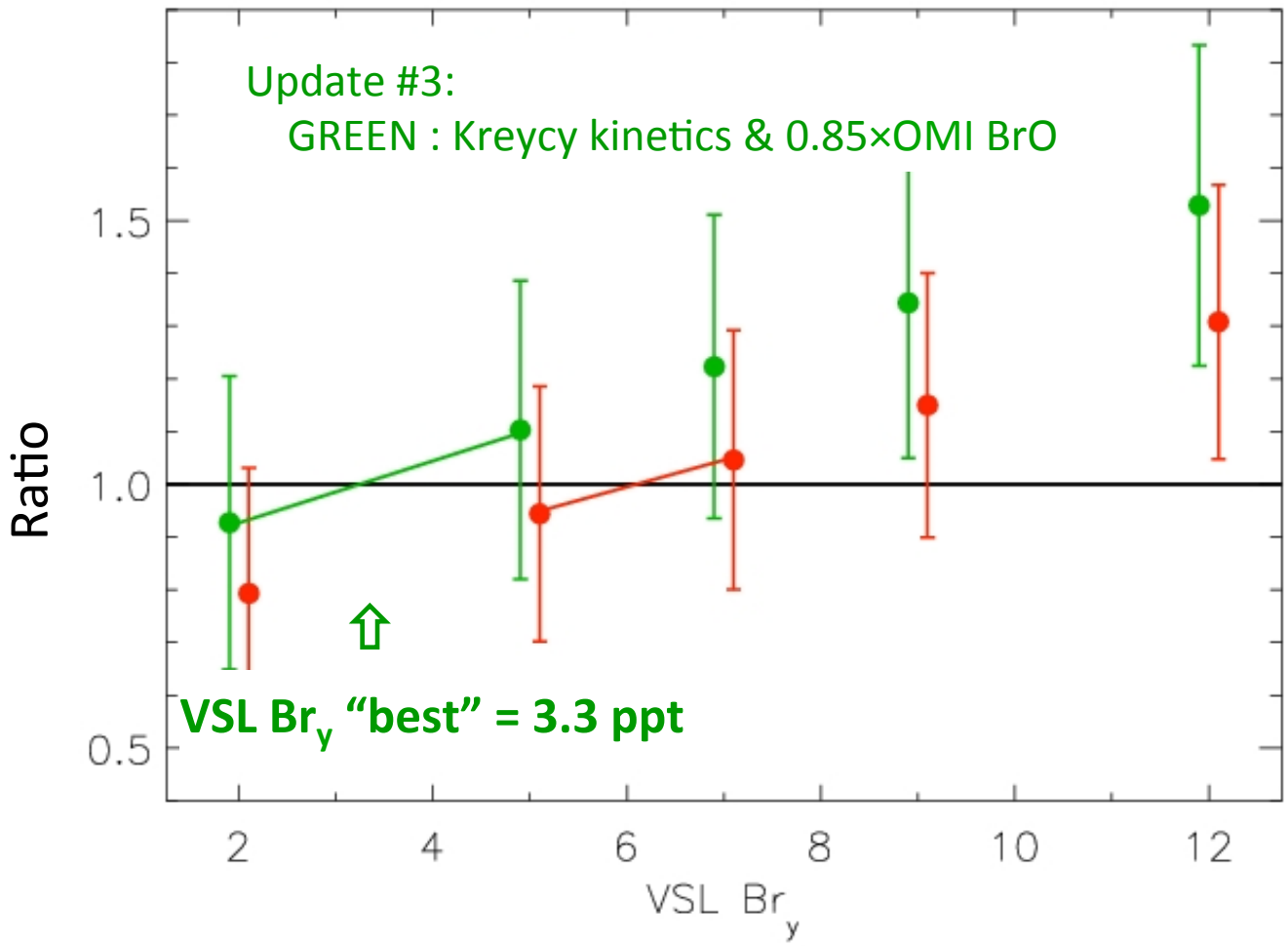
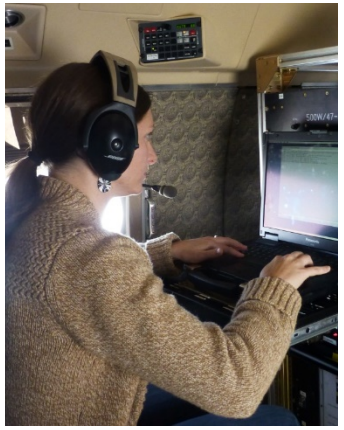


