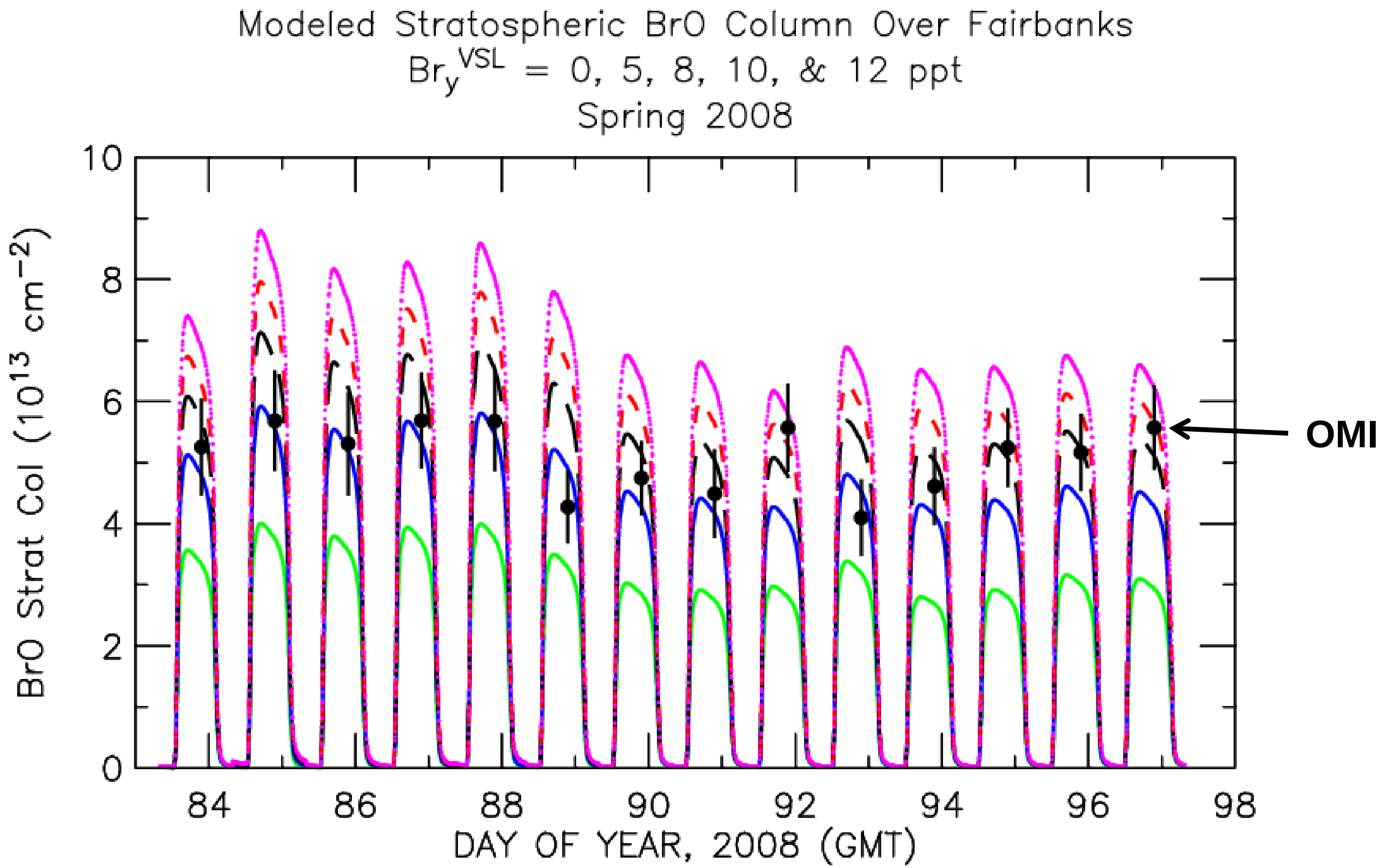
On the Interpretation of Satellite Observations of BrO

Tim Canty, R. Salawitch, S. Choi, J. Liao, L.G. Huey, T. Kurosu, J. Joiner, R. Suleiman, K. Chance, P.F. Levelt, J. A. Neuman, J.B. Nowak, T. Ryerson, J. Dibb, G. Mount, E. Spinei, W. Simpson, D. Donohoue, R. McPeters, P.K. Bhartia, J. Herman, A. Cede, N. Abuhassan, B. Johnson, Q. Liang, A. da Silva, S. Pawson, S. Tilmes, and D. Kinnison, and **Nicolas Theys** !

Aura Science Team meeting
13-15 September 2011

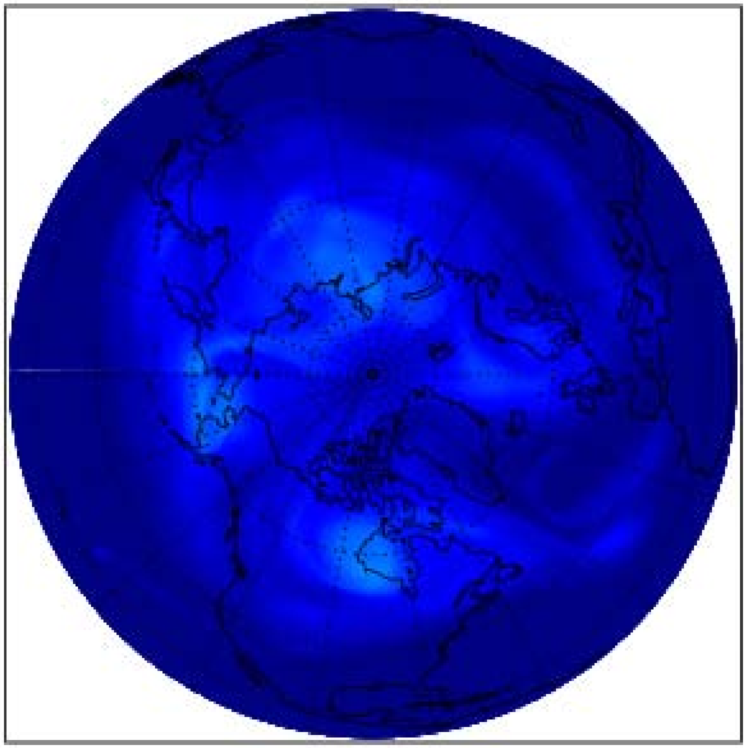
Column BrO, Fairbanks, Alaska (65ºN)



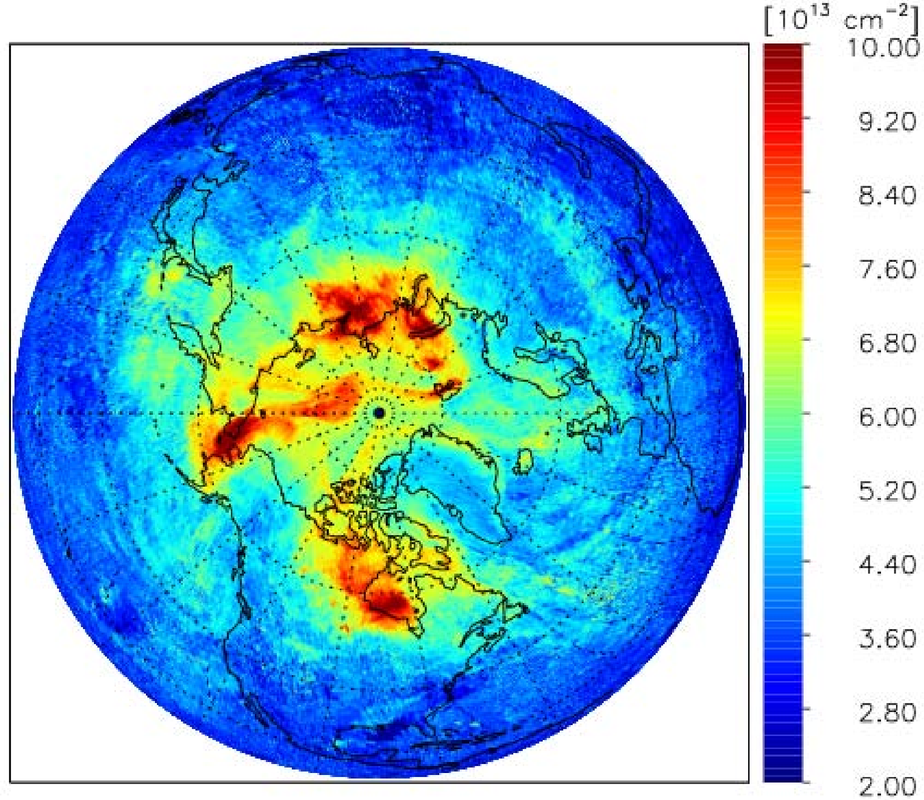
While uncertainty remains regarding the *magnitude* of observed column BrO, we believe there is strong evidence indicating a stratospheric signature in the column BrO retrievals (Salawitch et al., 2010).

Modeled and Measured Column BrO, 5 April 2008

Model Stratospheric Column BrO, VSL=0 ppt

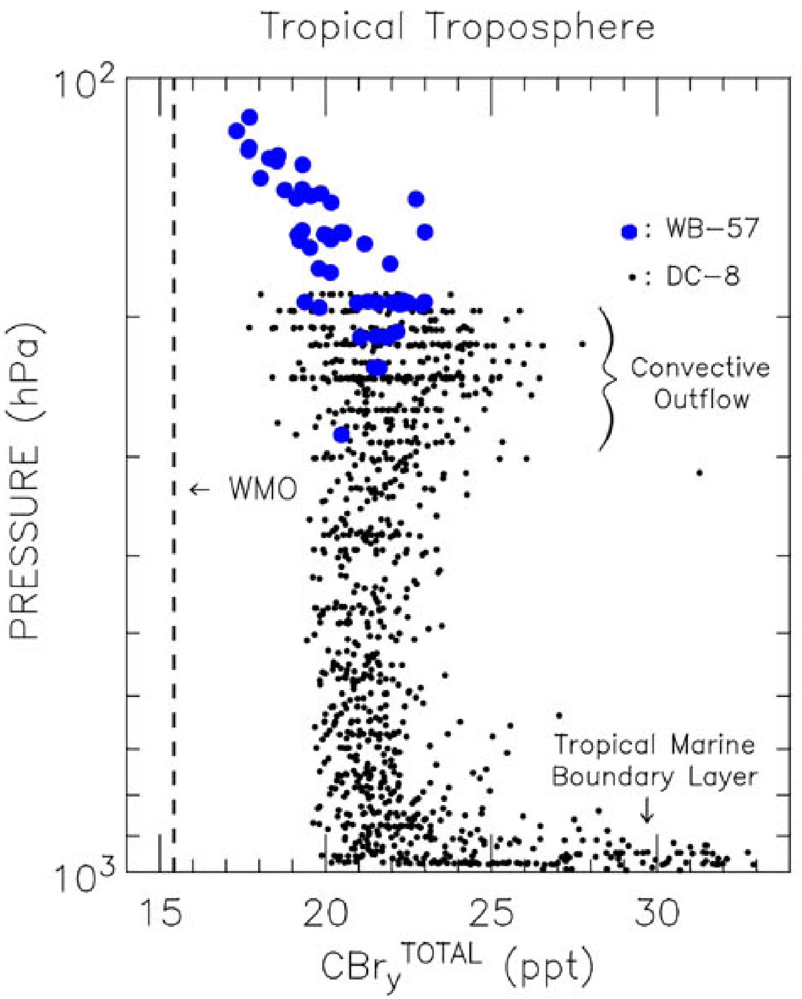


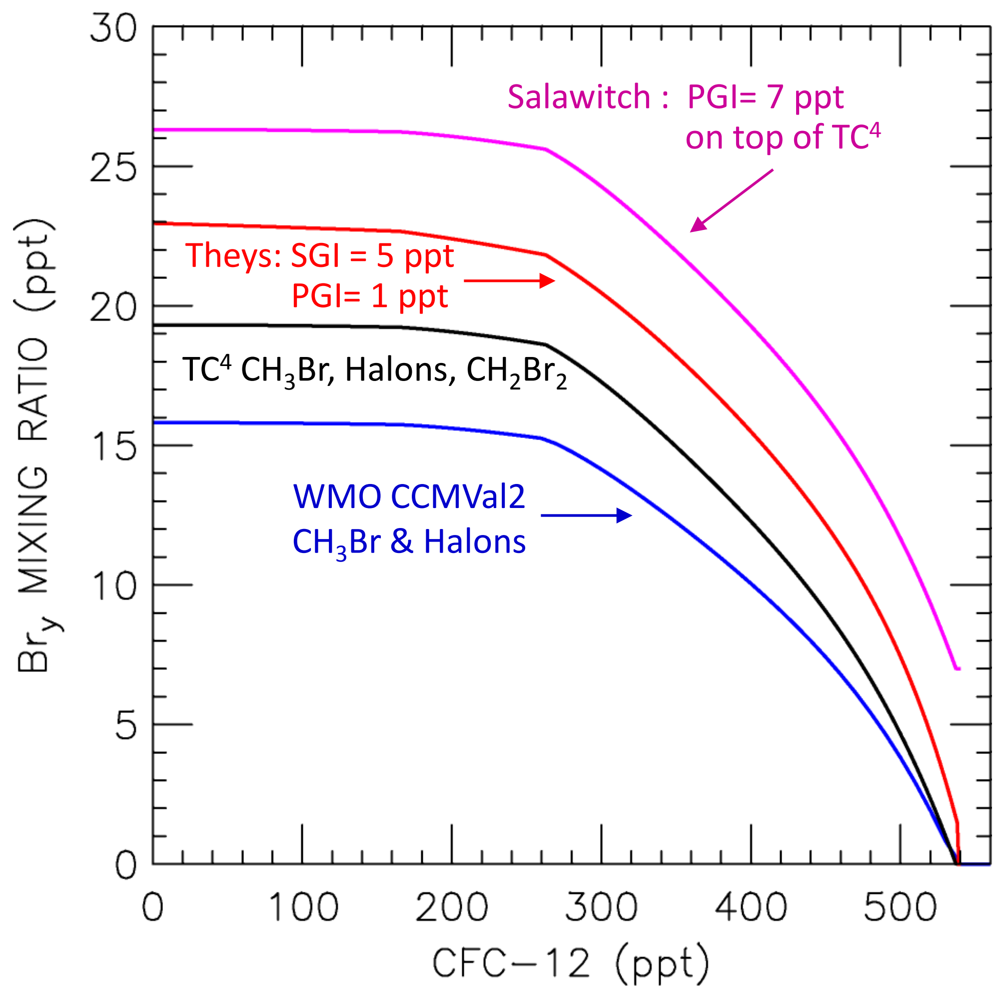
OMI Total Column BrO



Salawitch et al., GRL, 2010

Bromine from VSL (very short lived) Sources





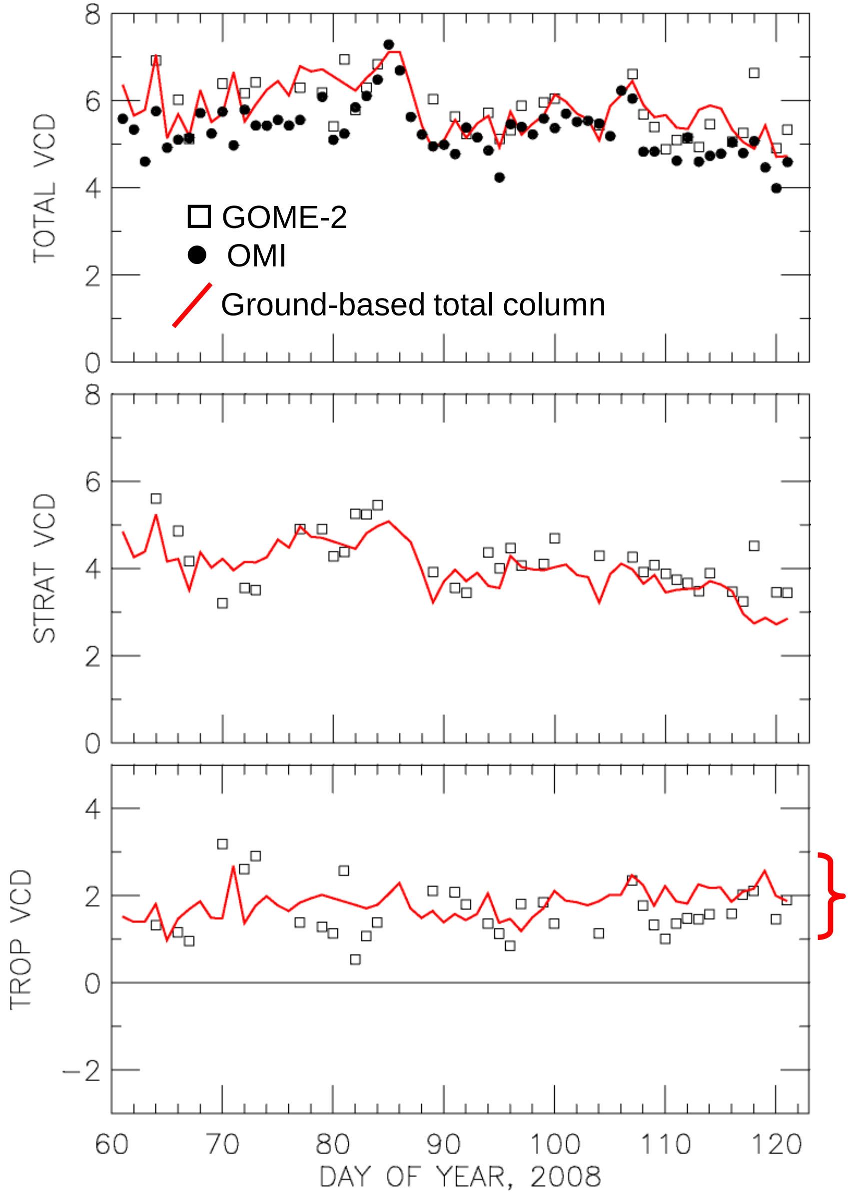
TC[4] ***tropospheric*** data indicate significant potential for VSL species to supply Br_y to stratosphere

Salawitch et al., GRL, 2010

Salawitch et al., GRL, 2010 & Theys et al., ACP, 2009
Theys et al., ACP, 2011

Ground Based BrO, Harestua, Norway (60ºN)

