Halogen Simulations in CAM-Chem and Impact on Ozone Chemistry

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CONTRAST, Boulder, CO

Outline

- Description of Halogen Chemistry in the CAM-Chem
- UTLS Inorganic Bromine in the Western Pacific
  - Abundance
  - Partitioning
- What to expect during CONTRAST
  - Example model distributions of O_3, BrO, CH_2Br_2

Chemistry of Tropospheric Halogens

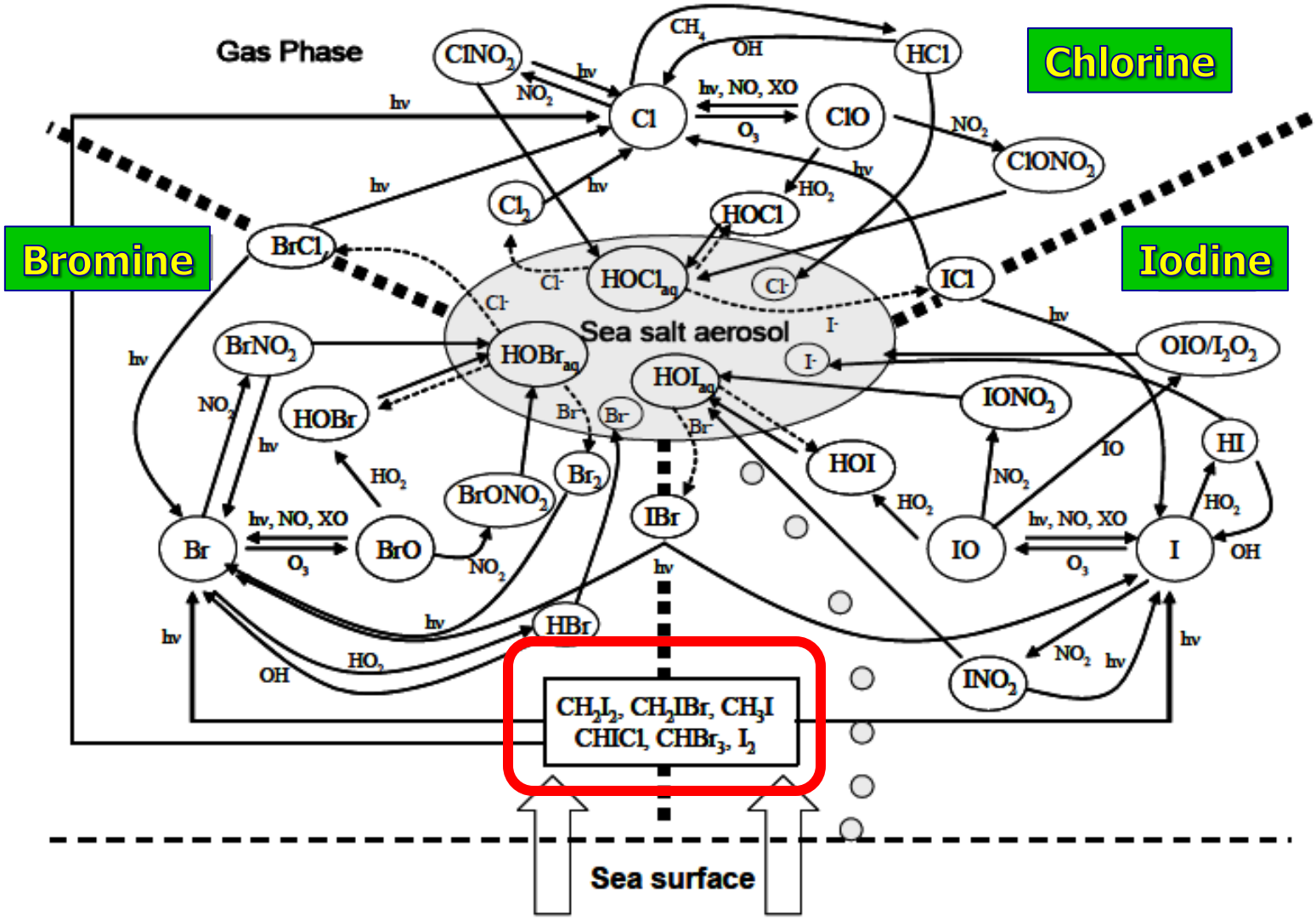


Figure courtesy of A. Saiz-Lopez

Modeling Very-Short Lived Species

NCAR CESM CAM-CHEM

- Global Chemistry-Climate Model
- 1.9° (lat) x 2.5° (lon) horizontal resolution
- 26 vertical levels (surface to ~ 4 hPa)