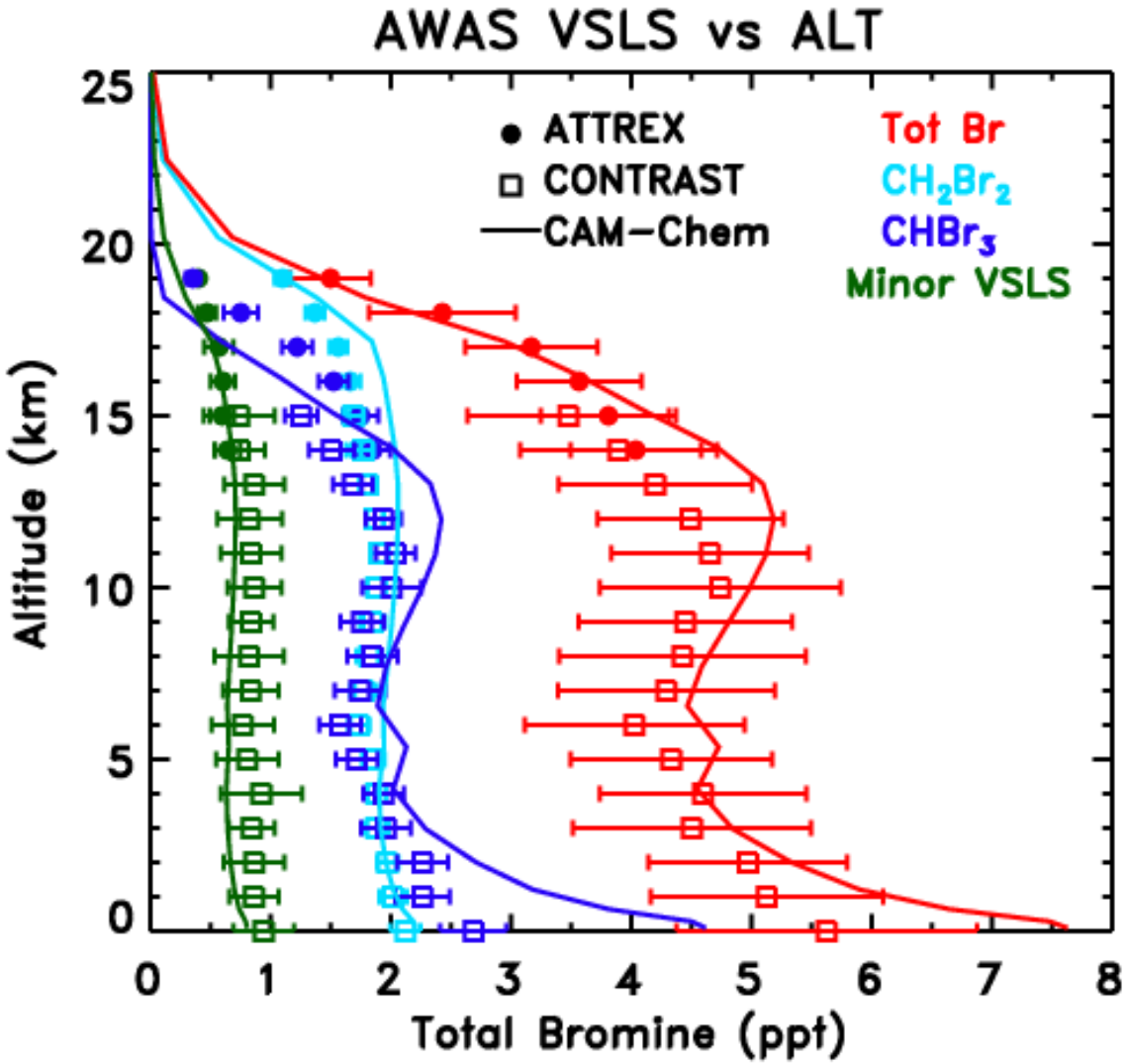
CONTRAST, CAST, & ATTREX:

Guam, Jan & Feb 2014

WAS & Airborne GC/MS measurements of halocarbons

DOAS & CIMS measurements of inorganic halogens





Model calculations: Fernandez et al., ACPD, 2014
Measurements: AWAS, Elliot Atlas et al.

Concluding Remarks

1. Proper knowledge of contribution of VSLs to stratospheric Br_y

   Considerable interest to the halogen community

   Important for our understanding of stratospheric and tropospheric ozone

2. Inference of VSL Br_y from OMI BrO depends on:

   Knowledge of tropospheric BrO burden

   Absolute accuracy of the retrieval of total column BrO

   Kinetics that govern formation and loss of $BrONO_2$

Kinetics	OMI Scaling	VSL Br_y Best Fit (ppt)
JPL 2011	1.0	8.3
Kreycy 2013	1.0	6.1
JPL 2011	0.85	5.1
Kreycy 2013	0.85	3.3

3. Measurements of bromocarbons (WAS, GC/MS) & BrO (DOAS, CIMS) from multiple instruments on 3 aircraft during ATTREX, CAST, CONTRAST will heavily influence future deter. of VSL Br_y , esp. injection of VSL decomp products

   ⇨ results will be discussed at: a) Boulder week of 20 Oct 2014 (joint science team meeting)