Units: 10^{13} molecules/cm^2

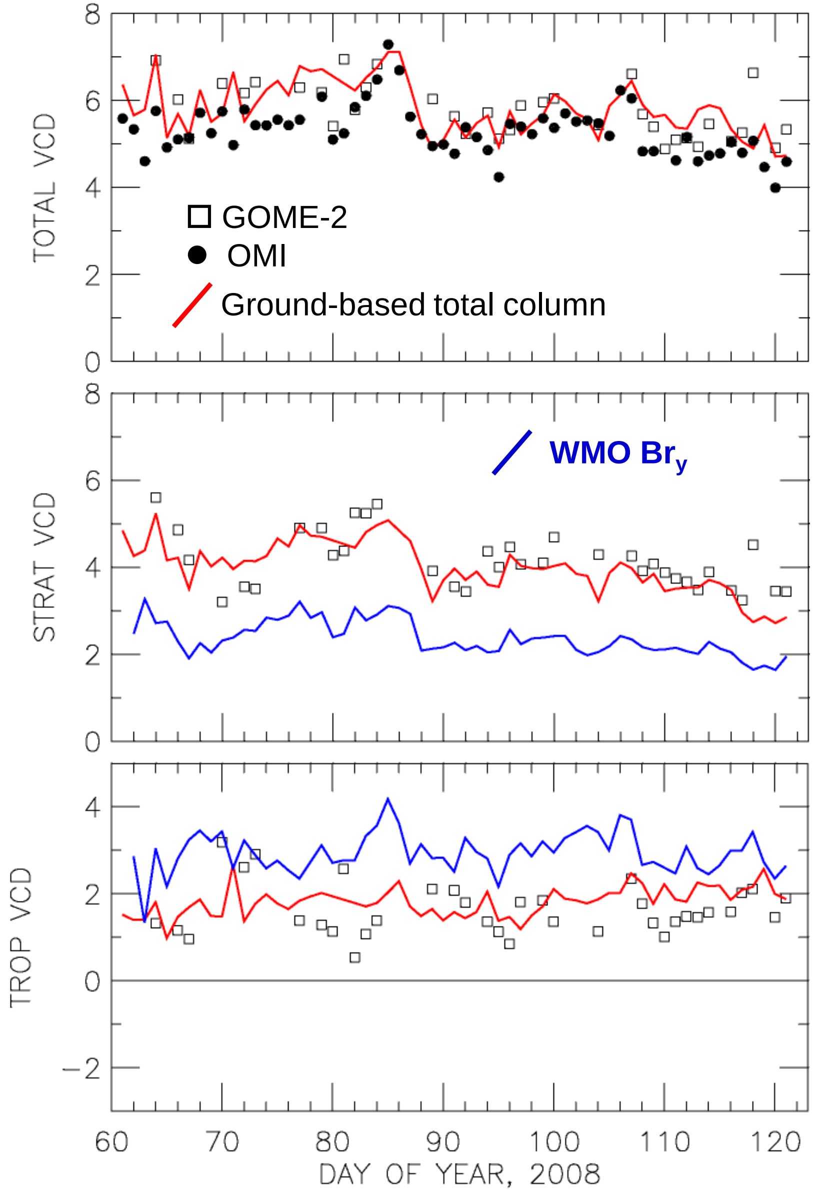


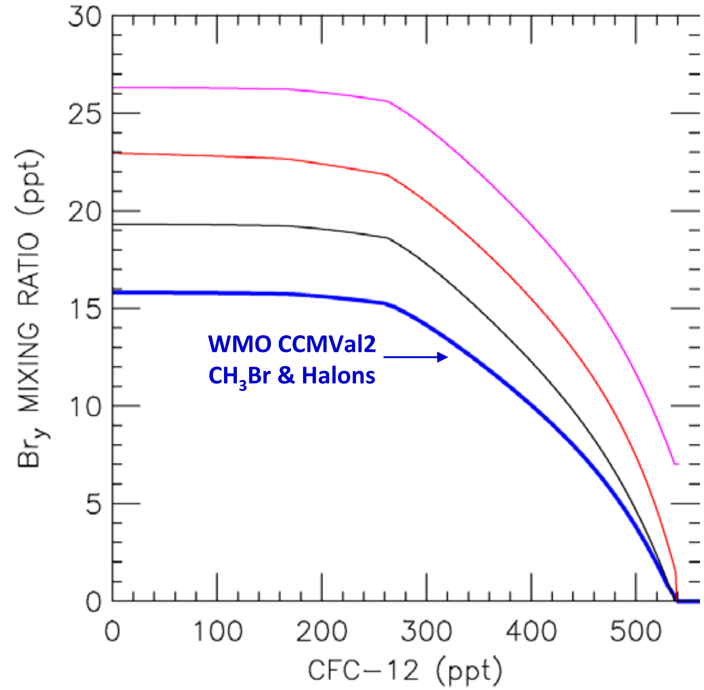
Global Trop Extra-Polar Col BrO of 1 to 3 10^{13}

Theys et al., ACP, 2011

Ground Based BrO, Harestua, Norway (60ºN)

Units: 10^{13} molecules/cm^2



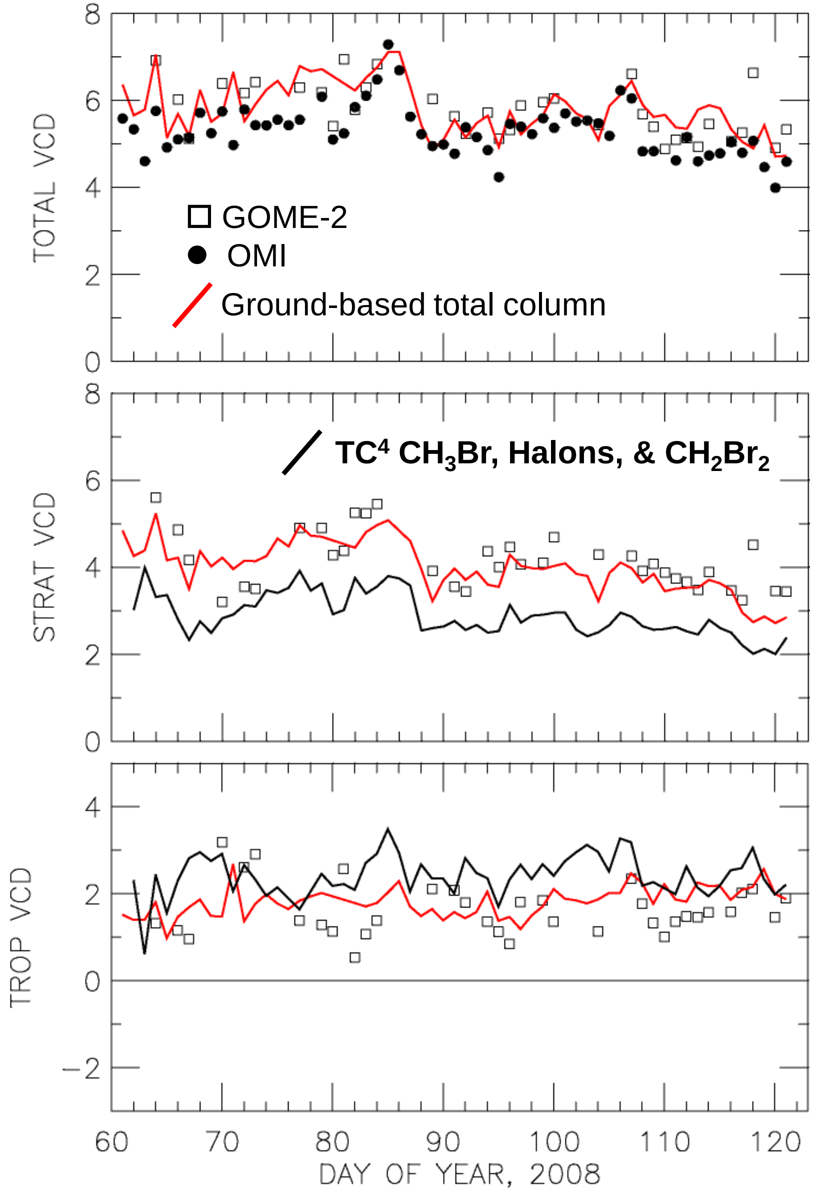


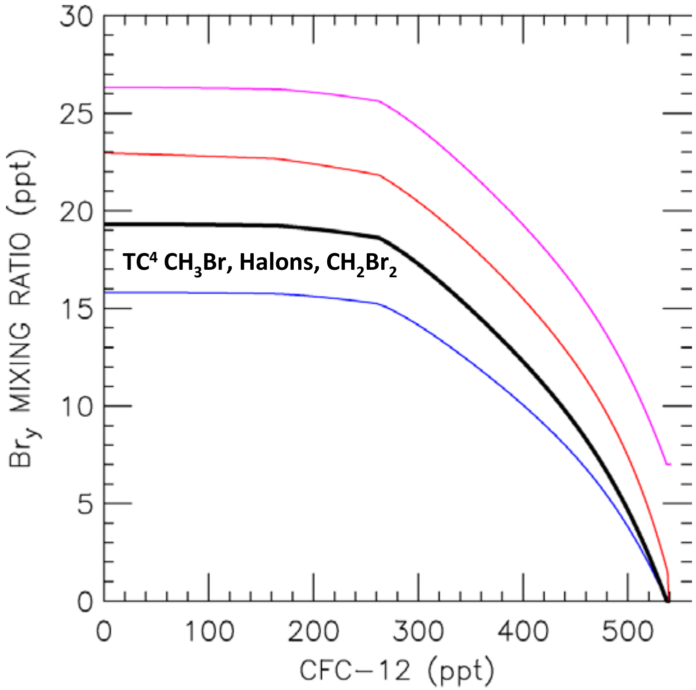
WMO Br_y implies higher trop burden than meas.

Theys, Canty, Hendrick, Van Roozendael, Chance, Kurosu, Suleiman & Salawitch

Ground Based BrO, Harestua, Norway (60ºN)

Units: 10^{13} molecules/cm^2



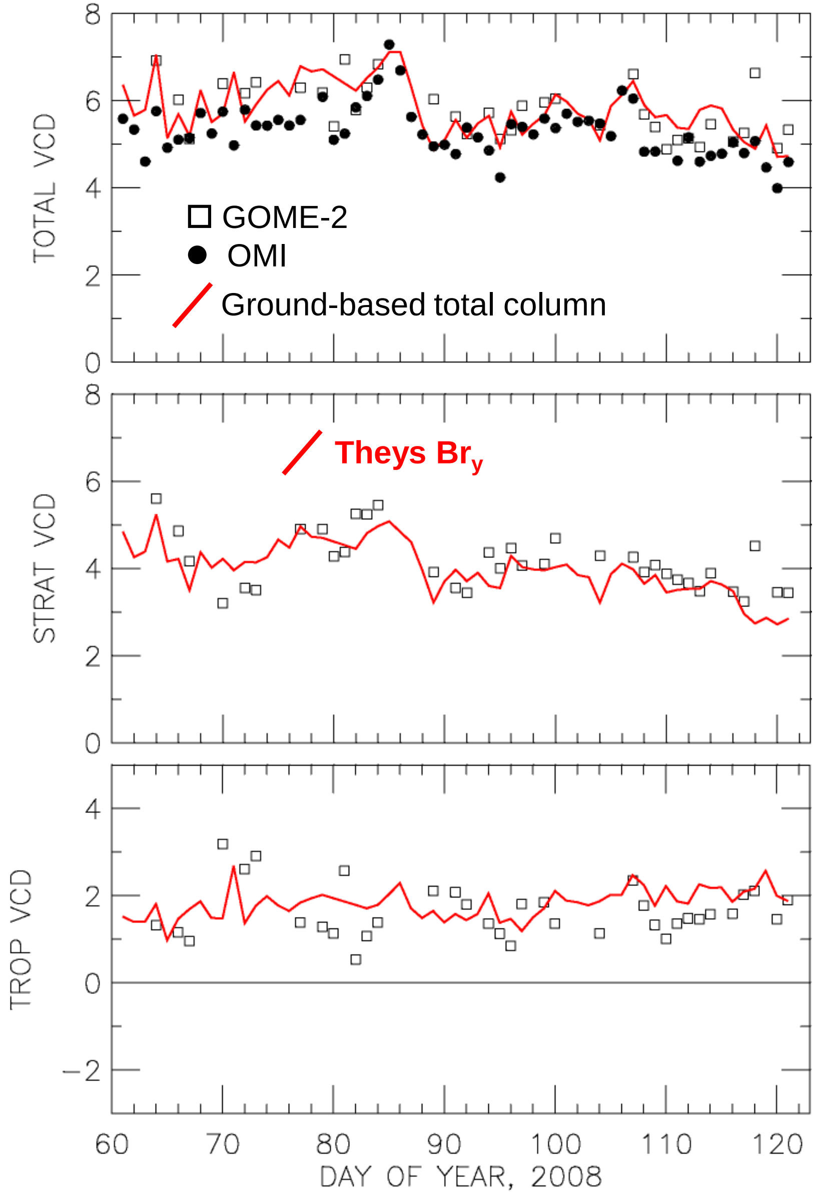


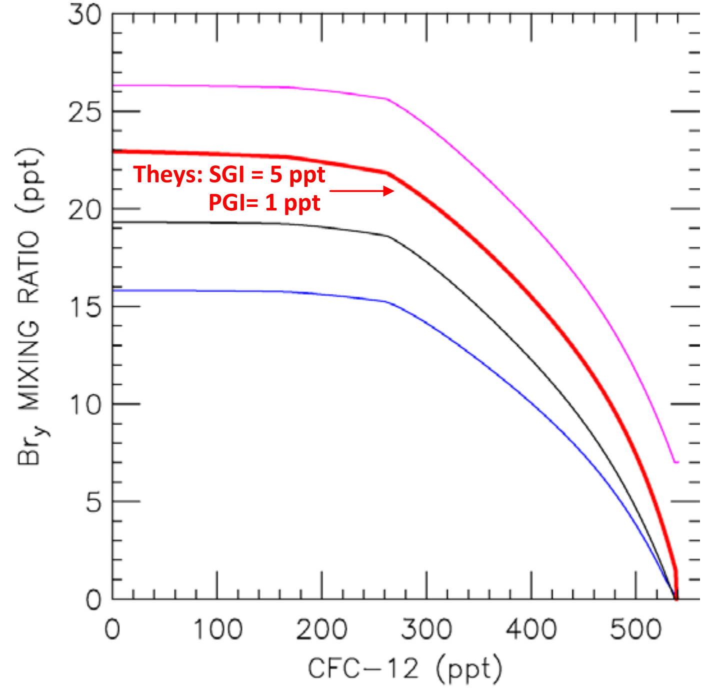
TC⁴ SGI Br$_y$ broadly consistent w/ meas trop BrO

Theys, Canty, Hendrick, Van Roozendael, Chance, Kurosu, Suleiman & Salawitch

Ground Based BrO, Harestua, Norway (60ºN)

Units: 10^{13} molecules/cm^2





Global Trop Extra-Polar Col BrO of 1 to 3 10^{13}

Theys et al., ACP, 2011

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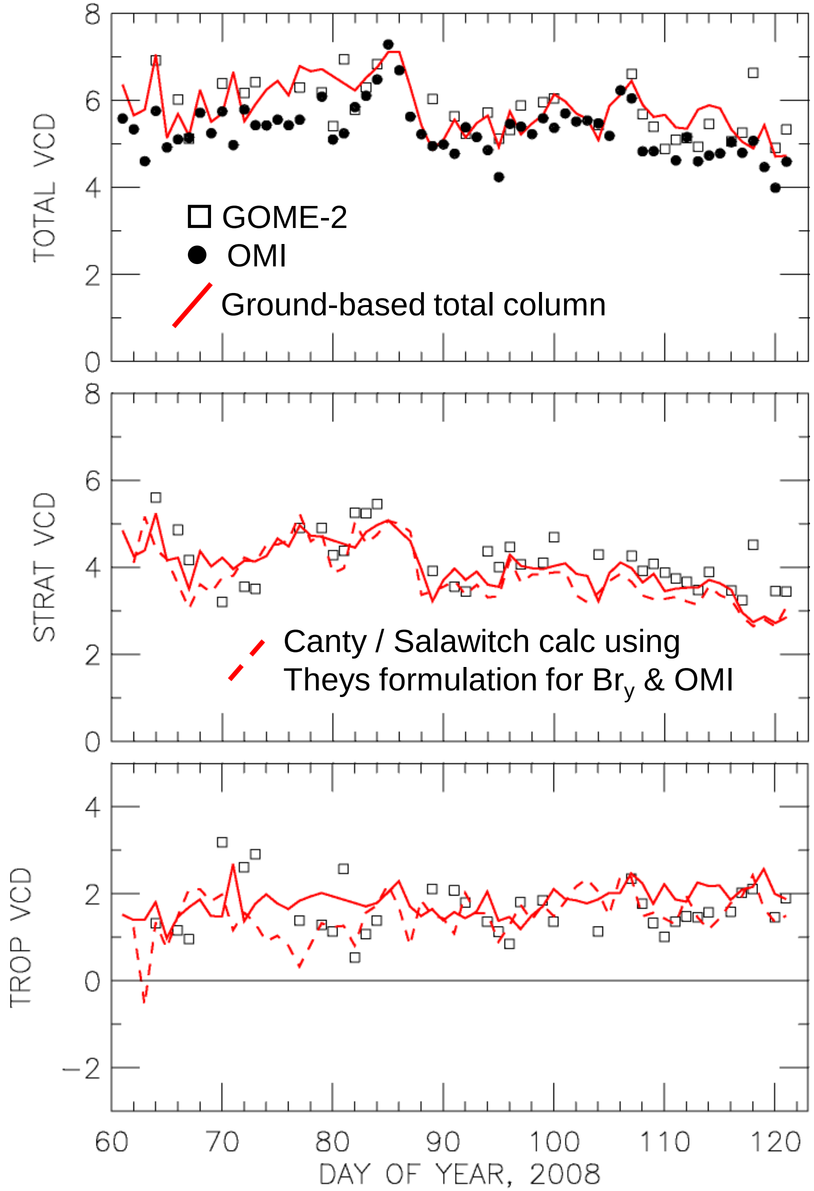