Lamarque et al., *Geosci. Mod. Dev.*, 2012

Tropospheric Halogen Chemistry

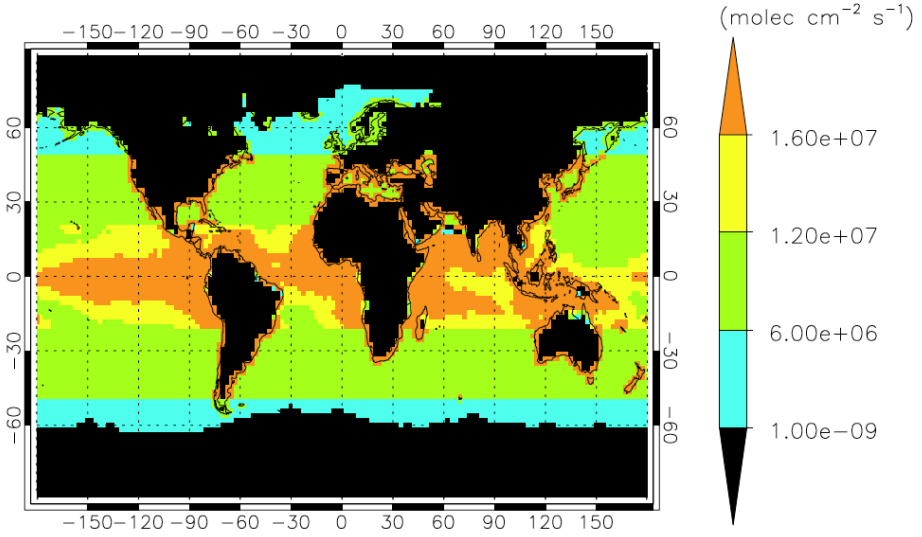
Halogenated sources from the ocean.

- Emissions following Chl-a over tropics
- Catalytic release from sea-salt
- Do NOT have polar emission processes

Chemical Processes

- Photochemistry (Cl, Br, and I)
- Dry / wet deposition
- 9 Additional vsl Organic species included.
- 160 species, 427 reactions