   b) S.F. fall 2014 AGU, UT/LS session

Back Up Material to Follow

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

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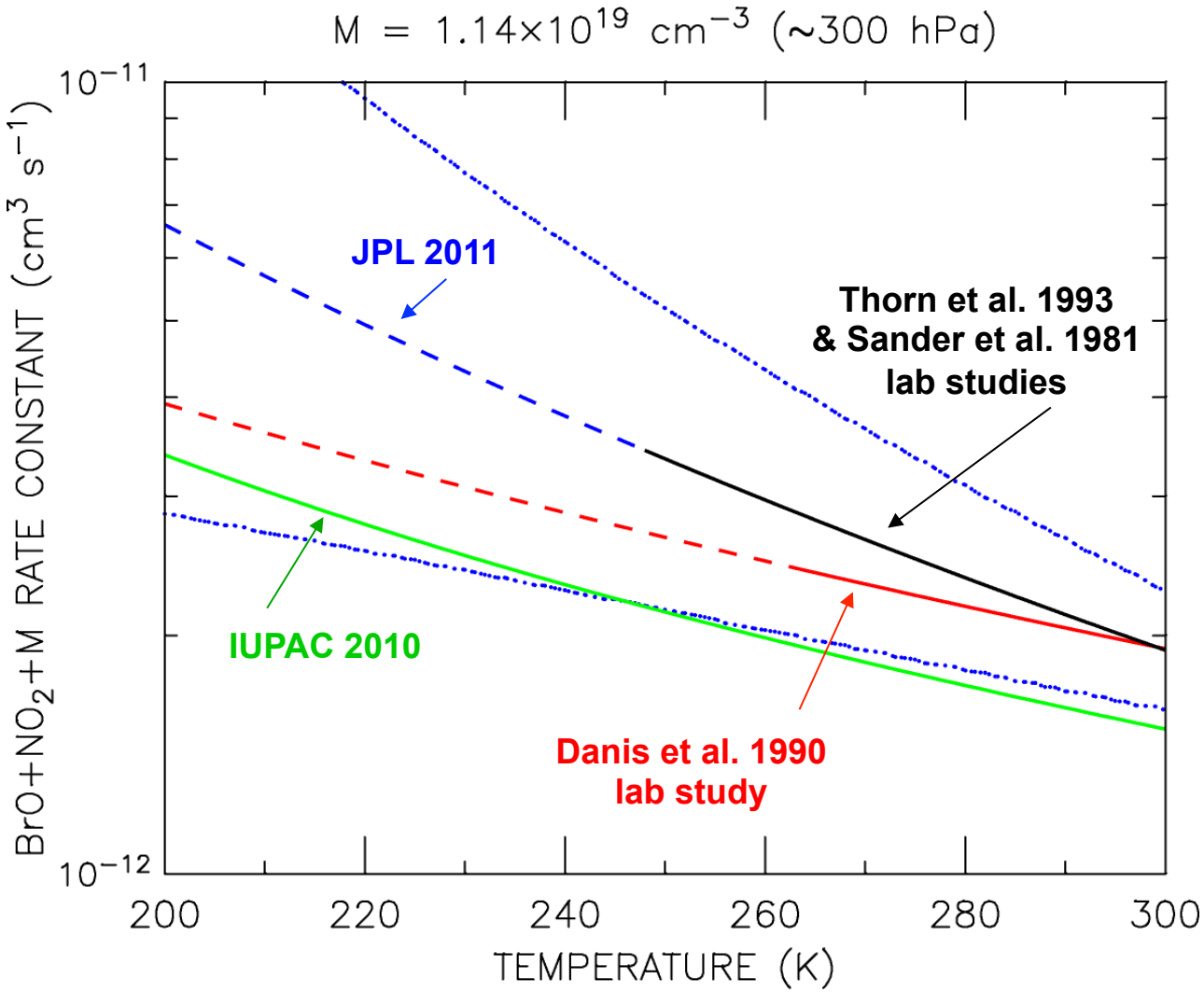
$BrONO_2$ cross section



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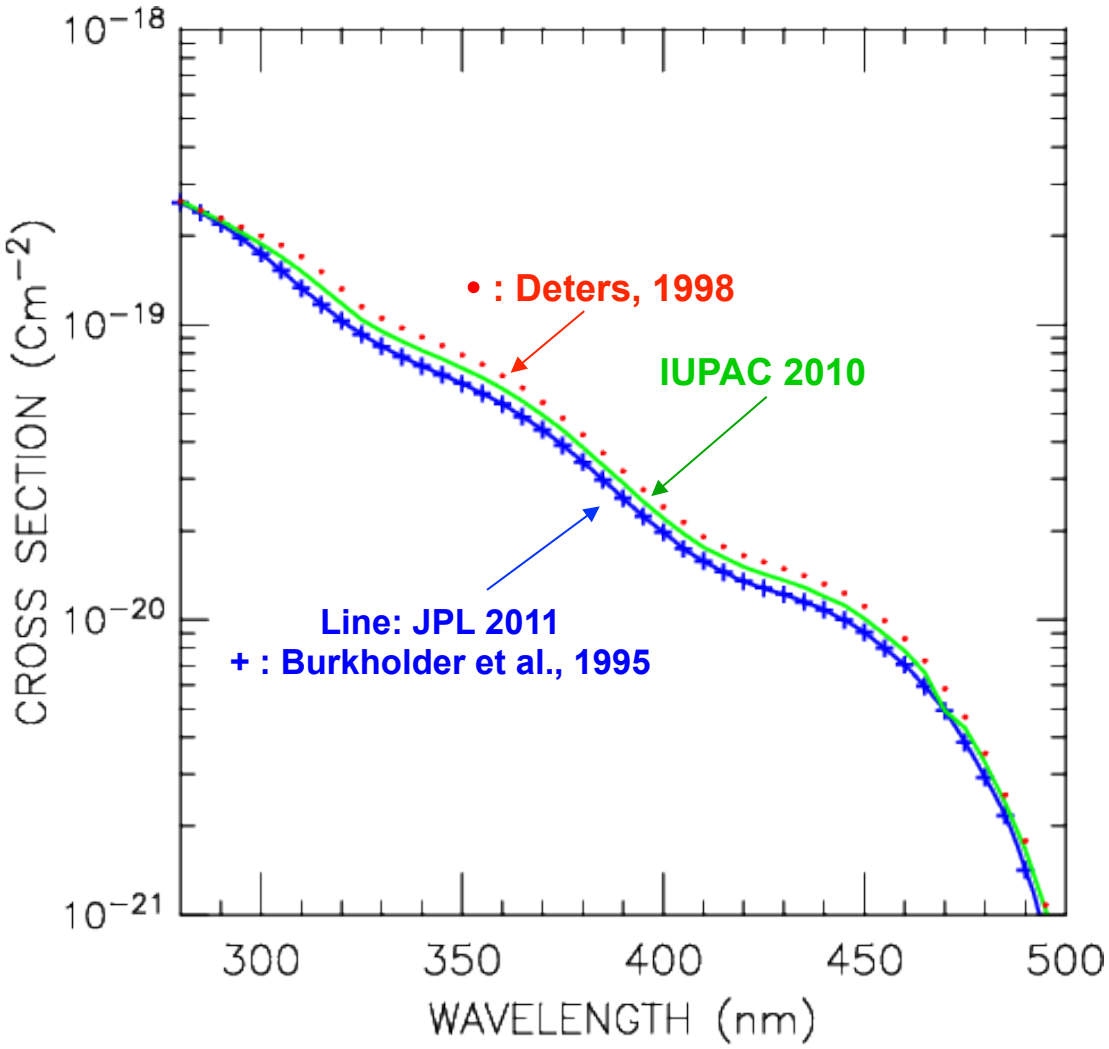