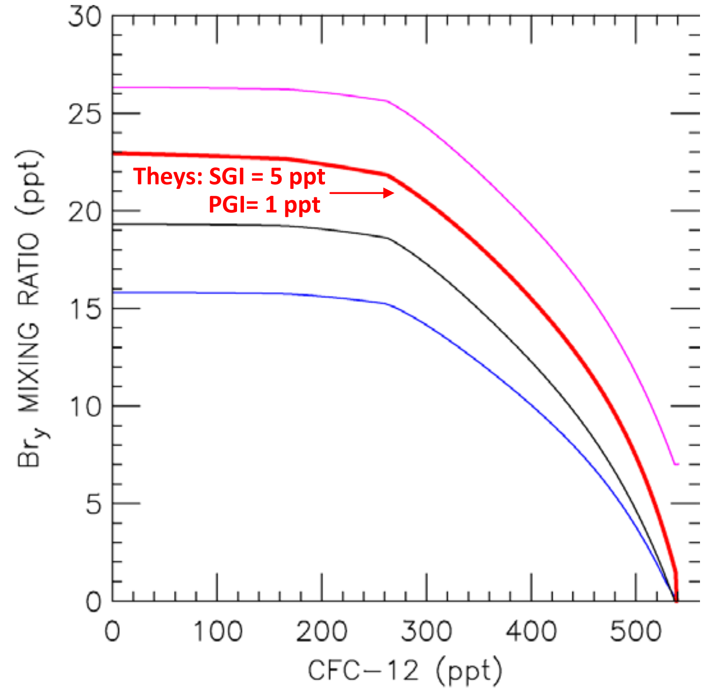

Global Trop Extra-Polar Col BrO of 1 to 3 10^{13}

Theys et al., ACP, 2011

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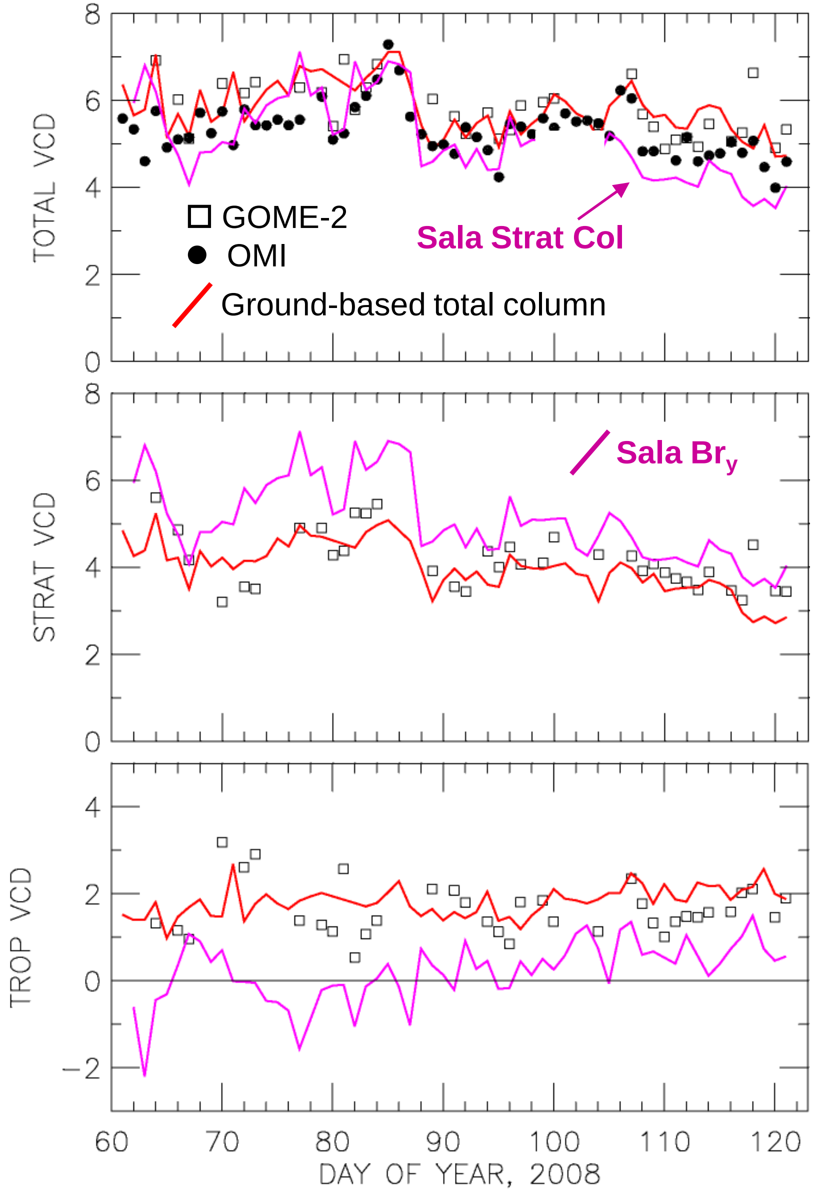
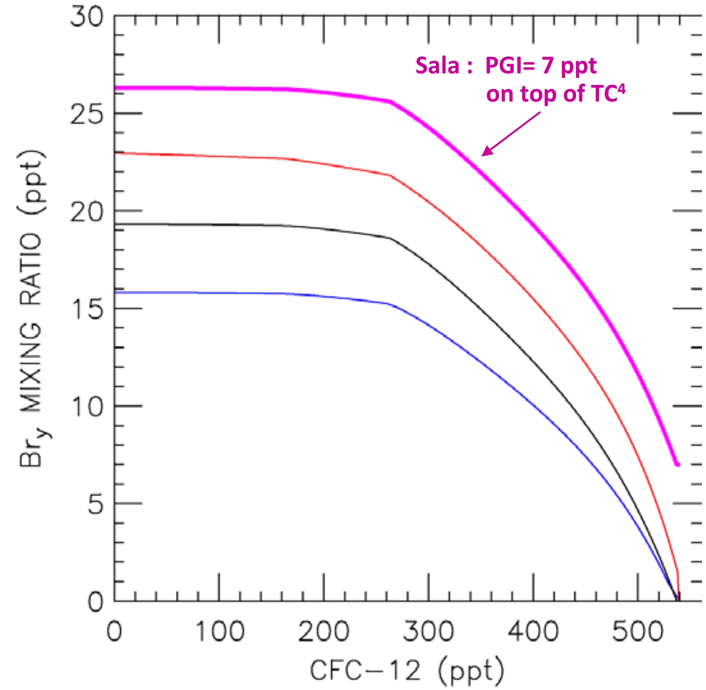
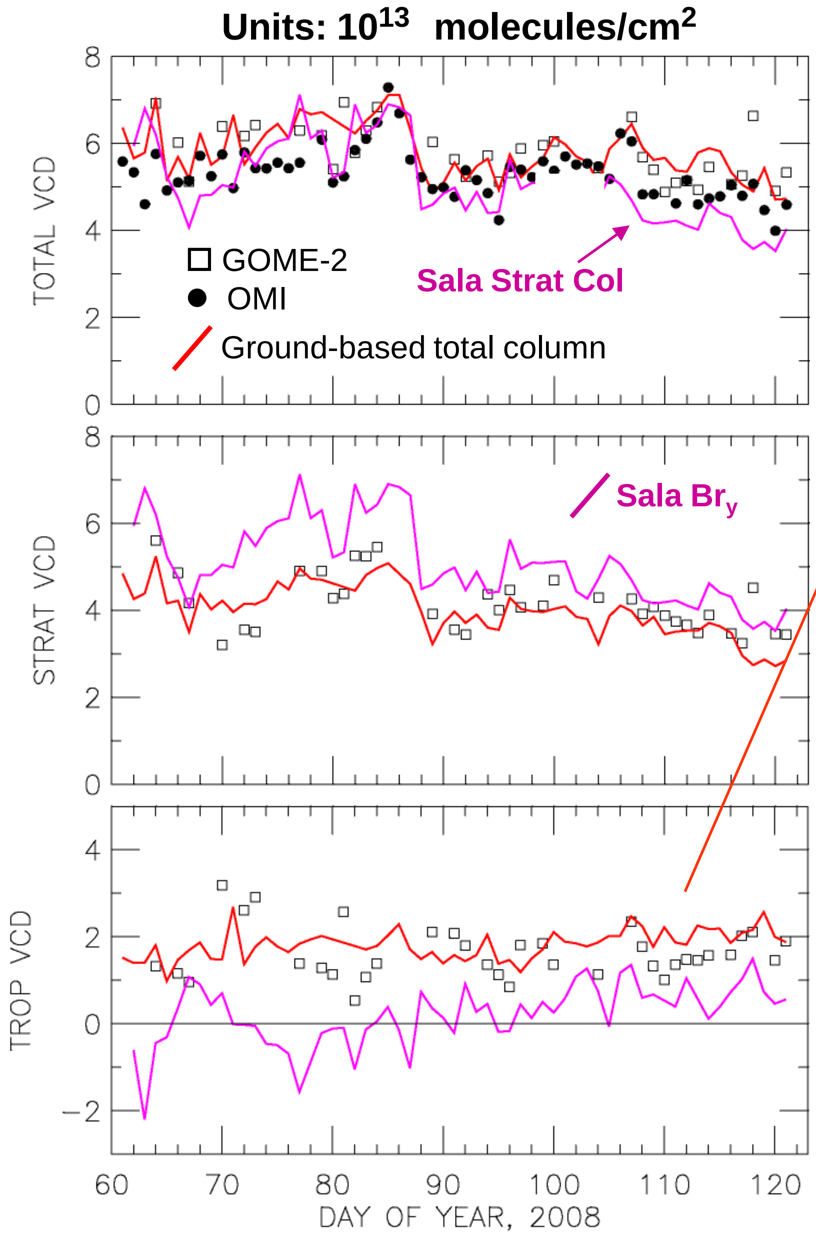




Salawitch Br_y Suggests Near-Zero
Global Tropospheric Extra-Polar Col BrO

Theys, Canty, Hendrick, Van Roozendael, Chance, Kurosu, Suleiman & Salawitch

Ground Based BrO, Harestua, Norway (60ºN)



Our tropospheric BrO background column of 1 to 3 10^{13} tends to confirm the findings of:

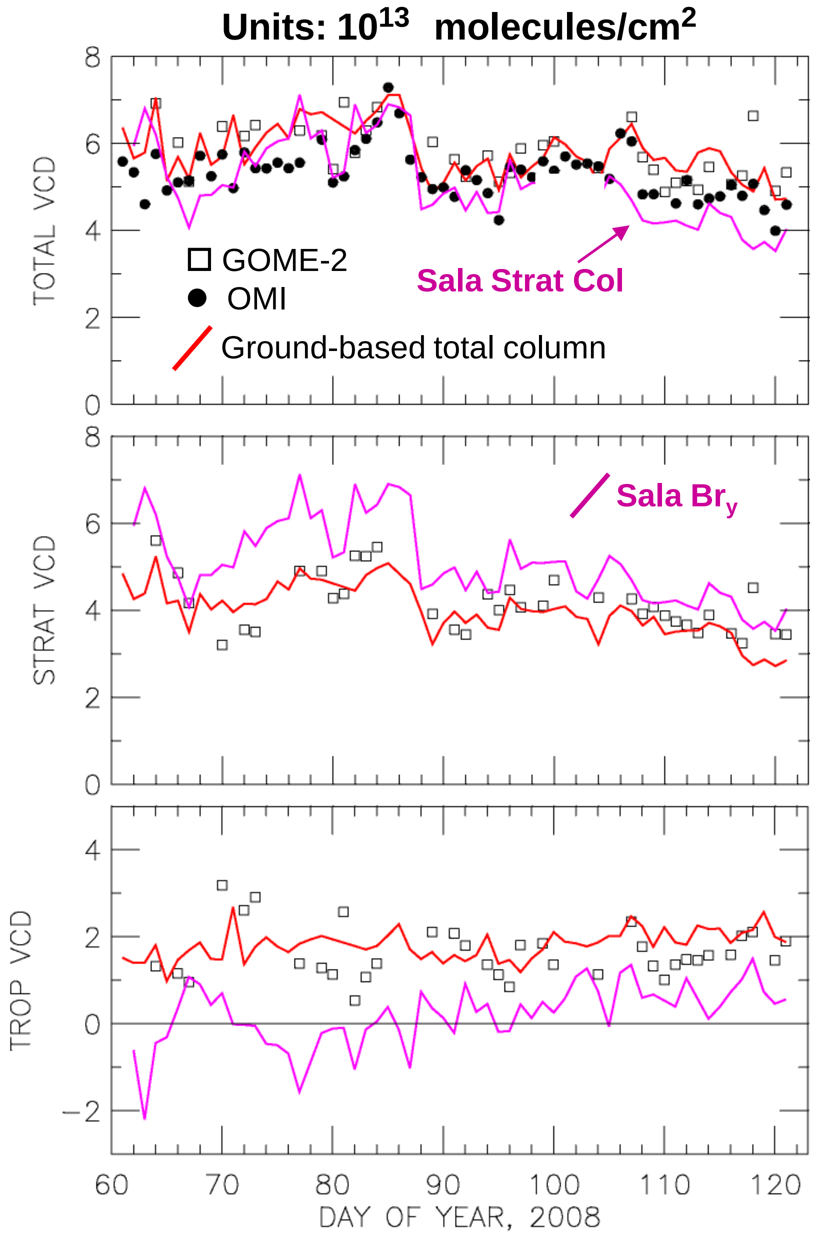
Fitzenberger et al., 2000
Wagner et al., 2001
Richter et al., 2002
Van Roozendael et al., 2002
Hendrick et al., 2007
Theys et al., 2009

Page 1807, Theys et al., 2011

Salawitch Br_y Suggests Near-Zero Global Tropospheric Extra-Polar Col BrO

Theys, Canty, Hendrick, Van Roozendael, Chance, Kurosu, Suleiman & Salawitch

Ground Based BrO, Harestua, Norway (60ºN)



Our tropospheric BrO background column of 1 to 3 10^{13} is in *contrast* to direct-sun spectral observations of:

Schofield et al., 2004 (Lauder, NZ)
Schofield et al., 2006 (Antarctica)
Dorf et al., 2008 (Tropics)

all showing tropospheric columns of 0.2 to 0.3 10^{13} molec/cm^2 … more study is needed

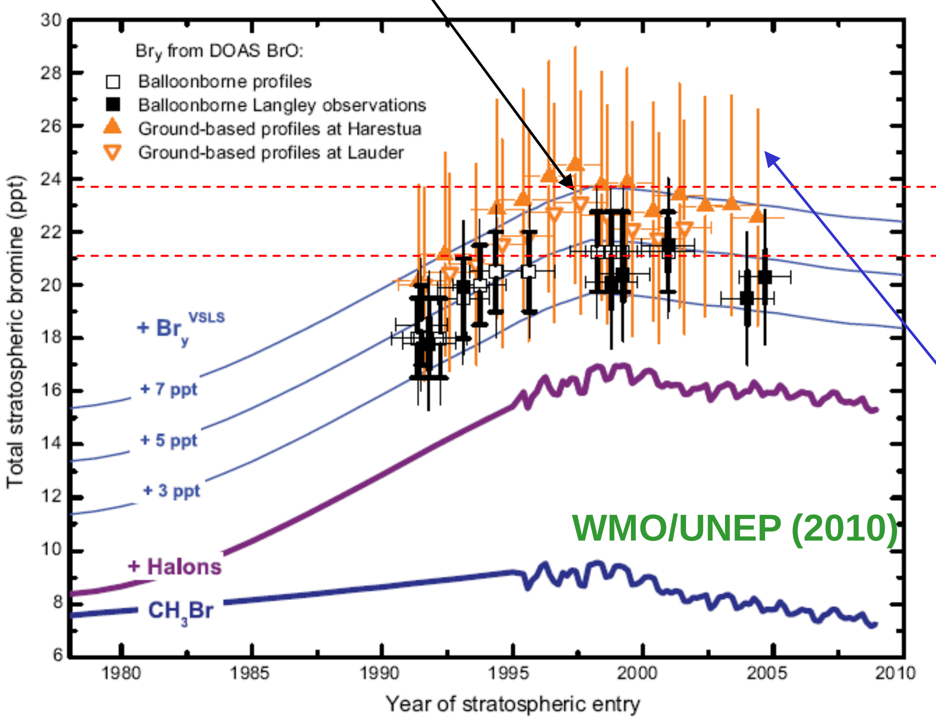
Page 1807, Theys et al., 2011

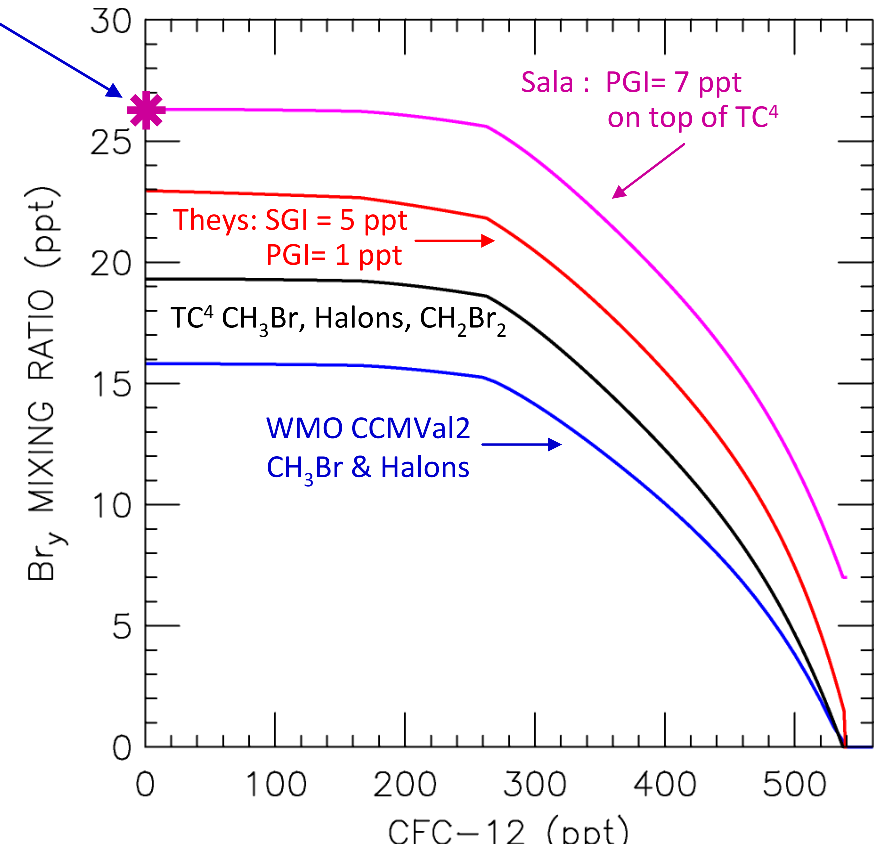
Salawitch Br_y Suggests Near-Zero Global Tropospheric Extra-Polar Col BrO

Theys, Canty, Hendrick, Van Roozendael, Chance, Kurosu, Suleiman & Salawitch

Can stratospheric bromine loading be this high ?!?

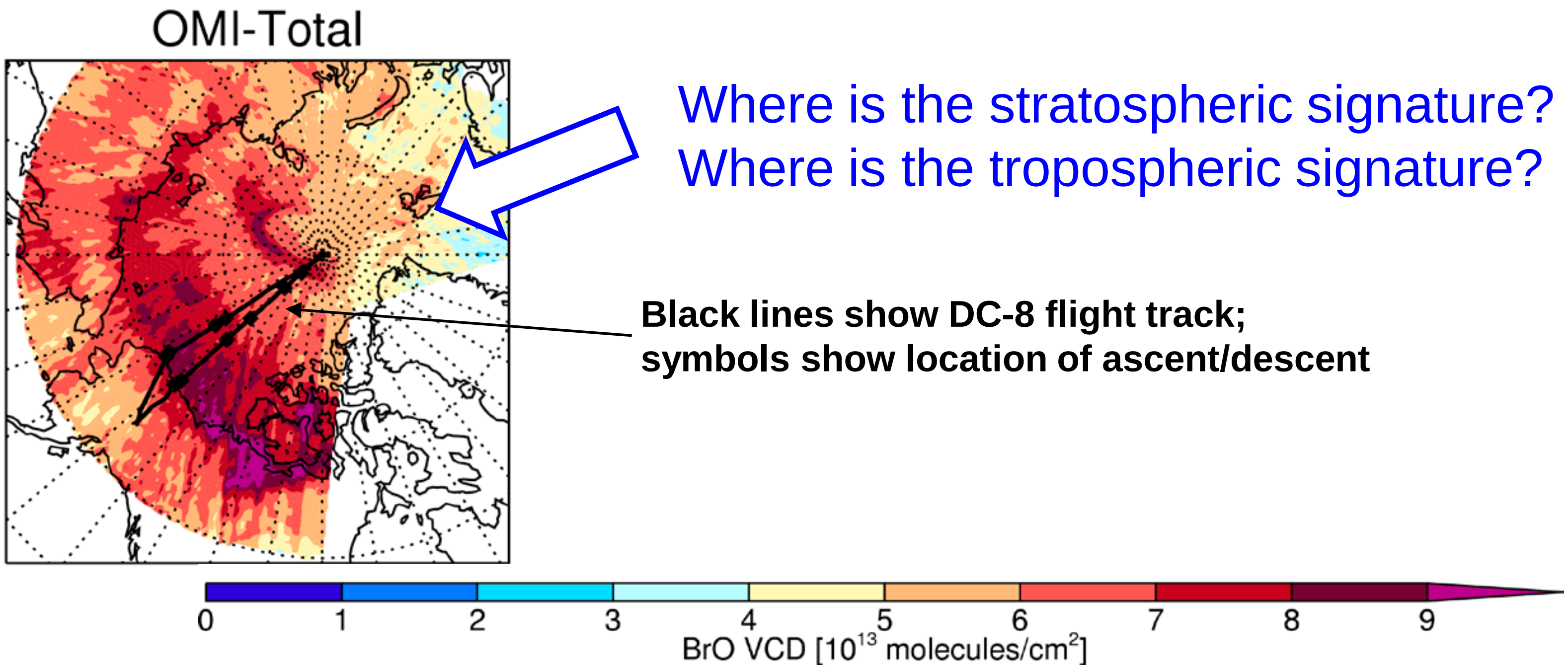
Total bromine inferred from upper stratos. BrO peaks at 21.5 to 24 ppt (depending on data source)