$CHBr_3$ Flux in CAM-Chem

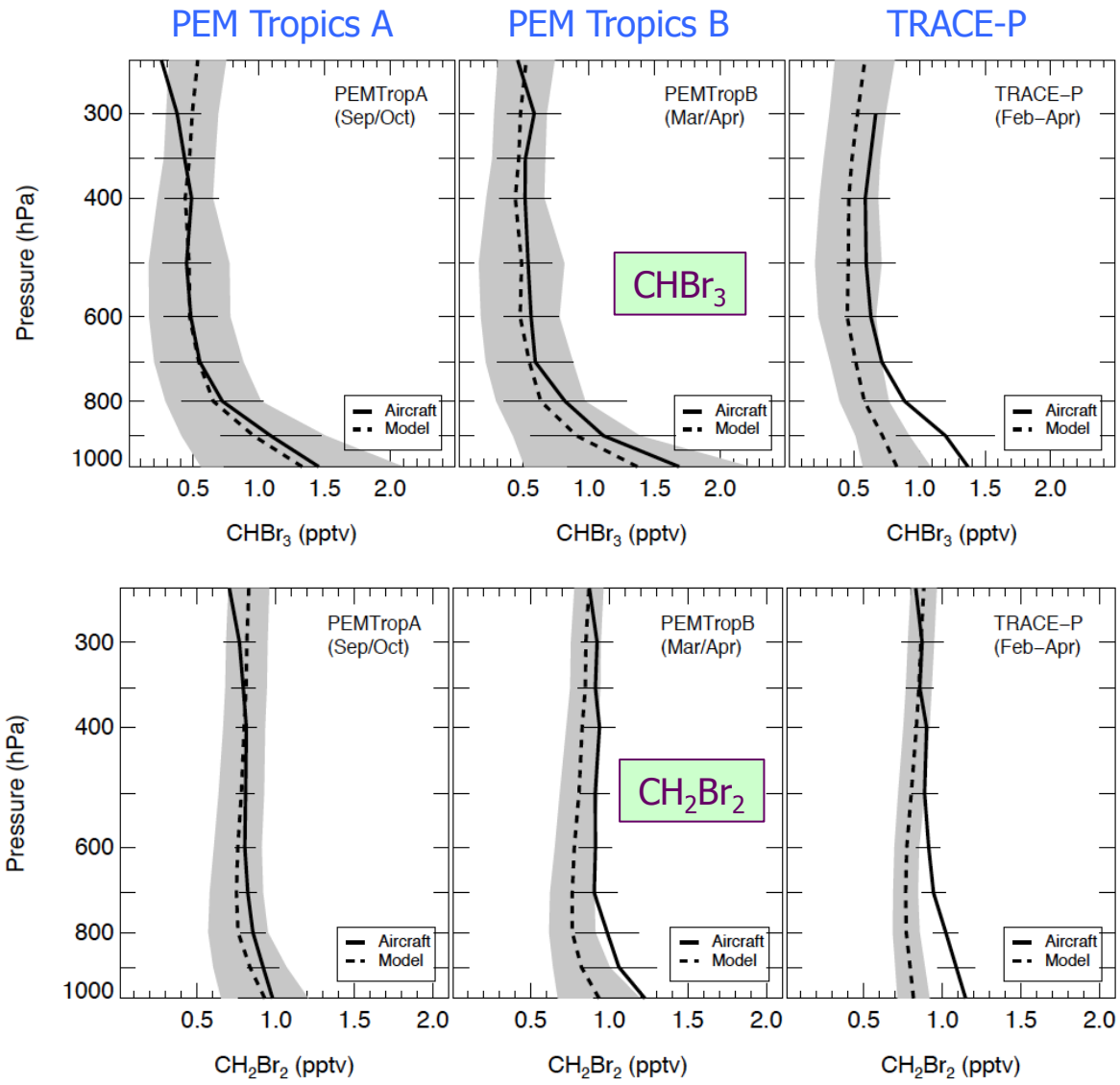


Source gas	Global annual flux (Gg yr^{-1})		Lifetime (this study)
	This study	Literature	
$CHBr_3$	533	400[a], 595[b], 448[d]	17 days
CH_2Br_2	67.3	113[c], 62[d]	130 days
CH_2BrCl	10.0	6.8[c]	145 days
$CHBr_2Cl$	19.7	23[c]	56 days
$CHBrCl_2$	22.6	16[c]	46 days
CH_3Br*	climatology	131[c]	1.6 yr[g]
CH_3I**	303	304[e]	5 days
CH_2ICl	234	236[f]	8 h
CH_2IBr	87.3	87[f]	2.5 h
CH_2I_2	116	116[f]	7 min

Total Bromine: 632 Gg Br yr^{-1}
Total Iodine: 600 Gg I yr^{-1}

Ordoñez et al., ACP, 2012

Abundance of Organic Halogens in Pacific



Reasonable agreement with observations. However, we do seem to underestimate VSL species in TRACE-P.