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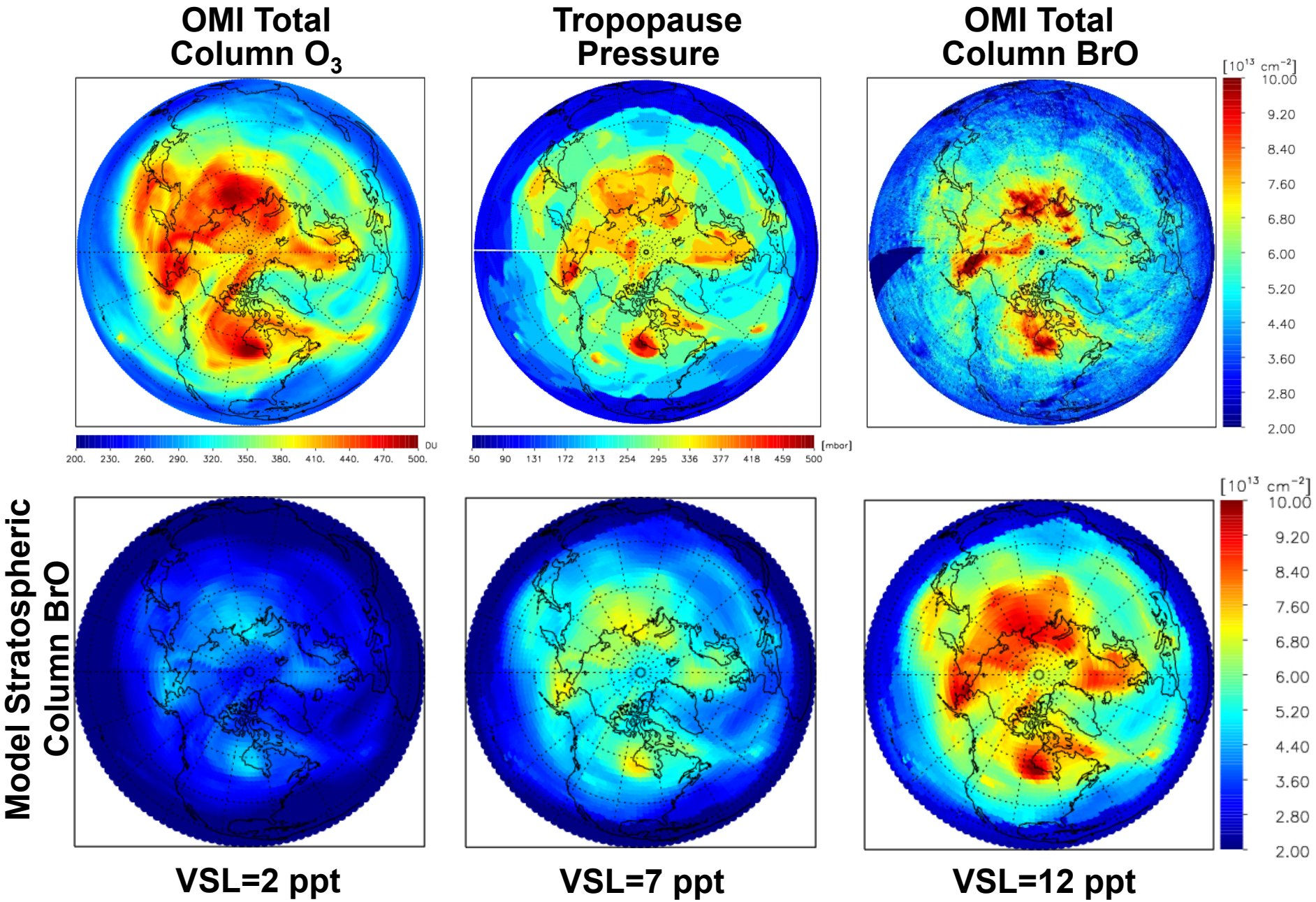
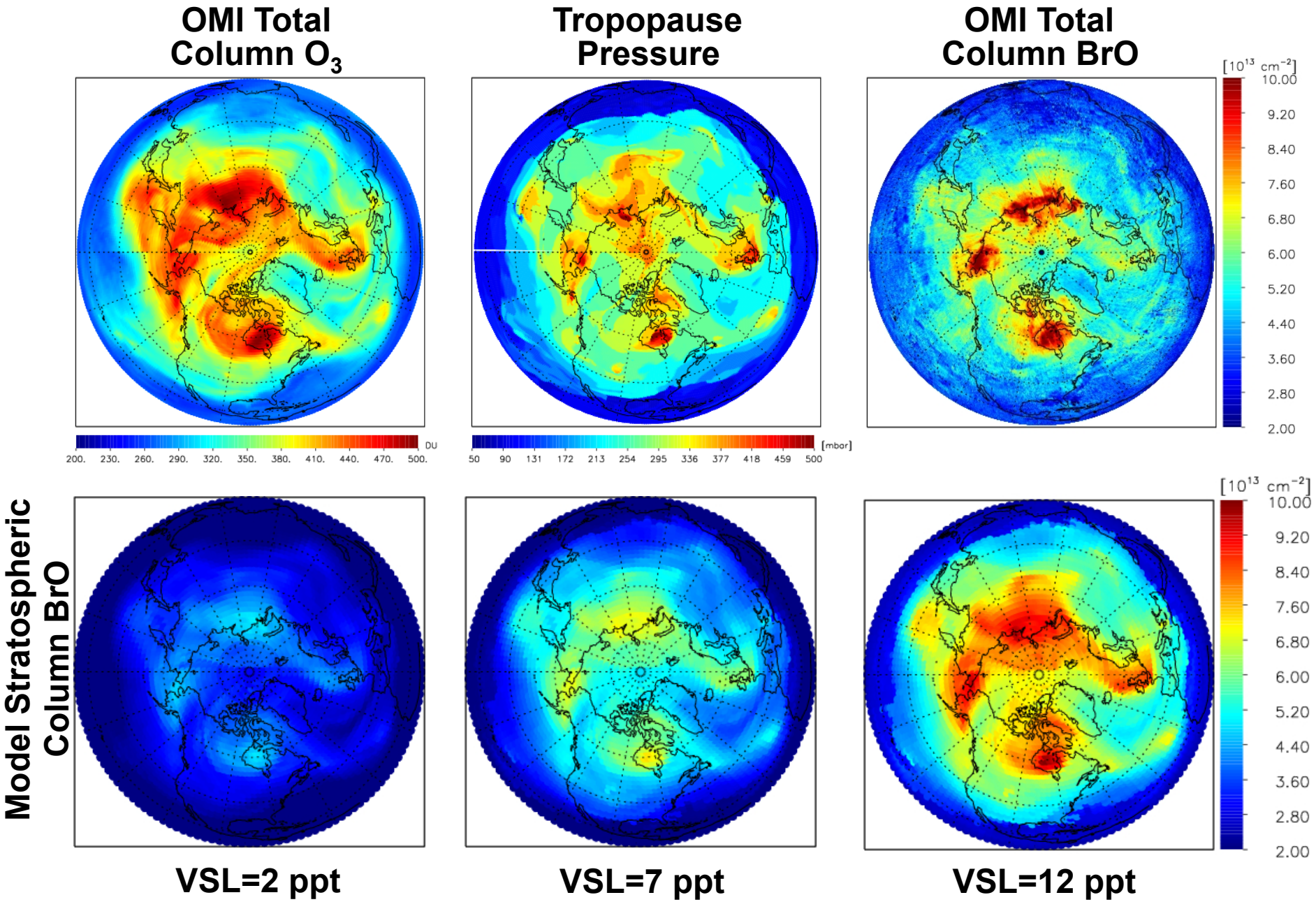