1. **Uncertainties of some inferences, which include meas. uncert & kinetics that govern BrO/Br_y in upper strat, encompass 26 ppt**
2. **Total column BrO from space uncertain at least by ~22%**
3. **BrO/Br_y in lower strat. sensitive to $k_{BrO+NO2+M}$ Rate constant reported by different lab groups varies greatly, especially at low temp.**

ARCTAS Flight of 17 April 2008



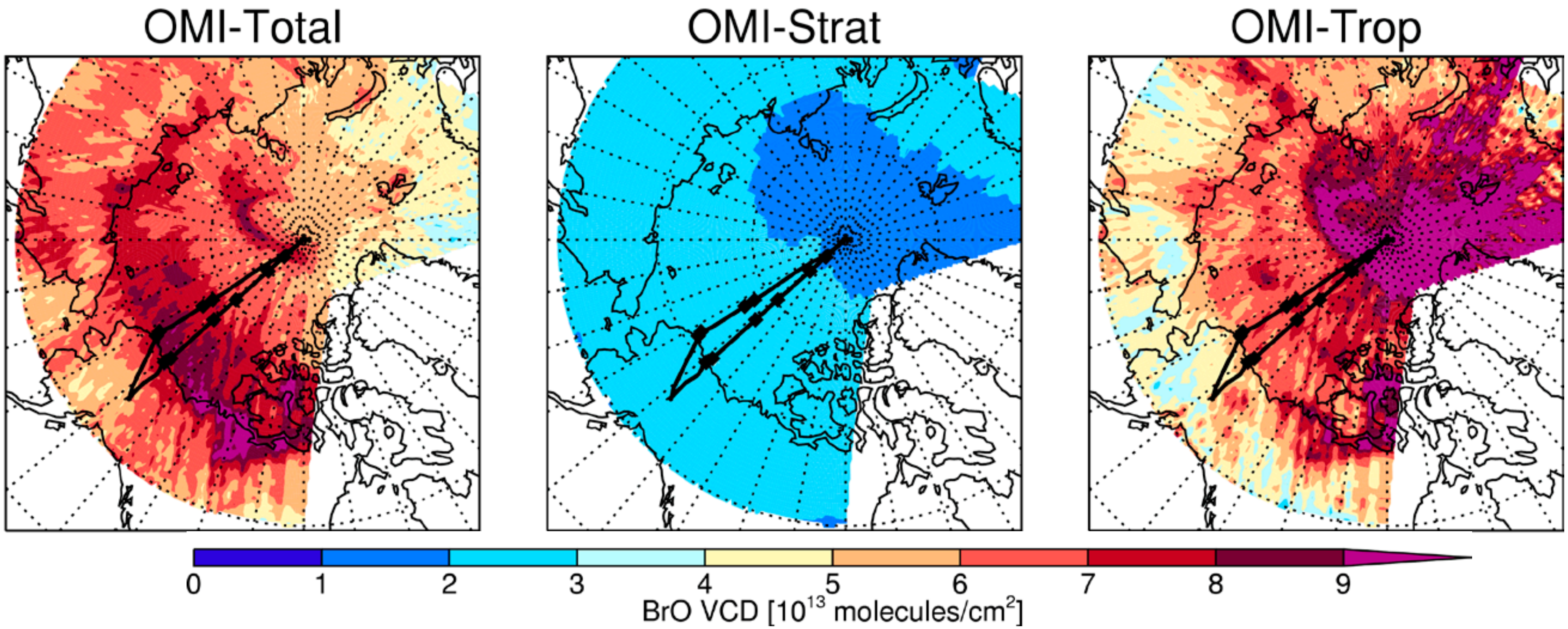
Where is the stratospheric signature?
Where is the tropospheric signature?

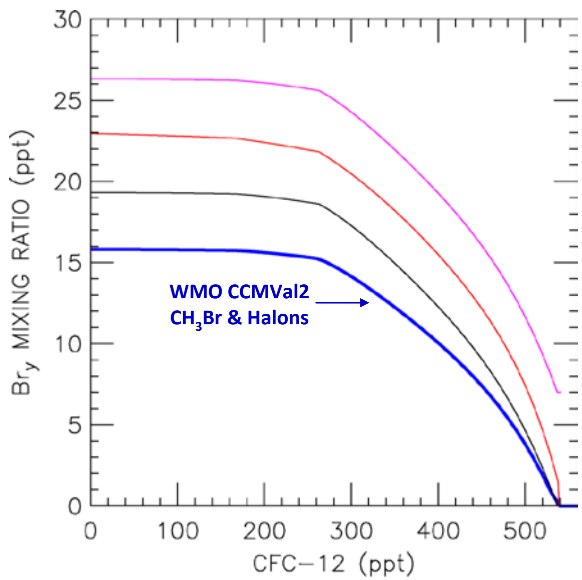
Black lines show DC-8 flight track; symbols show location of ascent/descent

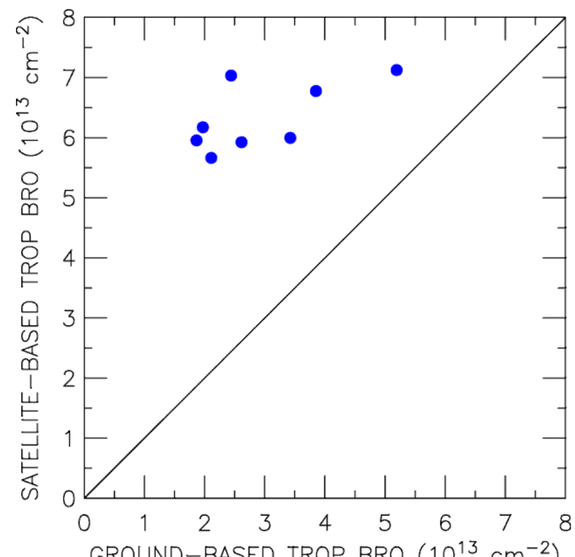
Sunny Choi & Joanna Joiner's analysis of clouds, viewing geometry, and surface albedo suggests *<u>17 April 2008</u>* provided IDEAL CONDITIONS for remote sensing of tropospheric BrO from space!

Choi et al., ACPD, 2011
Liao et al., ACPD, 2011

ARCTAS Flight of 17 April 2008

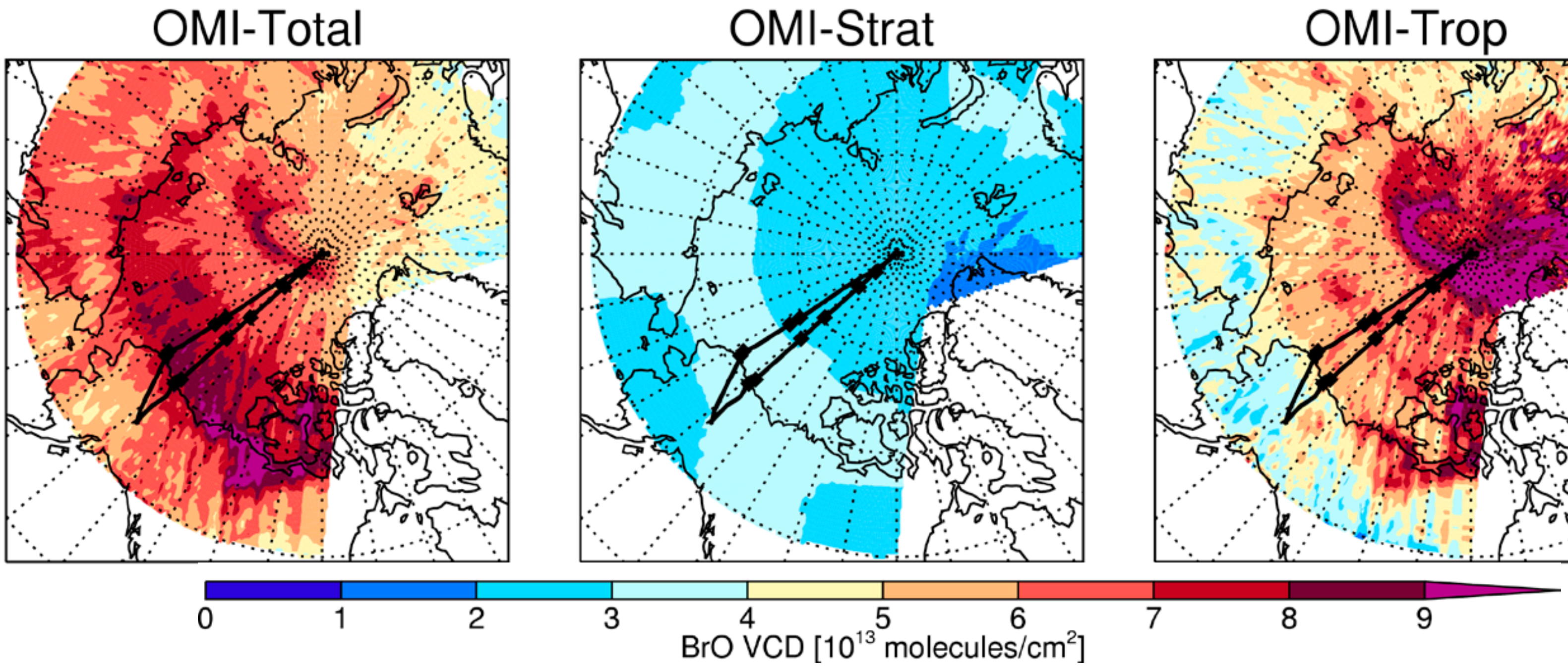


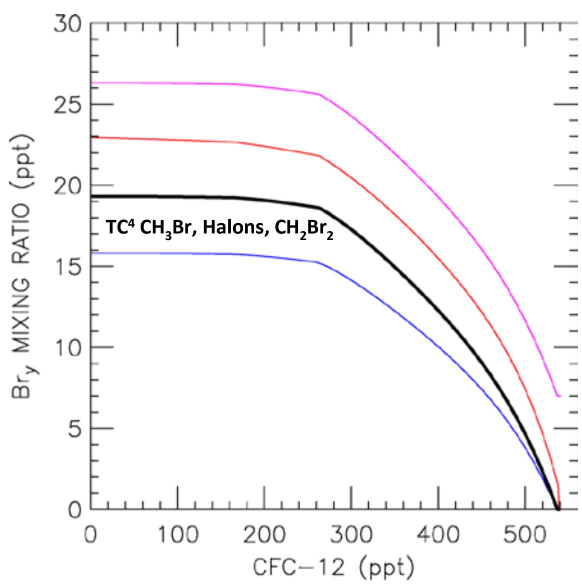


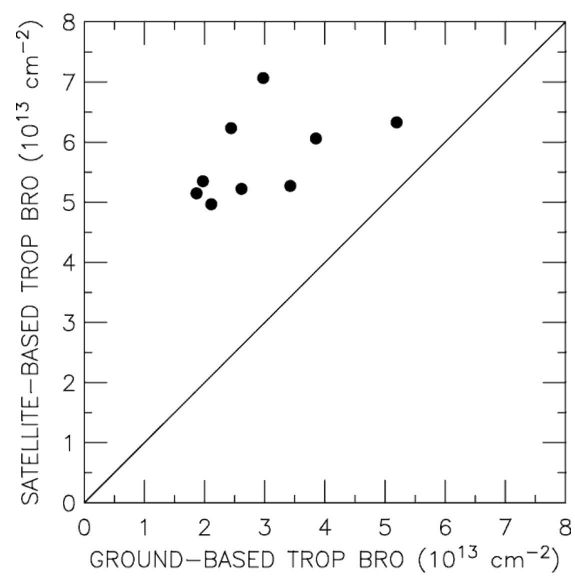


Choi et al., ACPD, 2011
Liao et al., ACPD, 2011

ARCTAS Flight of 17 April 2008







Choi et al., ACPD, 2011
Liao et al., ACPD, 2011

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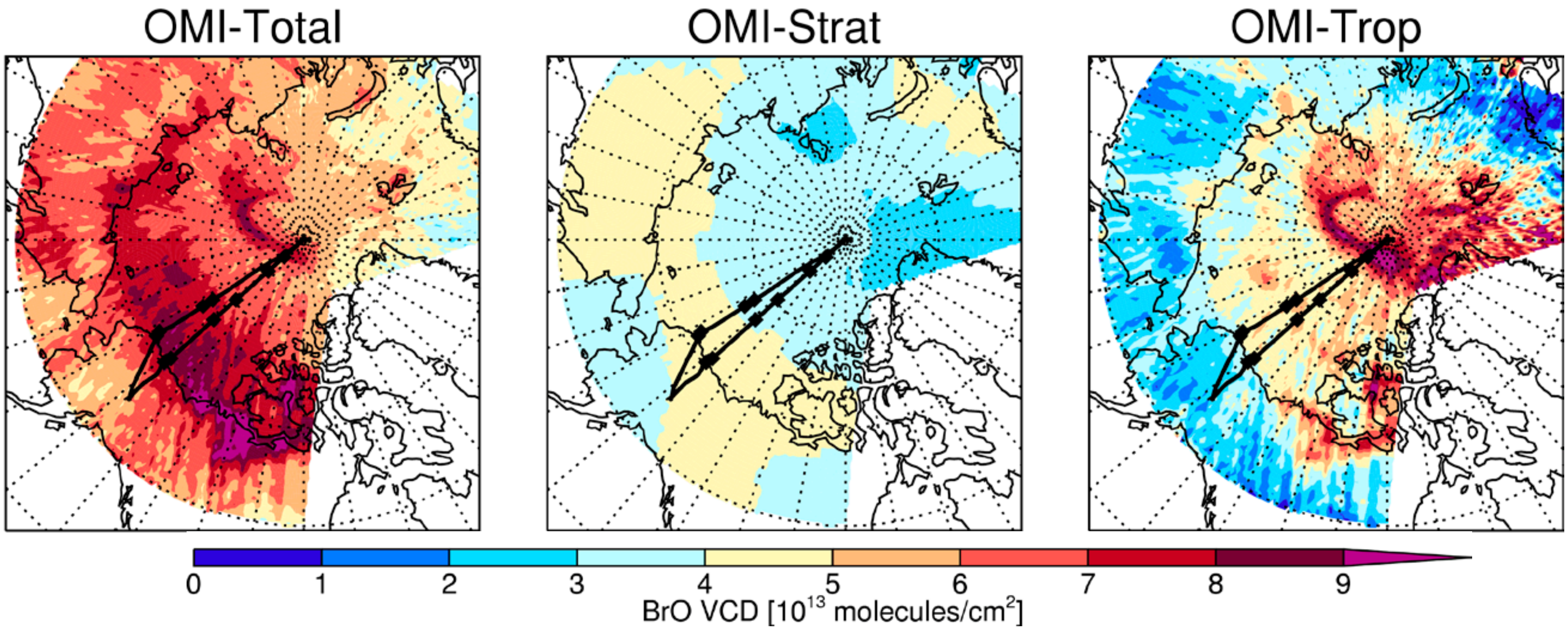
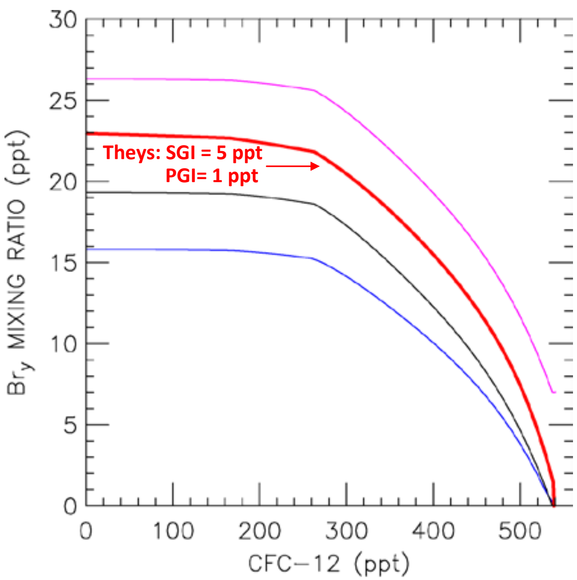
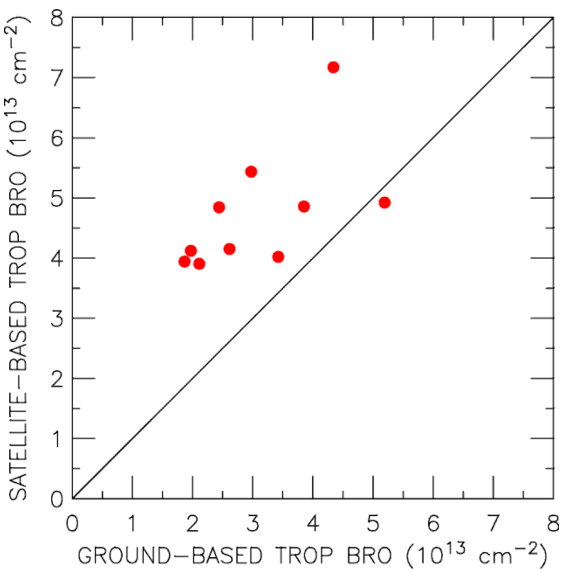
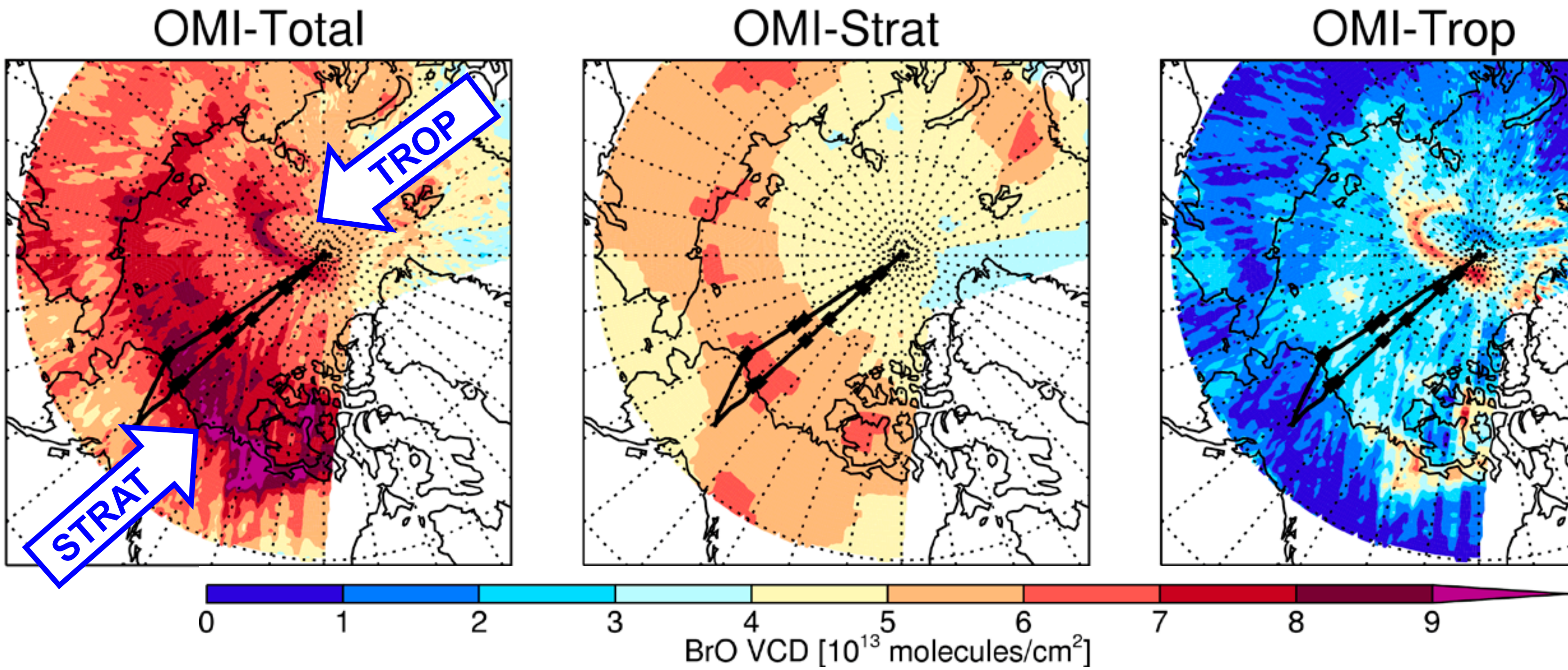