OMI Total Column O_3
Tropopause Pressure
OMI Total Column BrO
[10^{13} cm^{-2}]
10.00
9.20
8.40
7.60
6.80
6.00
5.20
4.40
3.60
2.80
2.00
DU
200. 230. 260. 290. 320. 350. 380. 410. 440. 470. 500.
[mbar]
50 90 131 172 213 254 295 336 377 418 459 500
Model Stratospheric Column BrO
VSL=2 ppt
VSL=7 ppt
VSL=12 ppt

6 Apr 2008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7 Apr 2008

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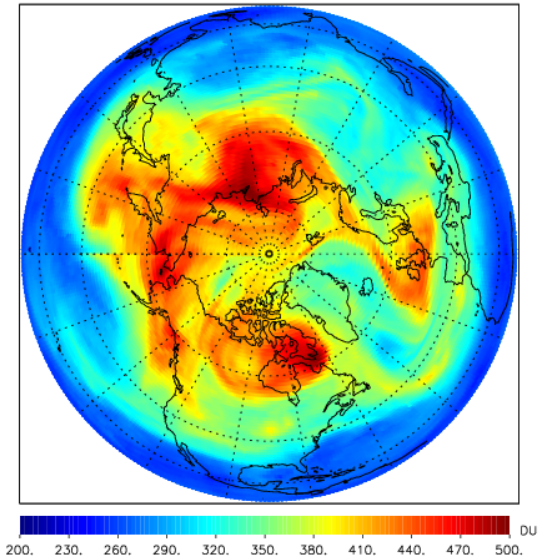

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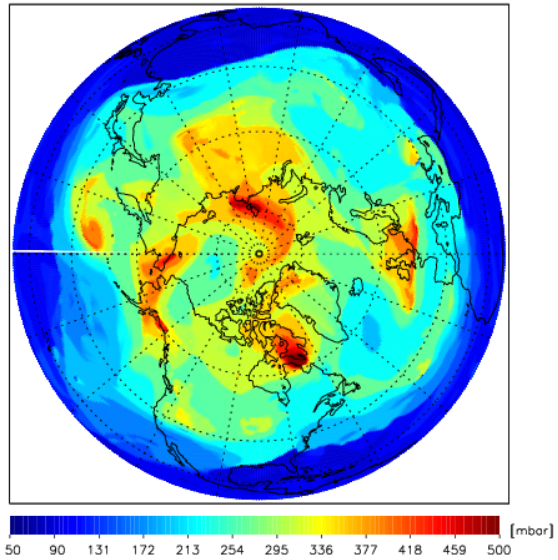

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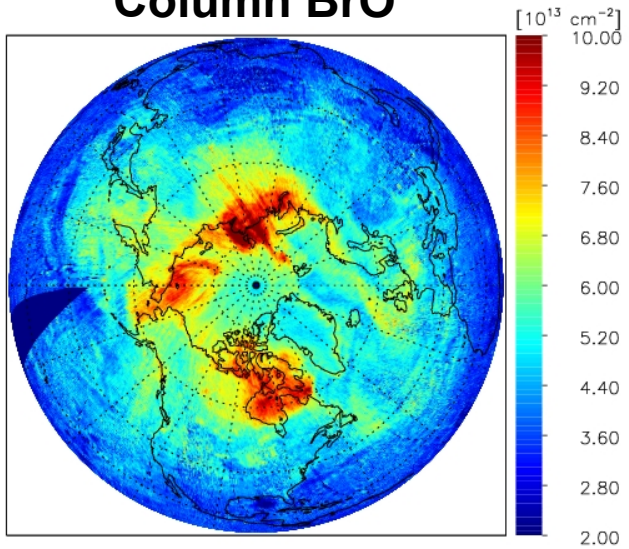

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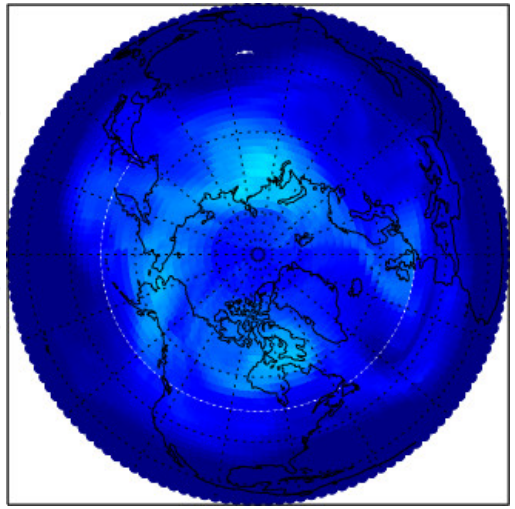
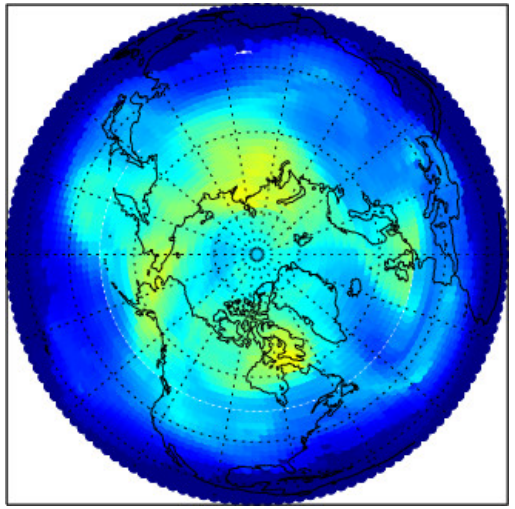
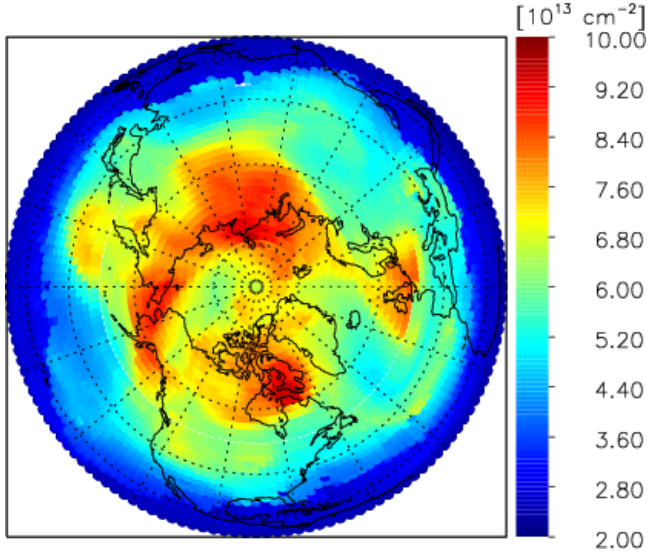