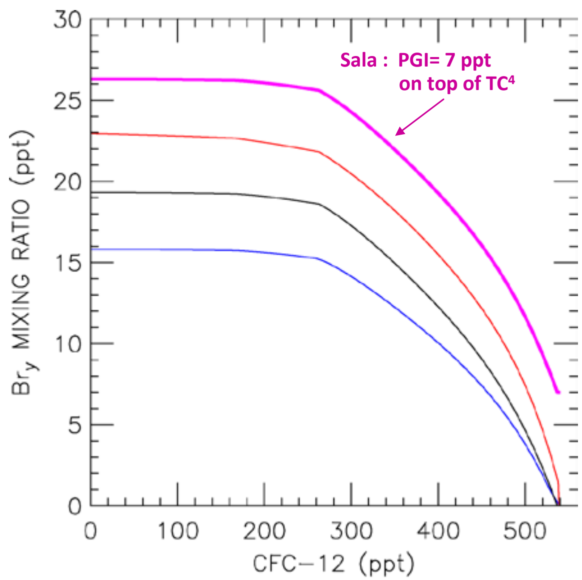


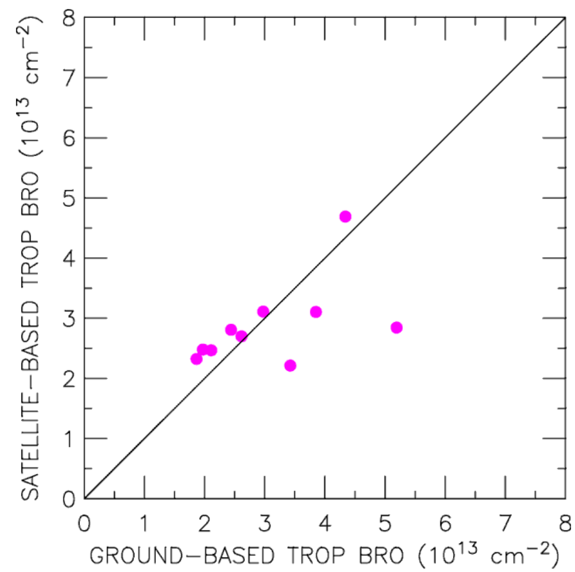


Choi et al., ACPD, 2011
Liao et al., ACPD, 2011

ARCTAS Flight of 17 April 2008

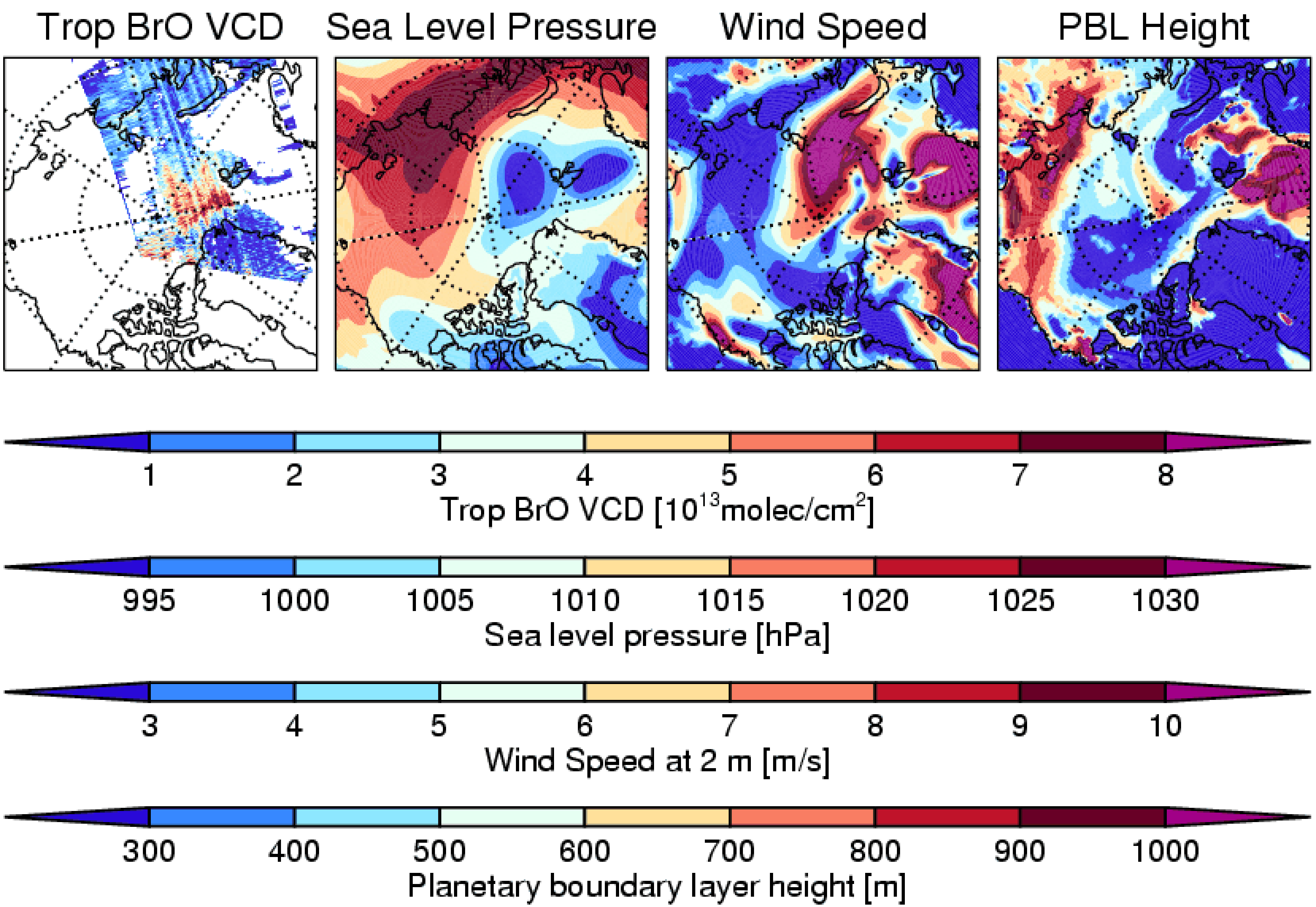






Choi et al., ACPD, 2011
Liao et al., ACPD, 2011

Apr 16 2008
07:17 (OMI orbit 19965)



Choi et al., ACPD, 2011

See poster by Choi et al. on Wednesday for more details!

Conclusions

Consensus:

1. **Stratosphere has more bromine than can be supplied by CH_3Br & Halons**
2. **Must account for spatial variability in stratospheric BrO when inferring tropospheric BrO from satellite measurements of column BrO**
3. **BrO "clouds" exist at high latitude in spring, associated with high wind blowing in regions of snow over first year sea ice**

Lack of consensus on how to handle stratospheric contribution

One school of thought:

Not much BrO just above tropop

Existence of global, ubiquitous, extra-polar tropospheric BrO of 1 to 3 10^{13} cm^{2} (2 to 3 ppt) with important consequences for:

- **Tropospheric O_3**
- **Hg**
- **DMS**

Another school of thought:

Lots of BrO just above tropop with important consequences for:

- **Polar Strat Ozone Depletion**
- **Mid-Lat Column Ozone Trends**

Global, ubiquitous, extra-polar tropospheric BrO small or perhaps non-existent

Conclusions

Consensus:

1. **Stratosphere has more bromine than can be supplied by CH_3Br & Halons**
2. **Must account for spatial variability in stratospheric BrO when inferring tropos… …BrO**
3. **BrO "c… …with high wind blowin…**

Lack of conse…

One school of… …ught:

Not much… …bove tropop

Existence… …nsequences for:
extra-pola… …zone Depletion
of 1 to 3… …mn Ozone Trends
with impo… …s, extra-polar
…small or perhaps

Tropo…
Hg
DMS

Must measure BrO and related species in:

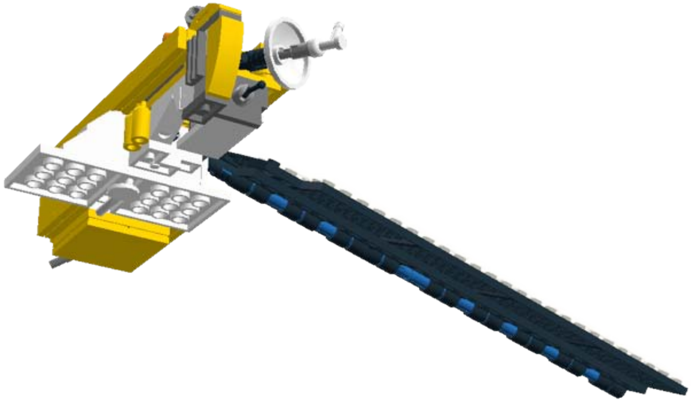
a) tropical tropopause layer (strat entry)
b) polar BL to lower strat
c) extra-polar troposphere

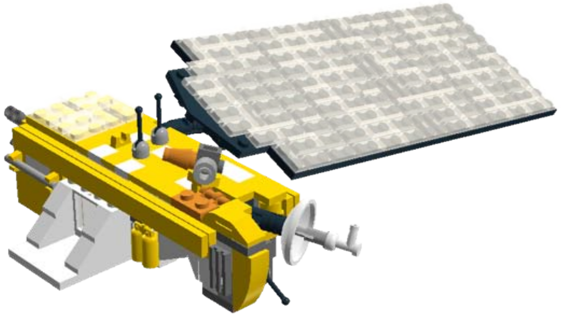
to sort this out !

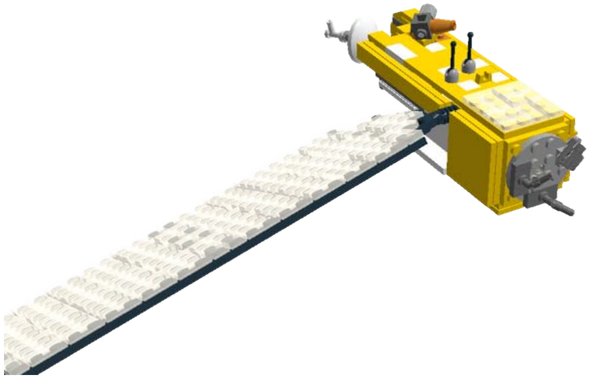
Future work:

Use MFDOAS data to define proportion of BrO col. In trop., strat.

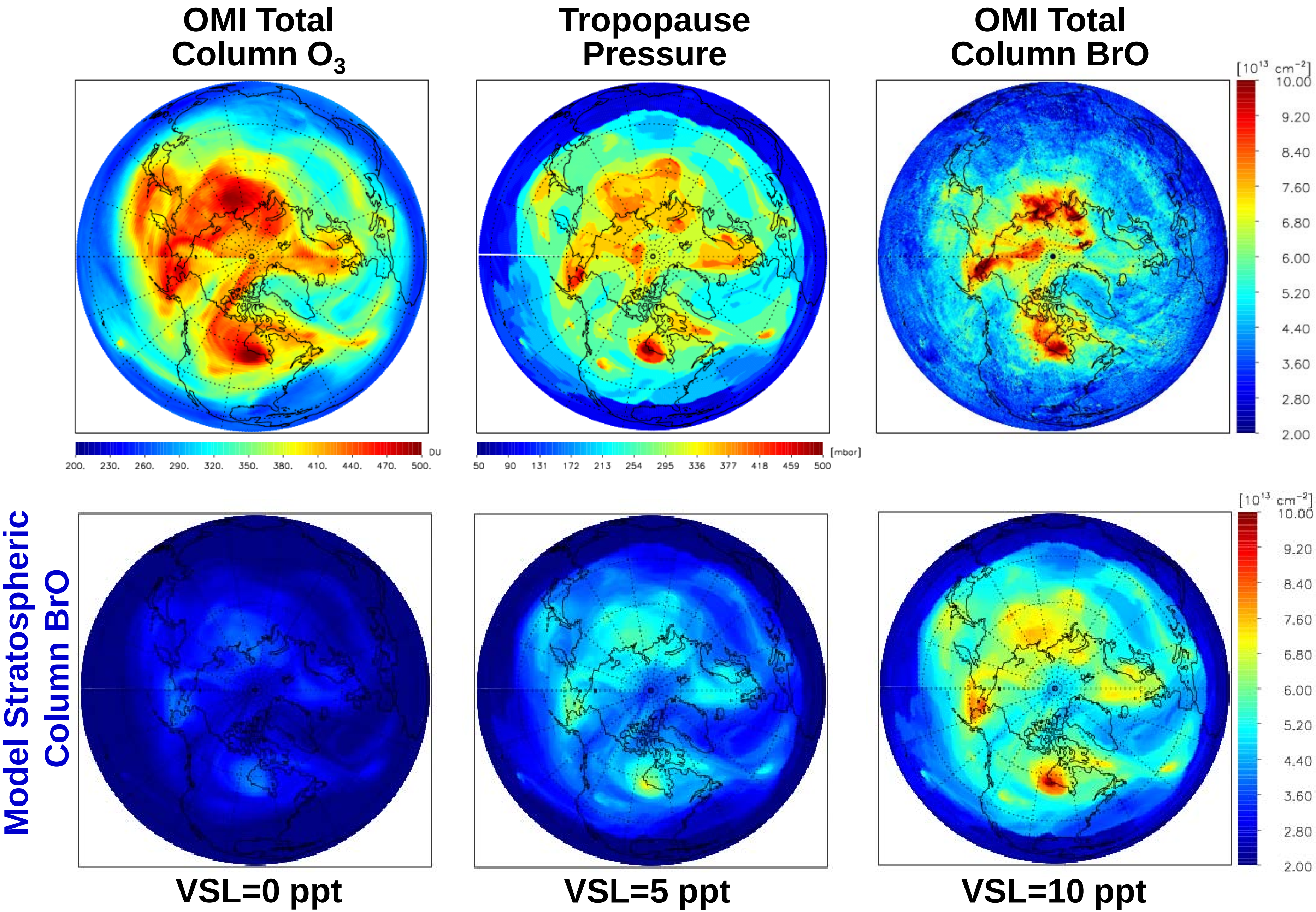
Thank You!