VSL=2 ppt

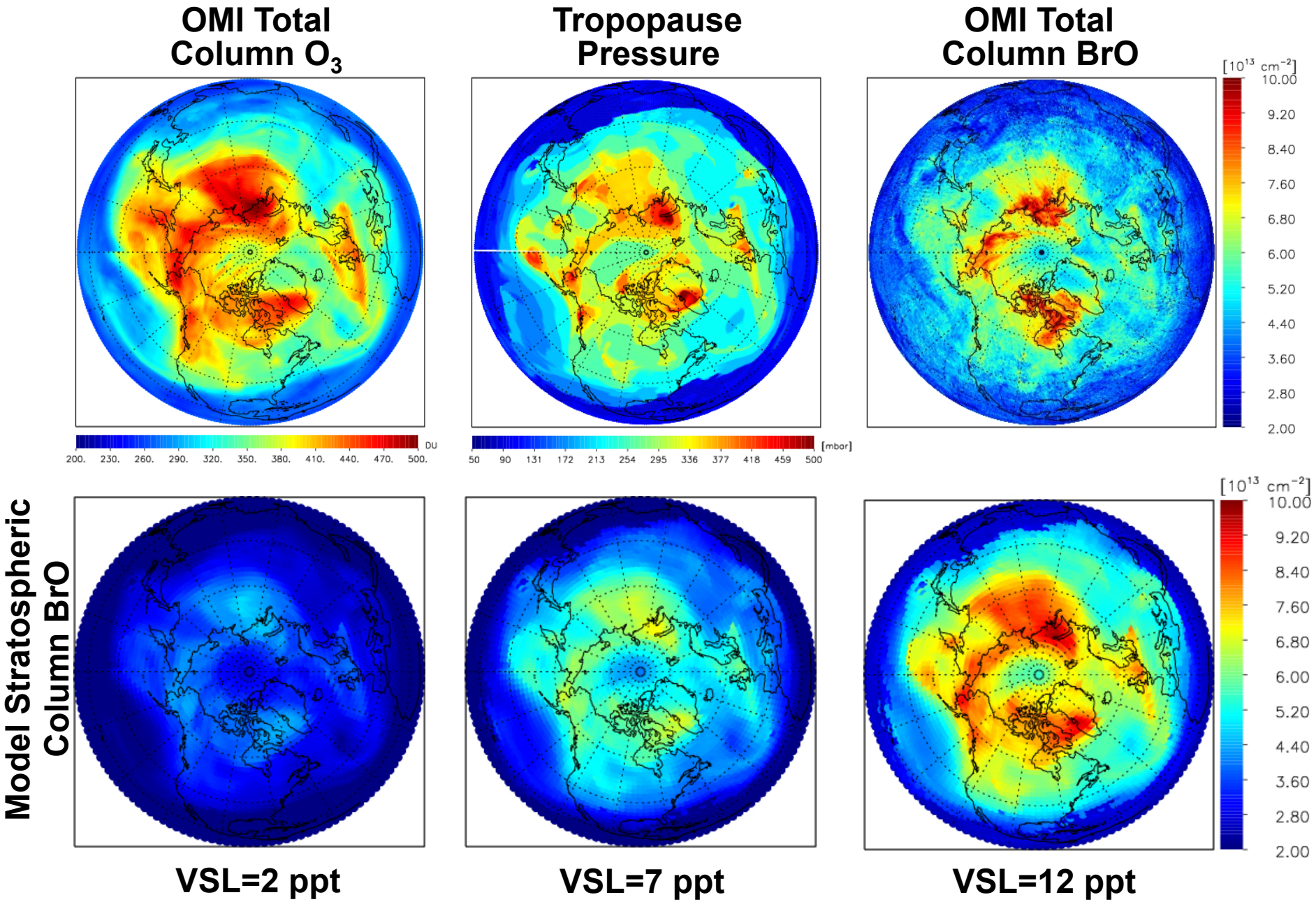


VSL=7 ppt



VSL=12 ppt

8 Apr 2008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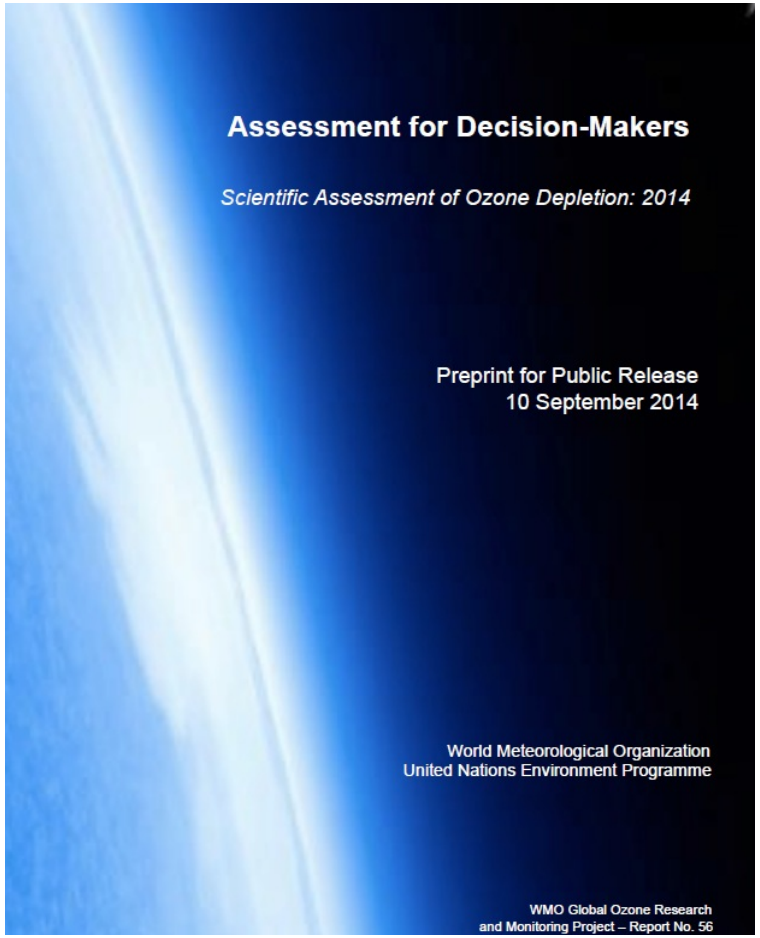
Supply of Stratospheric Bromine by Very Short Lived Substances (VSLs)

WMO/UNEP (2014) ADM, released 10 Sept 2014:

VSLs contribute ~5 (2–8) ppt toward the observed total stratospheric Br_y of ~20 ppt. The current estimate is slightly smaller than the 6 (3–8) ppt estimate reported in last Assessment primarily due to the revised estimates of the partitioning in the stratosphere between the observed BrO molecule and Br_y.



WMO/UNEP (2010) "Green Book" :

Table 1-14. Estimates of inorganic bromine from very short-lived substances (Bry^{VSLS}) contribution to stratospheric bromine derived from BrO measurements.

Should be 9 ppt using their def'n of VSLs

…..		
MLS satellite BrO profiles 55°S–55°N, 10–4.6 hPa	6.5	Kovalenko et al. (2007)
OSIRIS satellite BrO profiles 80°S–80°N, 20–34 km	5	McLinden et al. (2010)
OMI total column BrO	**7** [c]	Salawitch et al. (2010)
Ensemble	6 (**3–8**) [d]	

[c] Salawitch et al. (2010) has a different treatment of CH_2Br_2 than the other studies. Their estimate would be slightly higher (~ ≤1 ppt) if CH_2Br_2 were treated in the same manner as in the other studies.

[d] Average and range of the central values of the 12 estimates of Br_y^{VSLS}.

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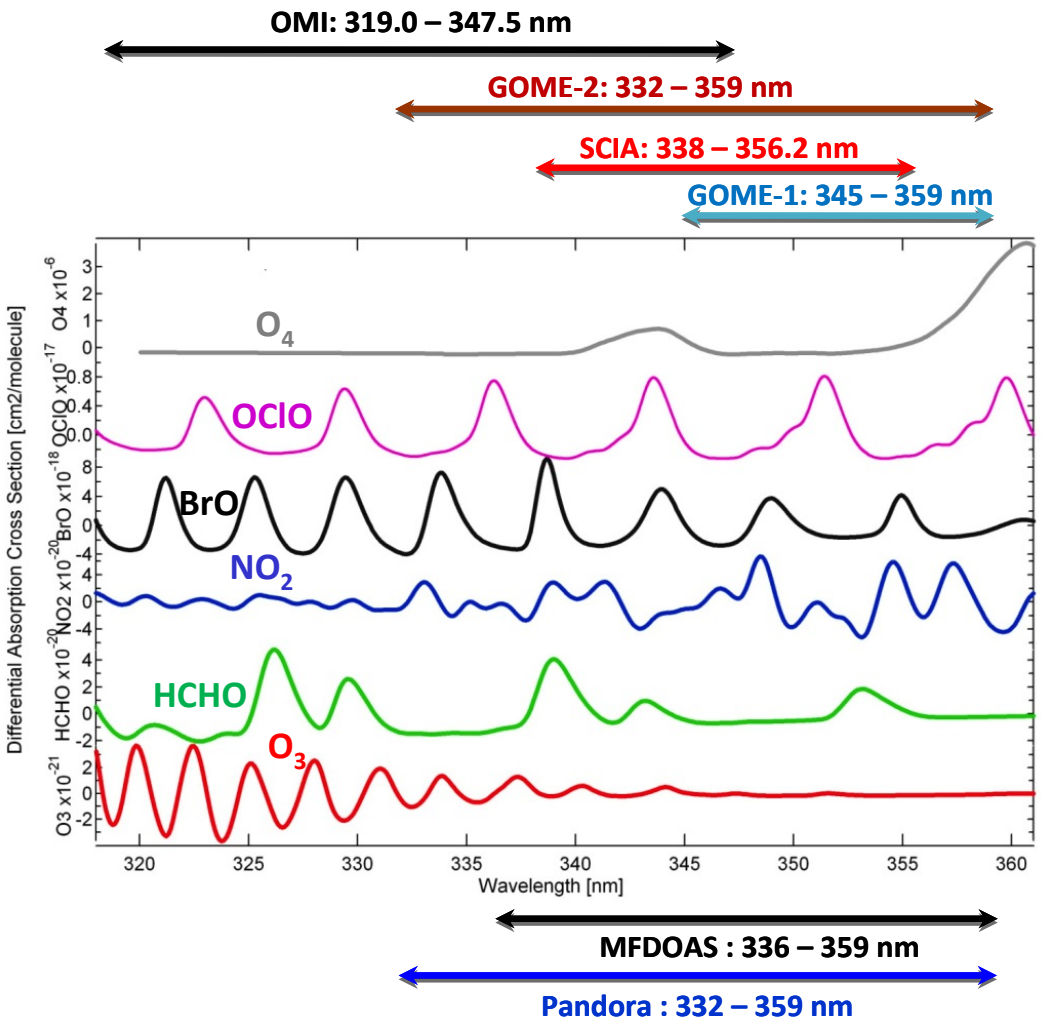
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