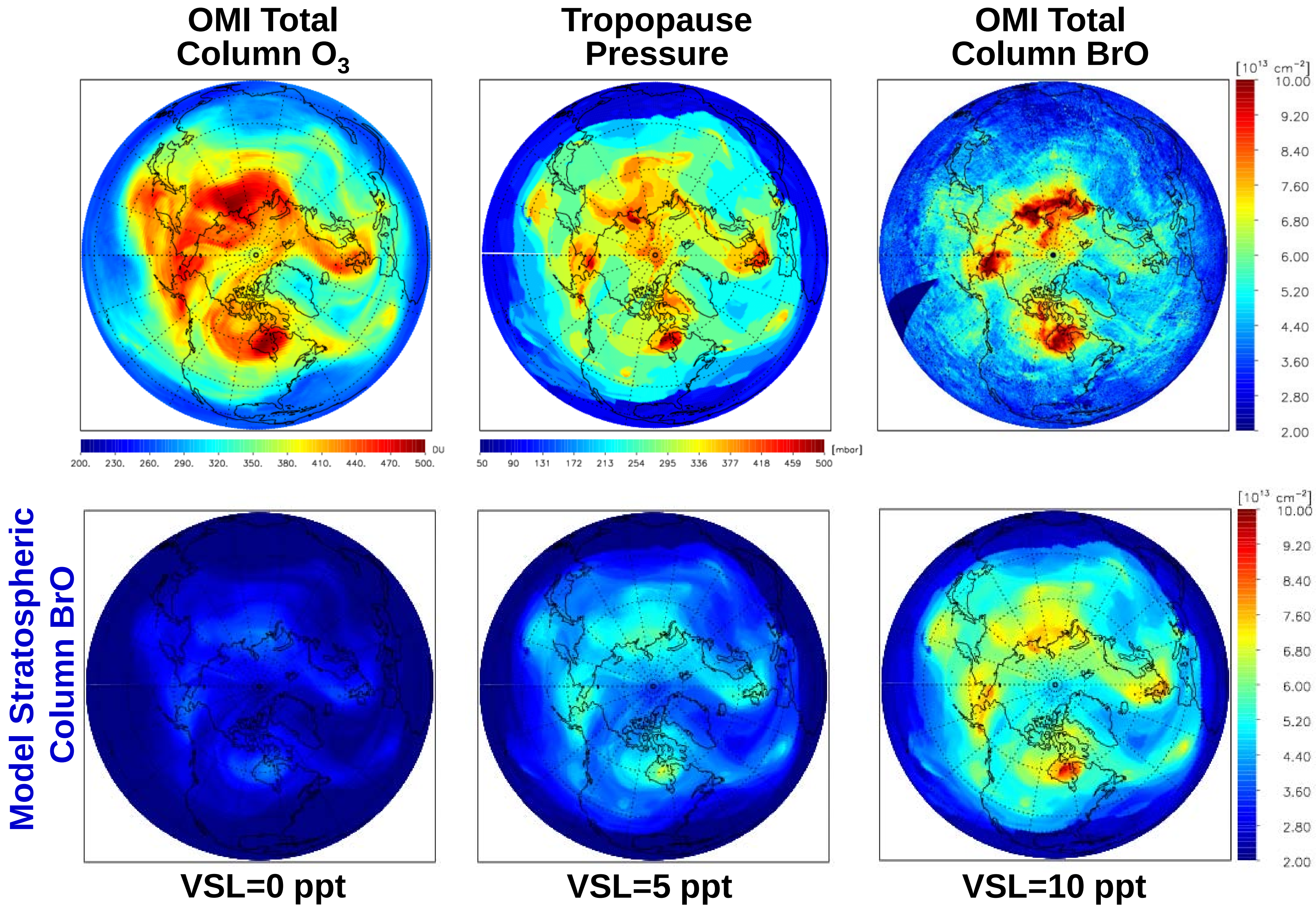


5 Apr 2008



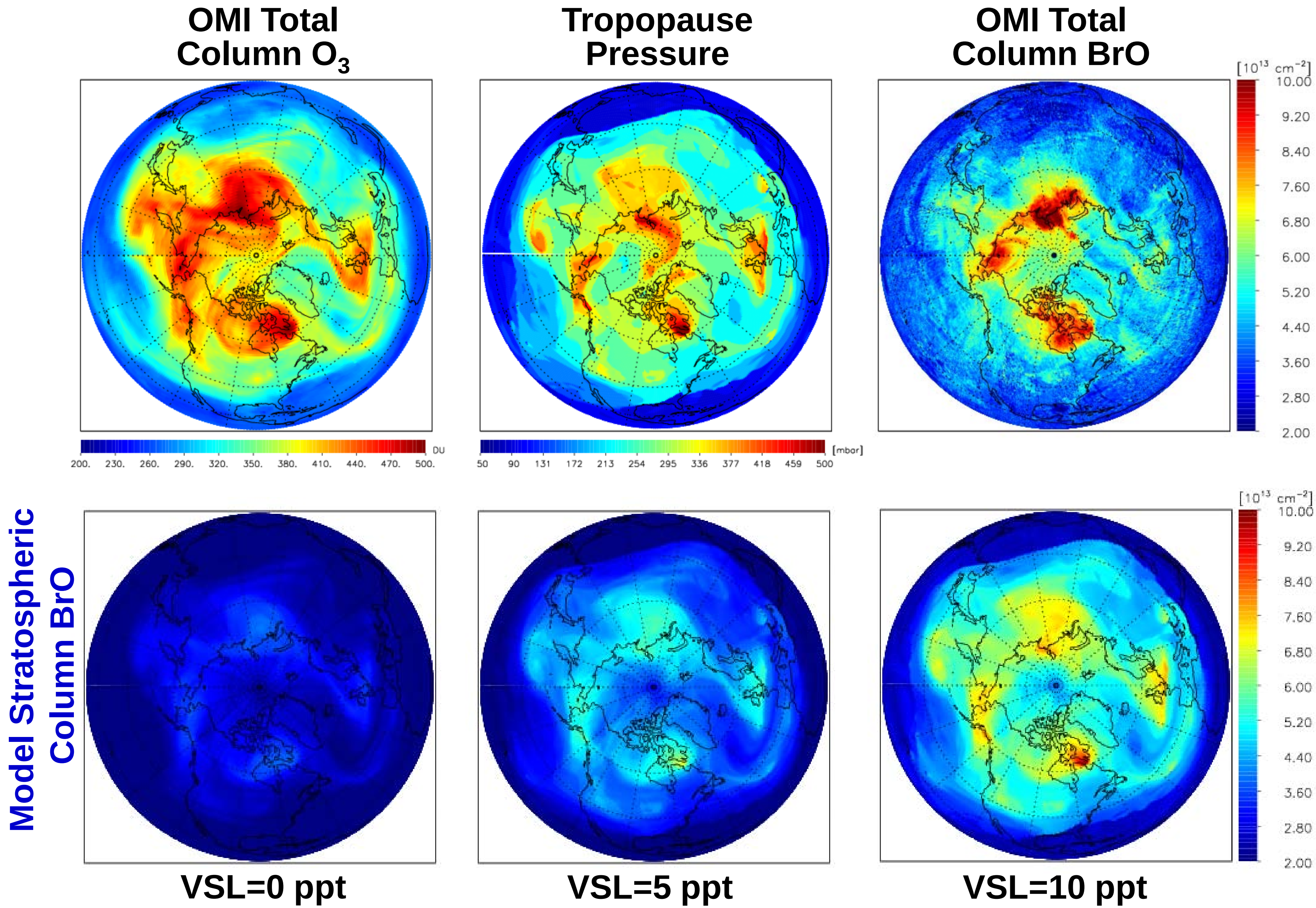
Salawitch et al., GRL, 2010

6 Apr 2008



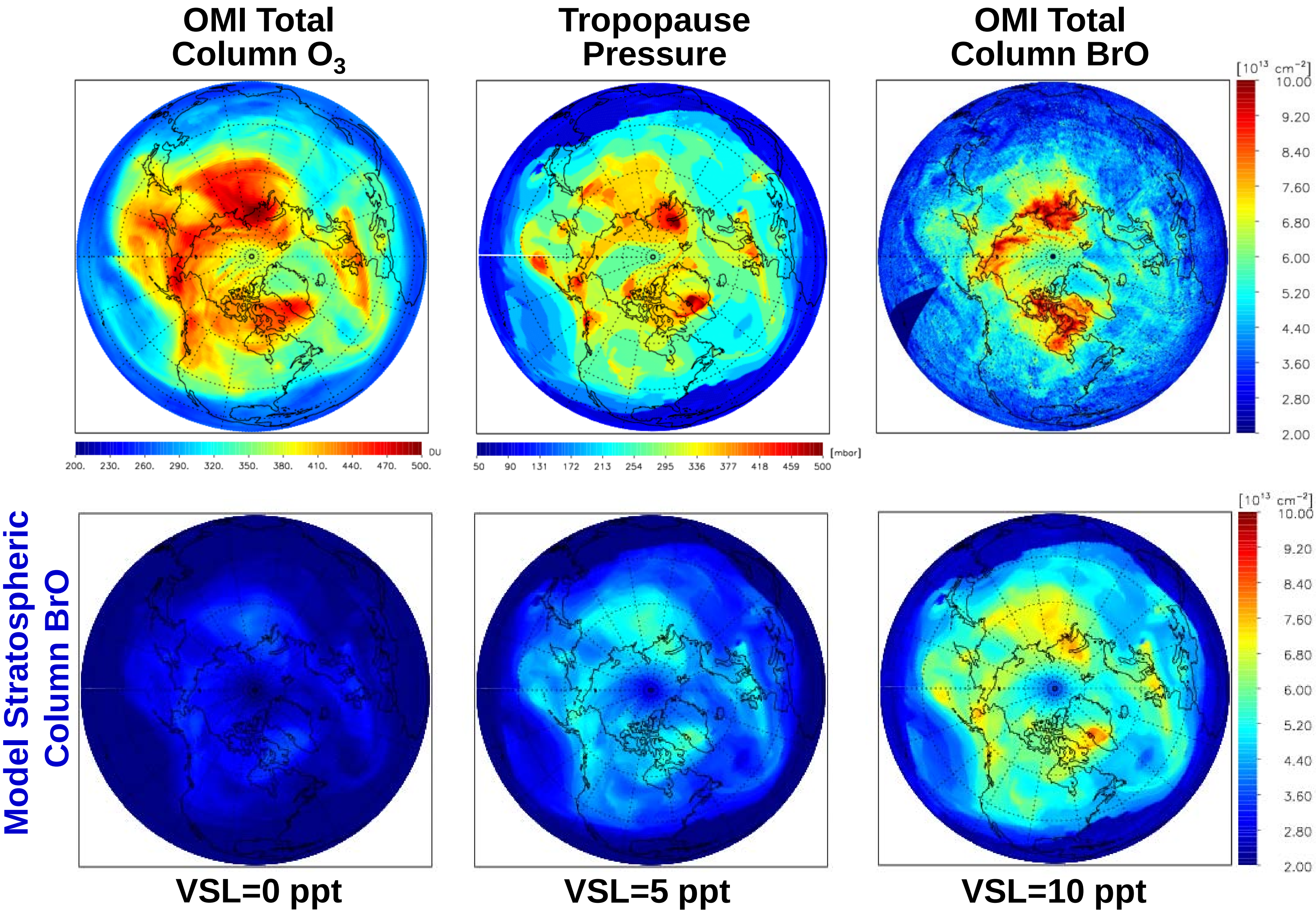
Salawitch et al., GRL, 2010

7 Apr 2008



Salawitch et al., GRL, 2010

8 Apr 2008



Salawitch et al., GRL, 2010

Data in Support of Salawitch & Theys Formulations

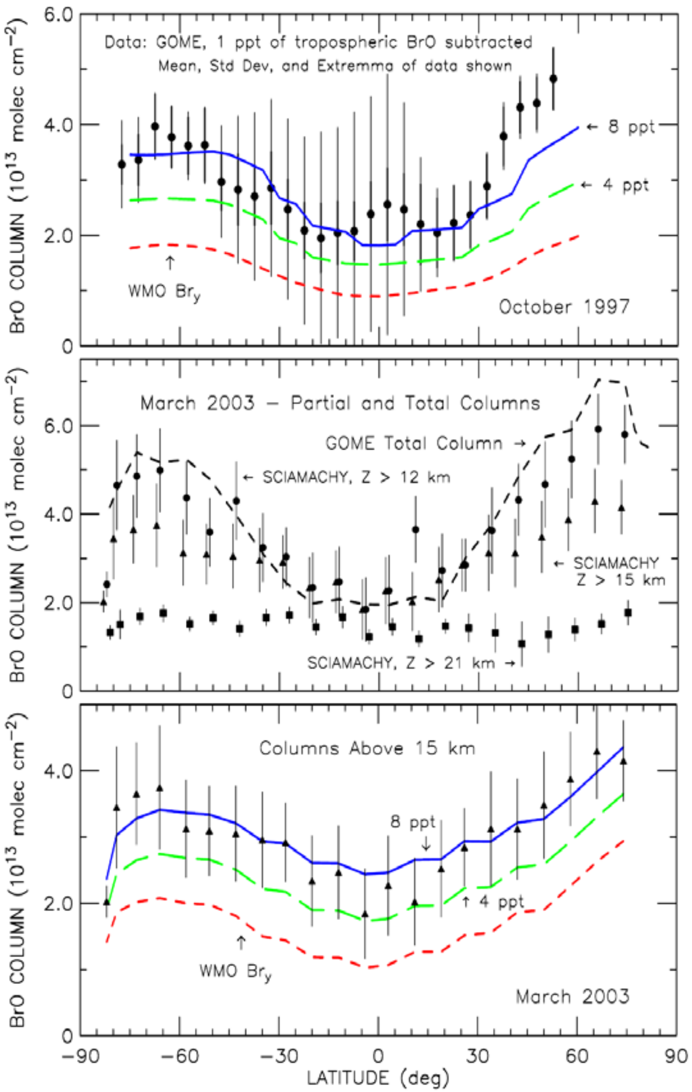


Figure 2-8, WMO/UNEP 2006, based on SCIAMACHY BrO retrievals of Sioris & Chance, **supports Salawitch formulation**

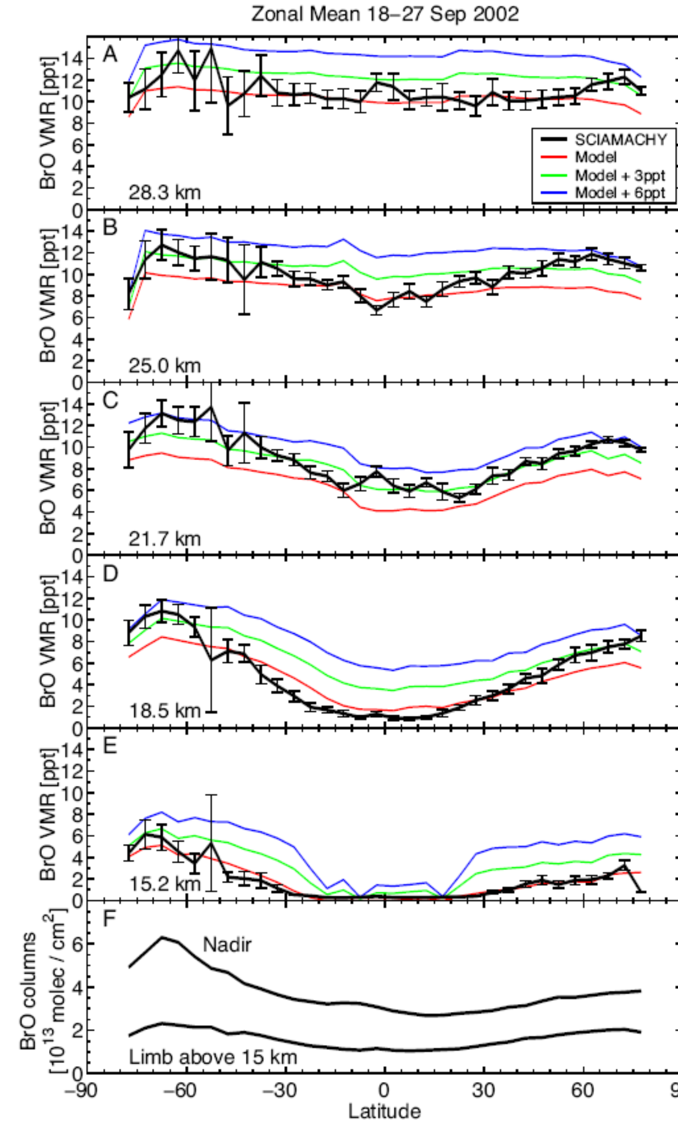


Figure 2-9, WMO/UNEP 2006, based on SCIAMACHY BrO retrievals of Rozanov & Sinnhuber, **supports Theys formulation**

15 to 22 April 2001: vertical displacement of dynamical tropopause strongly associated with synoptic disturbances controlling surface meteorology

A constant BrO mixing ratio of 3 ppt (6 ppt of Br_y) between 200 to 500 hPa (Salawitch) together with a tropospheric BrO background (Theys) could help reconcile tropospheric BrO columns simulated by GEM-AQ (blowing snow generates bromine explosion) and tropospheric BrO columns inferred from GOME

Toyota et al., ACP, page 3967, 2011

Based on relation between OMI Total Column BrO

and

Tropospheric Column BrO (many dozens of ARCTAC/ARCPAC) profiles

+

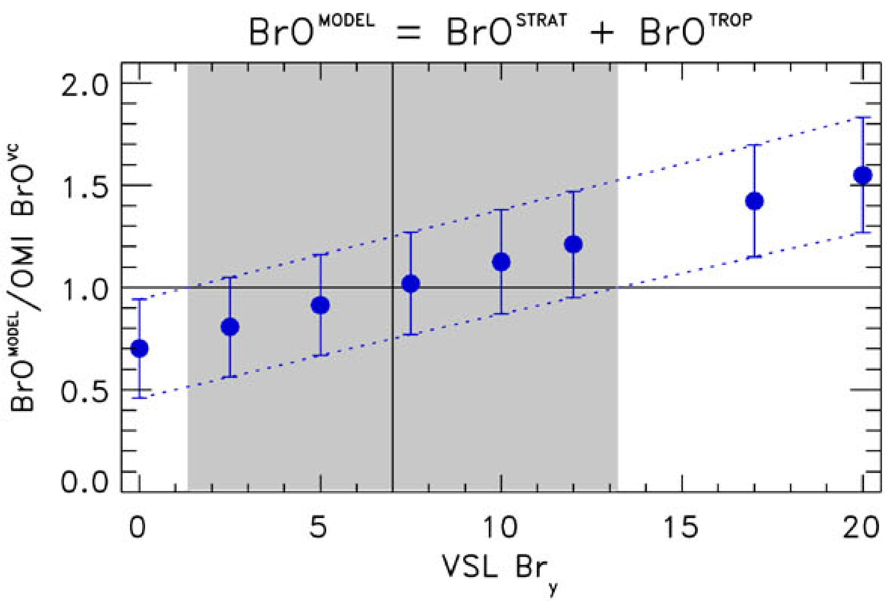
Stratospheric Column BrO (as a function of VSL Br_y)

Salawitch et al. 2010 concluded

Product Gas Injection (PGI) of 7 ppt of Br_y from VSL sources

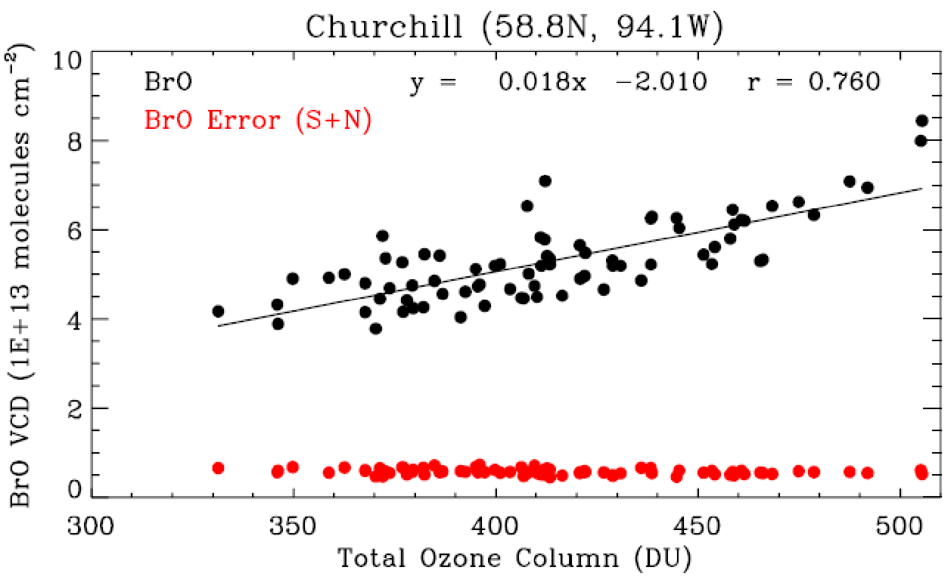
on top of the Wamsley Br_y relation (adjusted to 2008) that includes Source Gas Injection (SGI) of 2 ppt by CH_2Br_2

provides best overall fit to observations



Salawitch et al., GRL, 2010

Scientific conclusions depend on veracity of satellite column BrO



Calculations by **Xiong Liu** (UMBC):

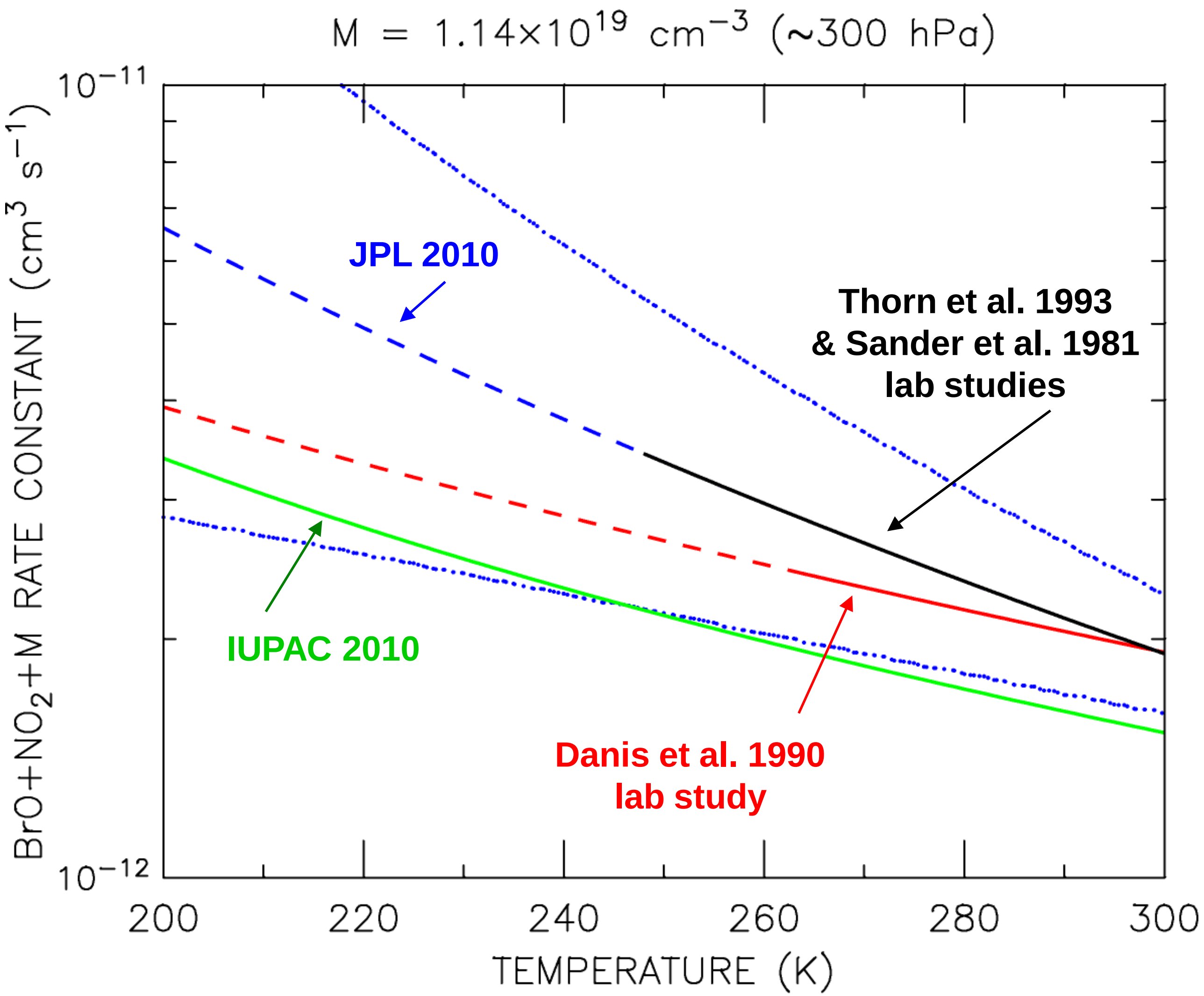
- Substantial correlation between column BrO and column O_3
- Small error (fitting residual) for column BrO
- Correlation disappears for SZA > 85 , when BrO is largely in nighttime reservoirs
- Almost no cross correlation between BrO and fitting parameters for ozone, albedo, cloud fraction, etc.

⇨ ***this indicates correlation between BrO & O_3 is not a retrieval artifact !***

- Also: Liu column BrO ~20 to 30% less than values found by Kurosu retrieval

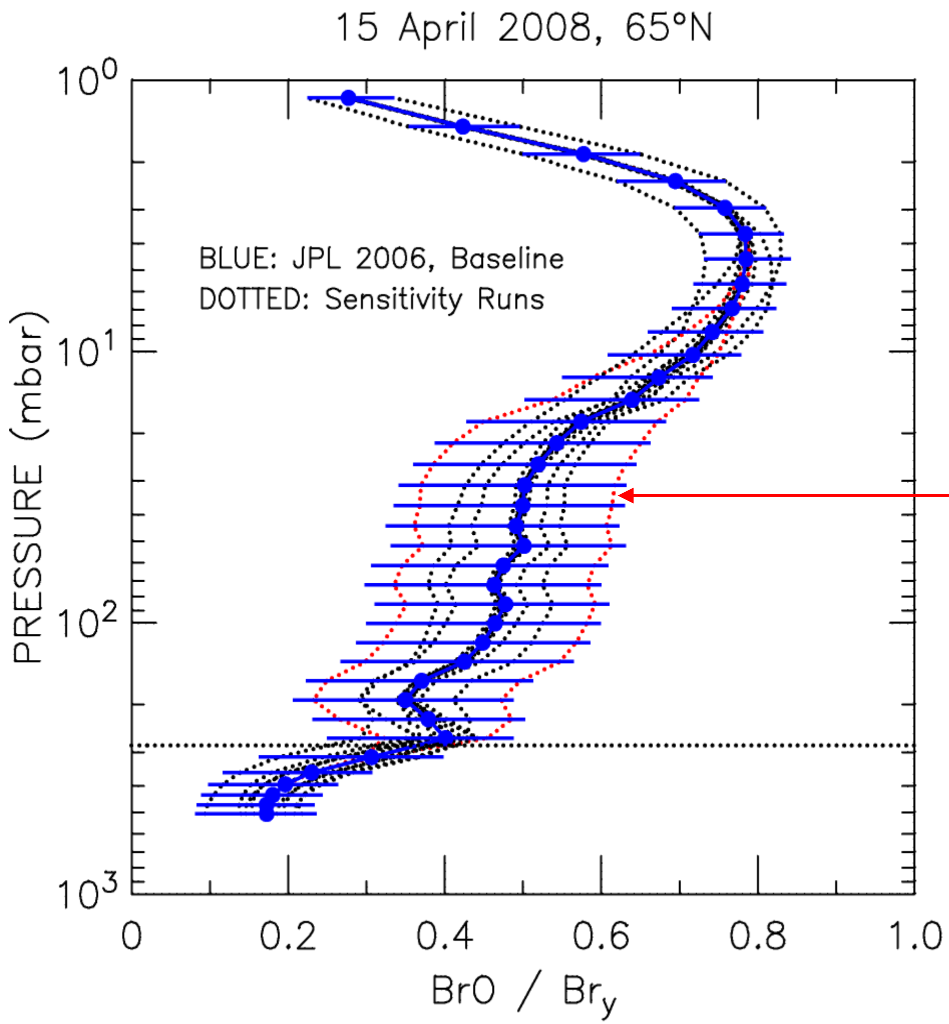
(column sensitive to fitting window, profile shape, cloud fraction, surface albedo)
Liu retrievals are preliminary!

BrO/Br_y in lowermost stratos sensitive to $k_{BrO+NO2+M}$



Model Uncertainty

Model BrO **depends on accuracy of kinetics that govern BrO/Br_y ratio**



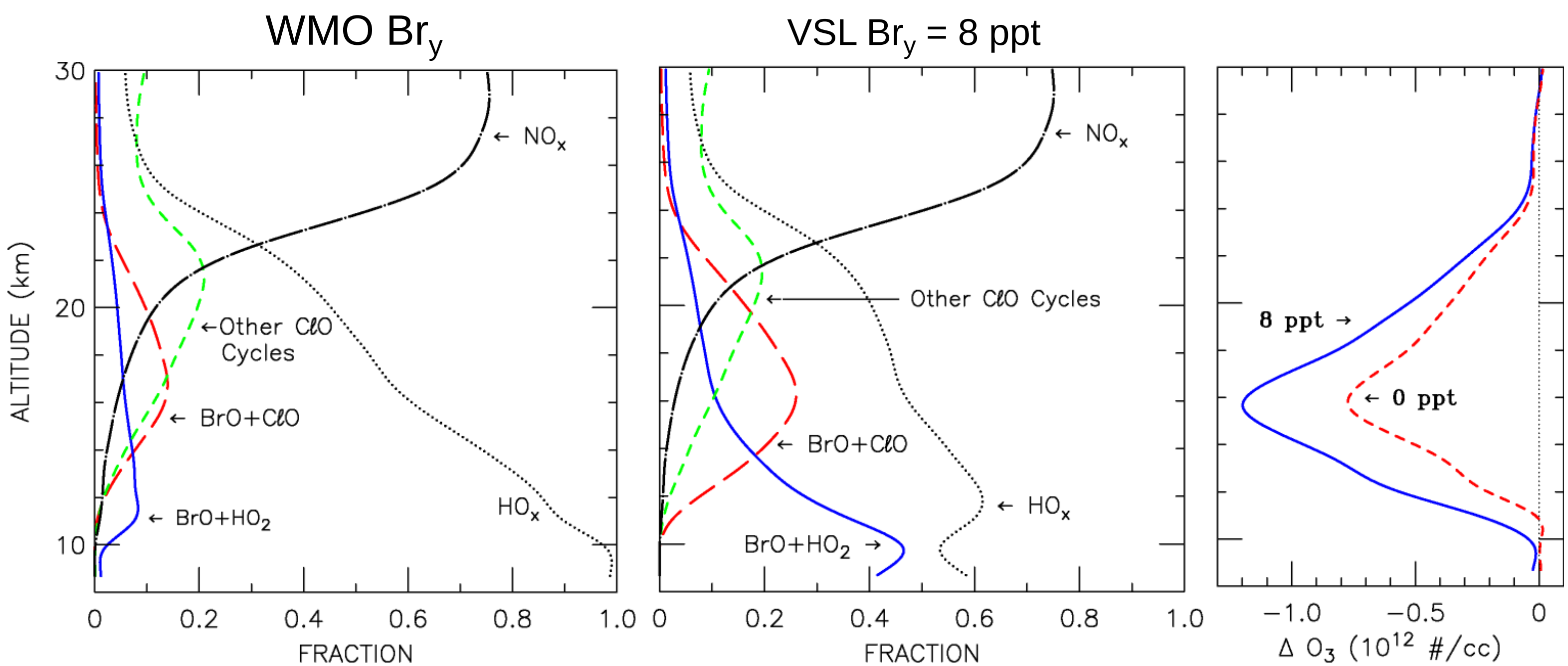
Reactions considered:

- $Br+HO_2$
- $Br+O_3$
- BrO+NO
- $BrO+NO_2$
- $Br+H_2CO$
- J_{BrNO3}
- J_{HOBr}

32

Stratospheric Ozone Photochemistry: Impact of VSL Br_y

Model Time Slice: 47 N, March 1993:



Salawitch *et al.*, GRL, 2005

Bromine supplied by VSL source species leads to:

Enhanced ozone depletion due mainly to BrO+ClO cycle

$BrO+HO_2$ catalytic cycle becomes significant O_3 sink below 16 km

Evidence that enhanced BrO is in the troposphere

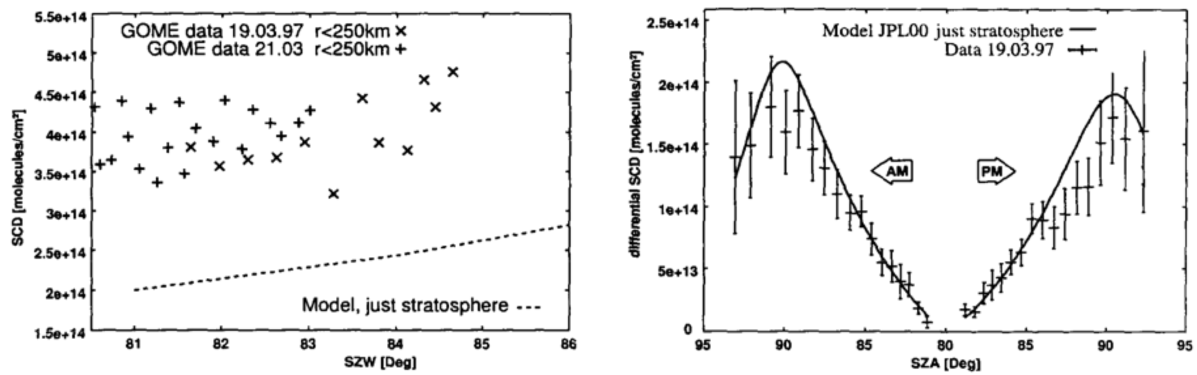


Fig. 3: Comparison of simulated SCD with observed SCD data. Left, GOME observations vs. simulations - right, ground based observations vs. simulations. Just stratospheric BrO is considered.

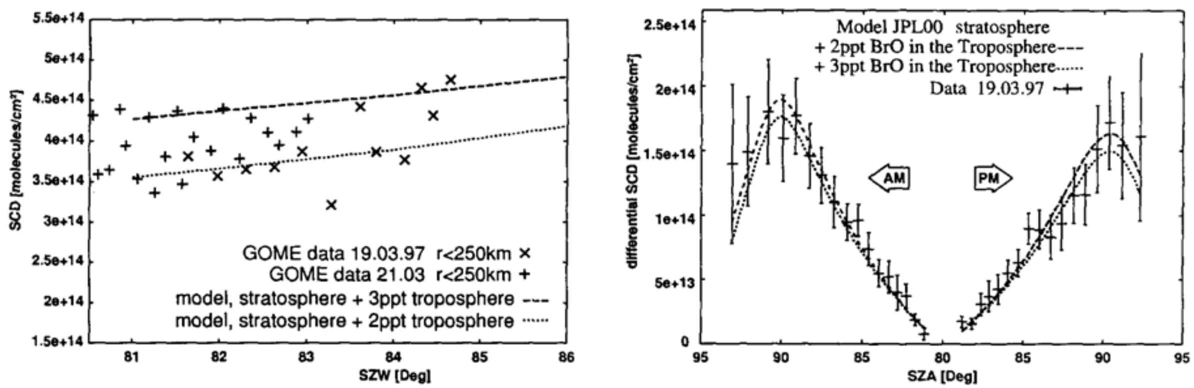


Fig. 4: Comparison of simulated SCD with SCD data for satellite based and ground based observations, with 2 pptv and 3 pptv BrO throughout the troposphere, which has been added to the stratospheric profiles.

Mueller et al., Adv. Space Res., 2002

Global, "ubiquitous" BrO of ~2 to 3 pptv throughout the troposphere needed to account for GOME slant column densities (SCD) and SZA dependence of BrO-SCD

Evidence that tropospheric BrO is not as high as 2 ppt everywhere

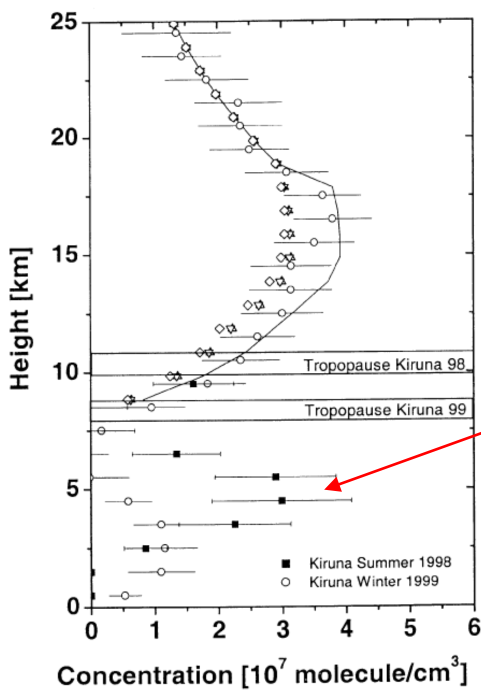
Tropospheric Column over Lauder, NZ (45 S)

	molecules cm^{-2}	ppt
Mean	0.2×10^{13}	0.2
Range	-0.6 to 1.2×10^{13}	-0.4 to 0.9
Standard Deviation	0.4×10^{13}	0.3

Upper limit of 0.9 ppt for tropospheric BrO

Retrievals based on twilight measurements of direct and scattered sunlight, clear-sky conditions

Schofield *et al.*, *JGR*, *109*, 2004



Peak VMR of 2 ppt

Fitzenberger *et al.*, *GRL*, *27*, 2000

Tropospheric Ozone Photochemistry : ~1 ppt of BrO

- **Tropospheric ozone:**
  - **zonal mean ⇓ 6 to 18% for a high-latitude VSL source**
  - **local ⇓ up to 40%, maxim. in SH free trop during summer**

    (von Glasow et al., ACP, 2004)
    (Yang et al., JGR, 2005)

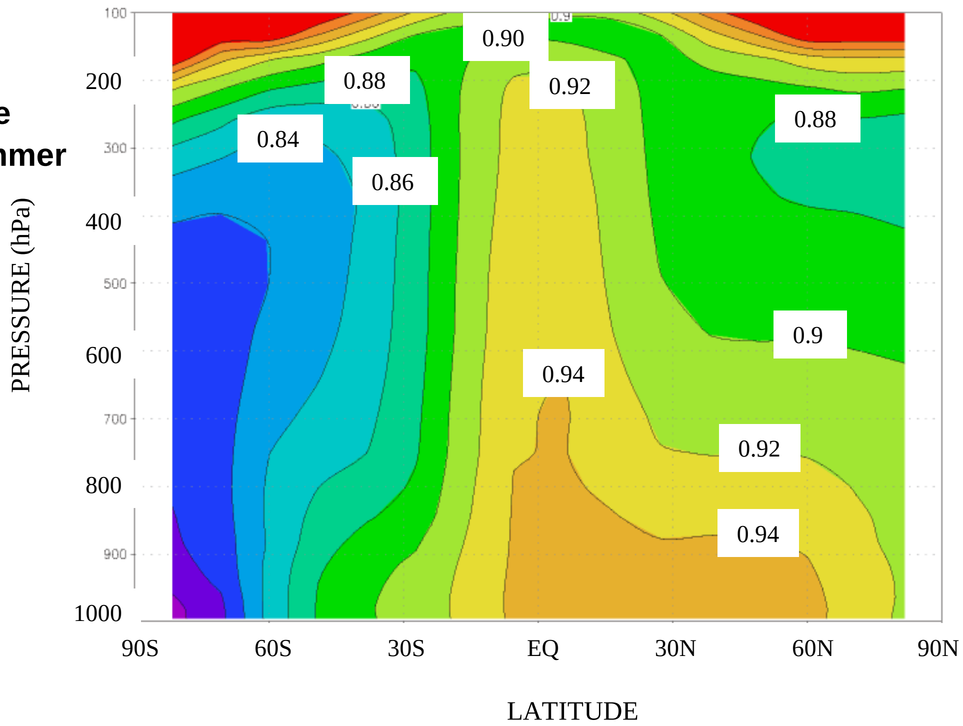


Figure 8. Ratio of O_3 in scenario "high latitude bromine source" to O_3 in "no halogen" scenario. Numbers are zonally and annually averaged.

von Glasow et al., ACP, 2004

Tropospheric Ozone Photochemistry : ~1 ppt of BrO

- Tropospheric ozone:
  - zonal mean ⇓ 6 to 18% for a high-latitude VSL source
  - local ⇓ up to 40%, maxim. in SH free trop during summer

    (von Glasow et al., ACP, 2004)

    (Yang et al., JGR, 2005)

- **DMS:**
  - **BrO + DMS becomes significant sink**
  - **DMS to SO_2 conversion efficiency dramatically ⇓**

    (von Glasow et al., ACD, 2003)

    (Boucher et al., ACP, 2003)

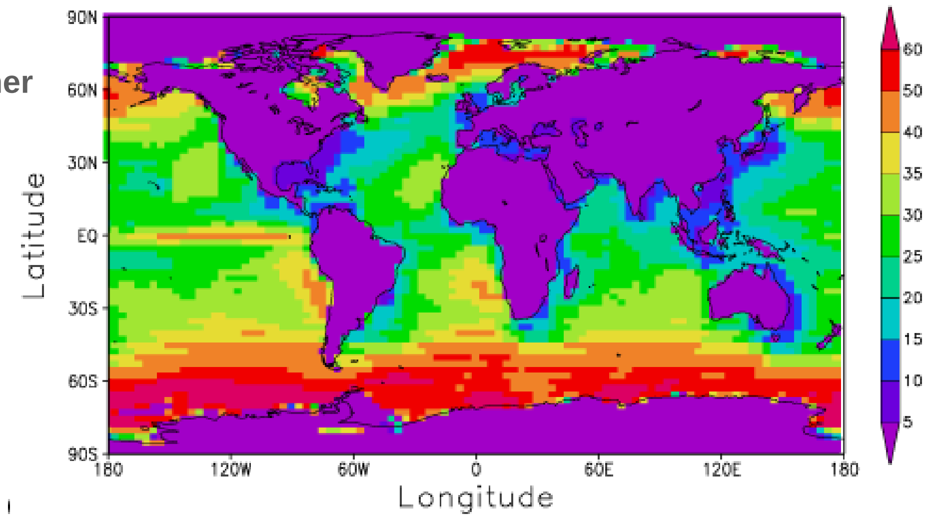


Figure 9. Relative contribution to vertically integrated DMS oxidation by BrO+DMS, for 1 ppt of tropospheric BrO

Boucher et al., ACP, 2003

Tropospheric Ozone Photochemistry: ~1 ppt of BrO

- Tropospheric ozone:
  - zonal mean ⇓ 6 to 18% for a high-latitude VSL source
  - local ⇓ up to 40%, maxim. in SH free trop during summer
    (von Glasow et al., ACP, 2004)
    (Yang et al., JGR, 2006)

- DMS:
  - BrO + DMS becomes significant sink
  - DMS to SO_2 conversion efficiency dramatically ⇓
    (von Glasow et al., ACD, 2003)
    (Boucher et al., ACP, 2003)

- **NO_x:**
  - **$BrONO_2$ hydrolysis significant source of HNO_3**
  - **Lower NO_x leads to lower ozone**
    (Lary, ACP, 2004)
    (Yang et al., JGR, 2006)

% Production of $HONO_2$ due to $BrONO_2$+H_2O

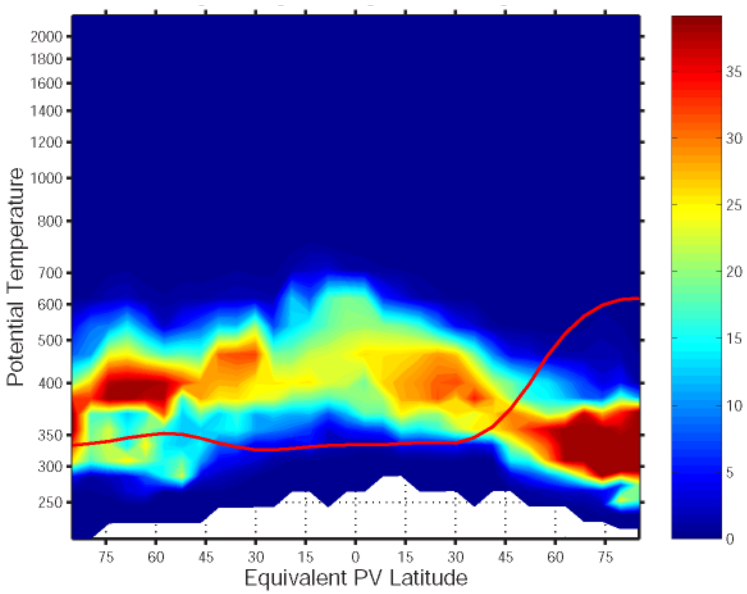
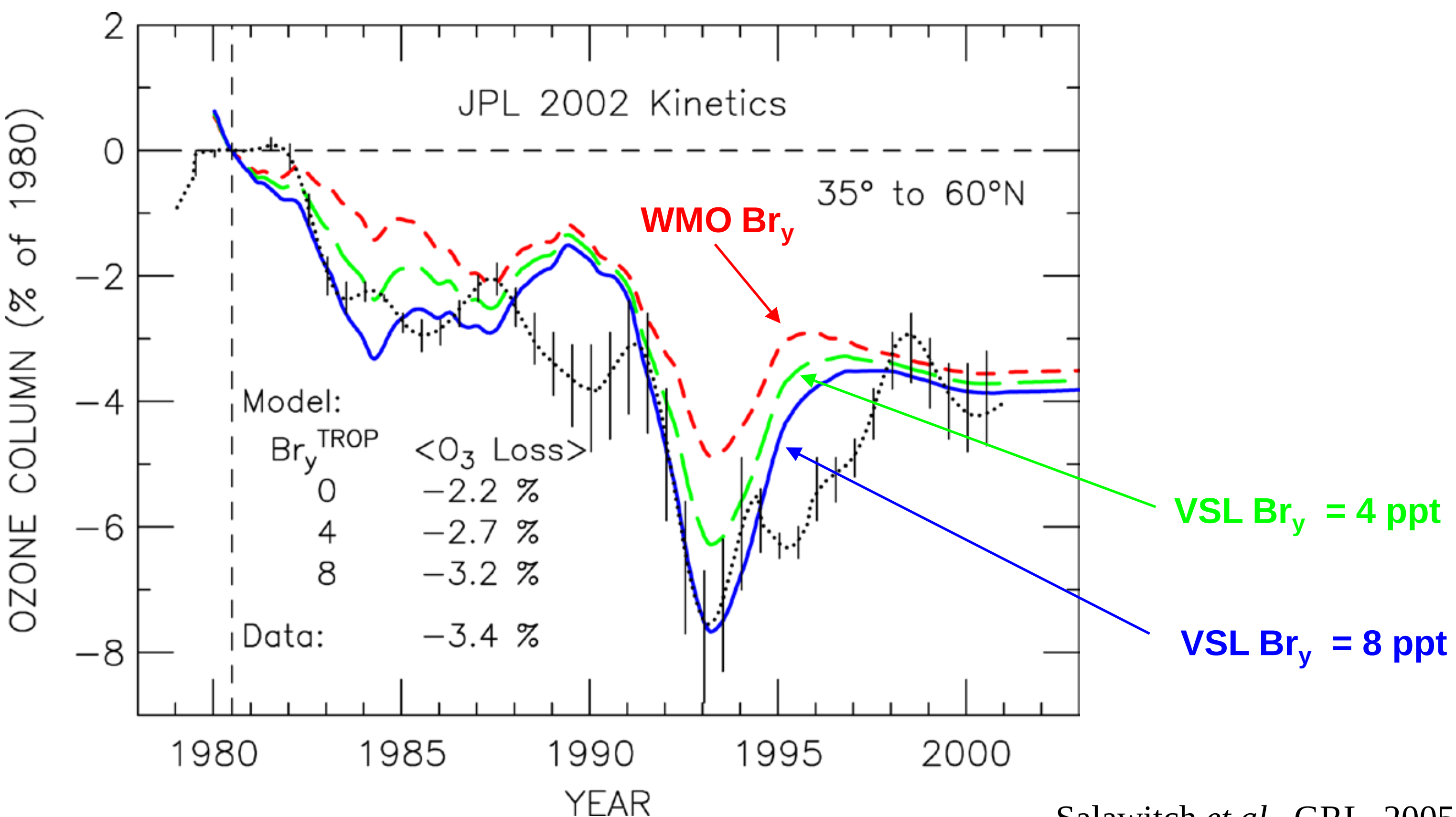


Figure 3c. Contribution of $BrONO_2$ + H_2O to the production of $HONO_2$

Lary et al., ACP, 2004

Stratospheric Ozone Photochemistry: Impact of VSL Br_y

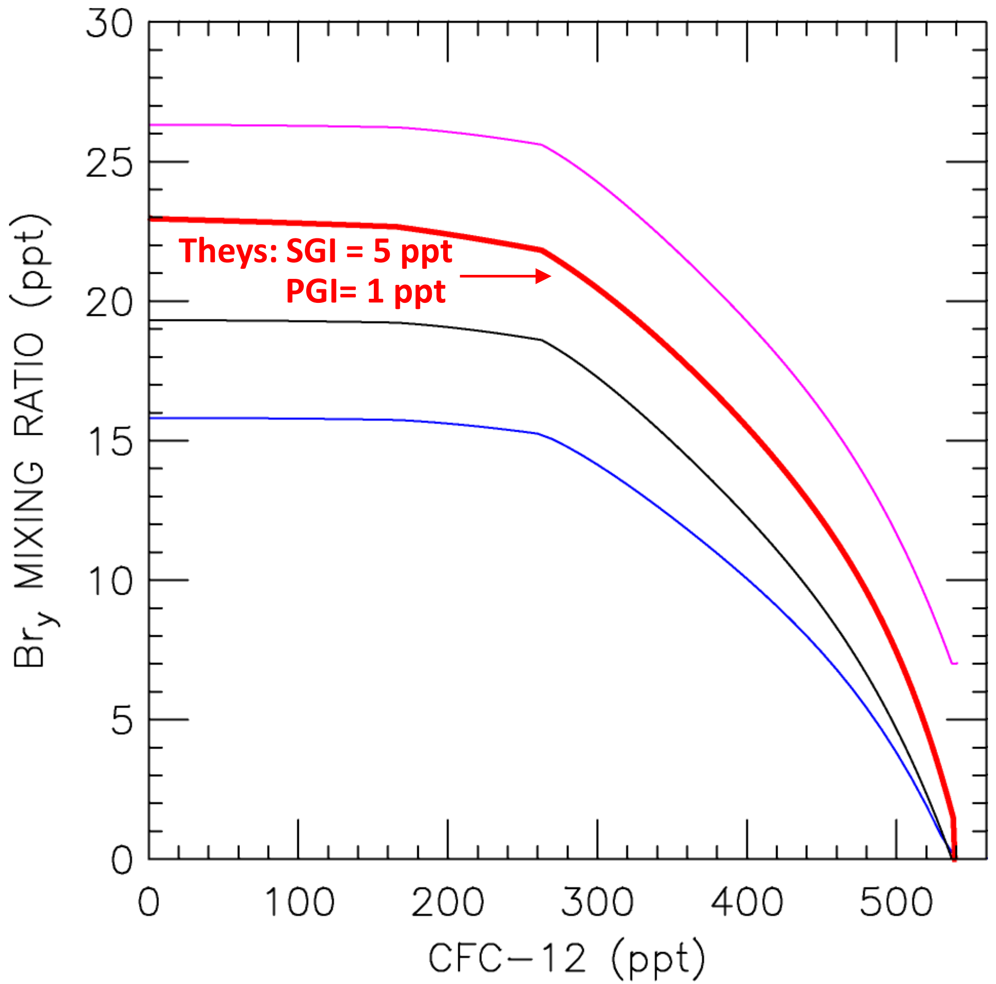


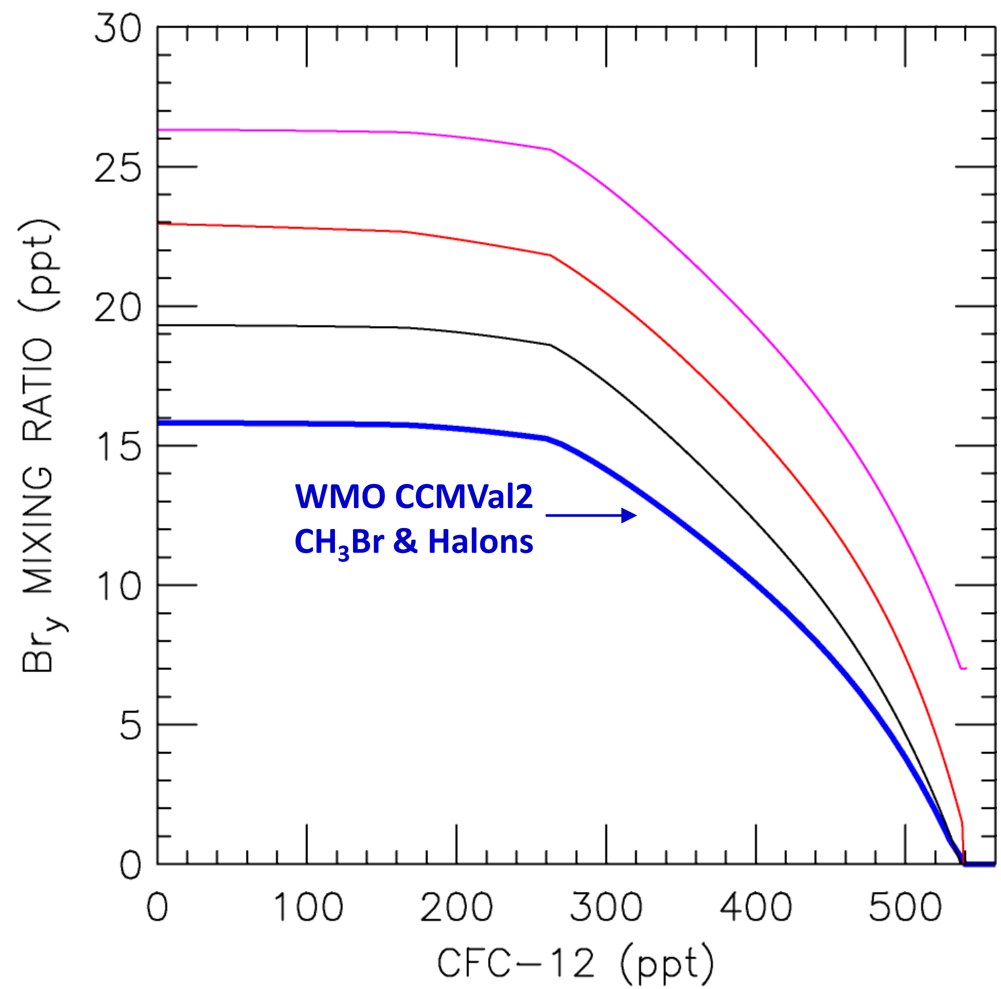
Salawitch *et al.*, GRL, 2005

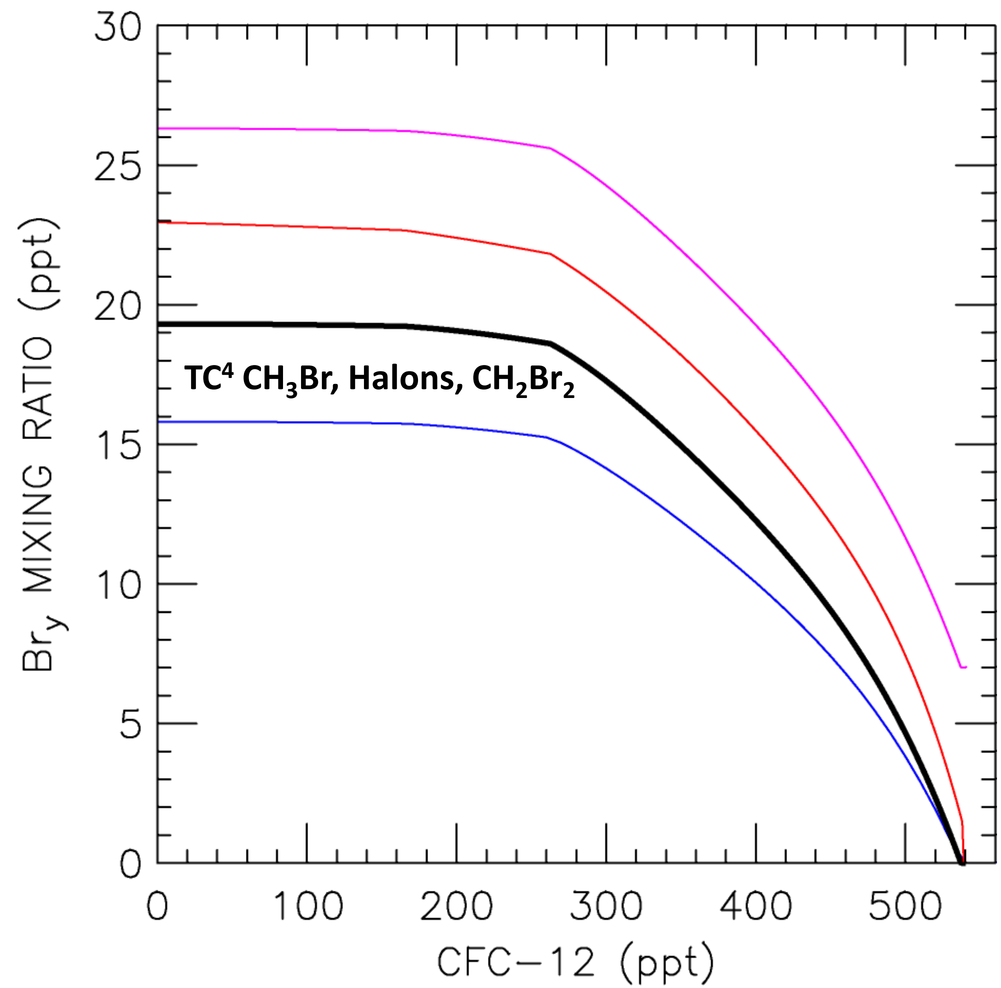
VSL bromine leads to:

Increase in computed ozone depletion

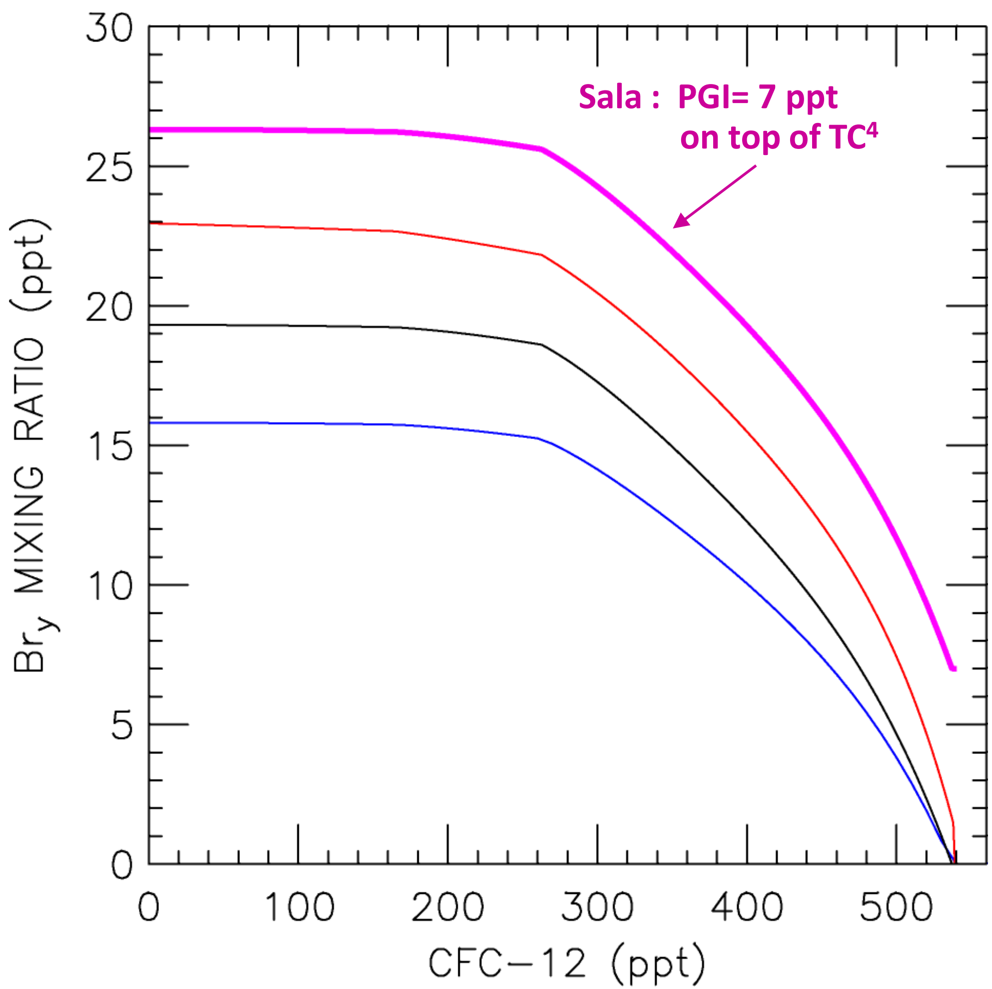
Better agreement with observed ozone changes


Theys: SGI = 5 ppt
PGI= 1 ppt
Br_y MIXING RATIO (ppt)
CFC−12 (ppt)
0
5
10
15
20
25
30
0
100
200
300
400
500


30
25
20
15
10
5
0
0
100
200
300
400
500
CFC−12 (ppt)
Br_y MIXING RATIO (ppt)
WMO CCMVal2
CH_3Br & Halons



30
25
20
15
10
5
0
Br_y MIXING RATIO (ppt)
TC[4] CH_3Br, Halons, CH_2Br_2
0
100
200
300
400
500
CFC−12 (ppt)


Sala : PGI= 7 ppt
on top of TC4
Bry MIXING RATIO (ppt)
CFC−12 (ppt)
0
5
10
15
20
25
30
0
100
200
300
400
500