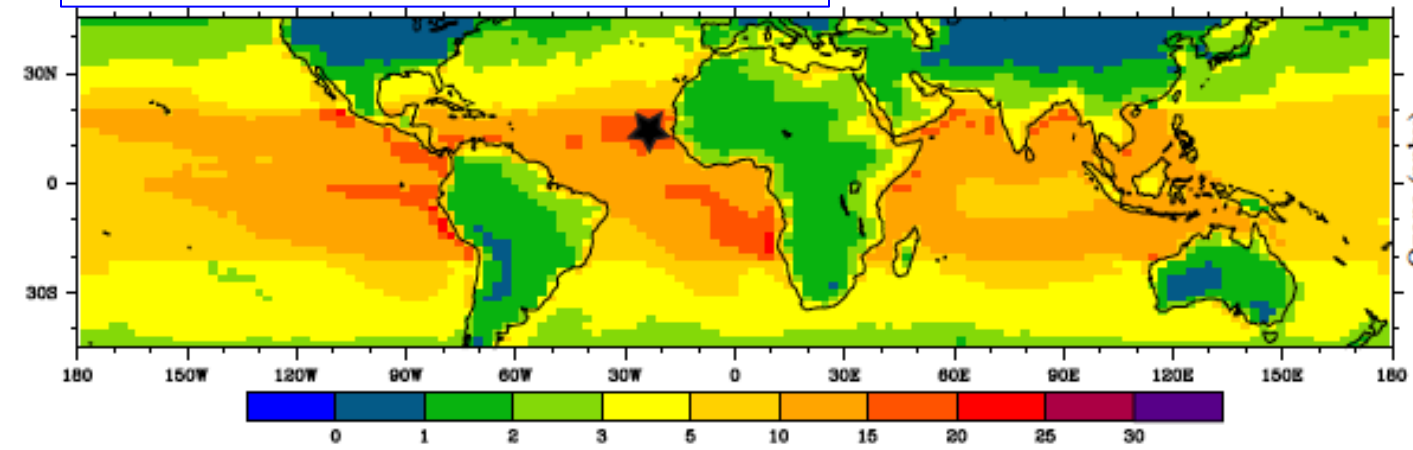
A detailed evaluation of the model vsl organic halogens is in:

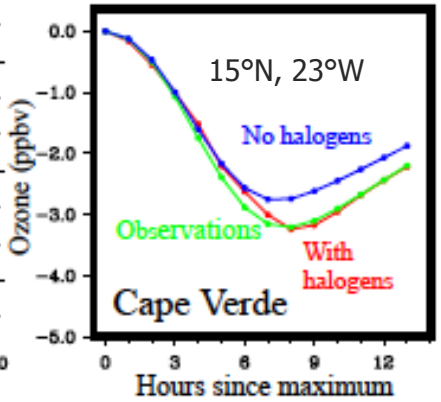
- Ordoñez et al., ACP, 2012; and
- Saiz Lopez et al., ACP, 2012.

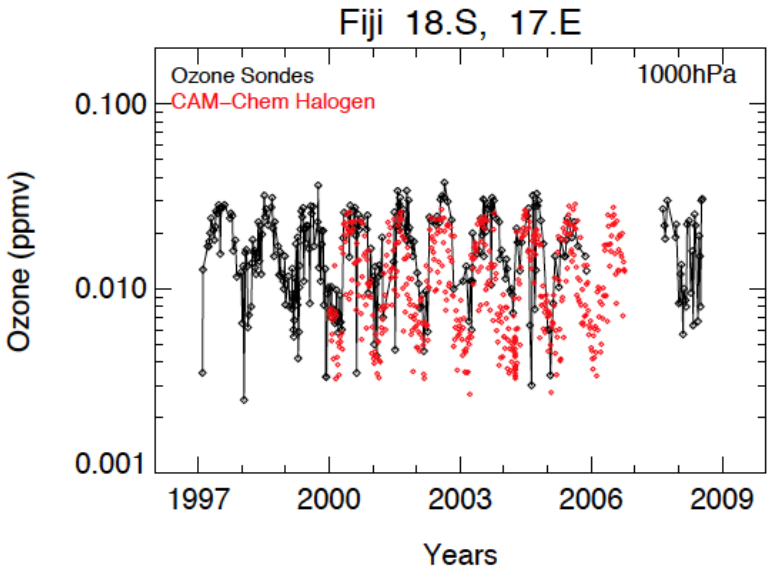
Saiz Lopez et al., ACP, 2012.

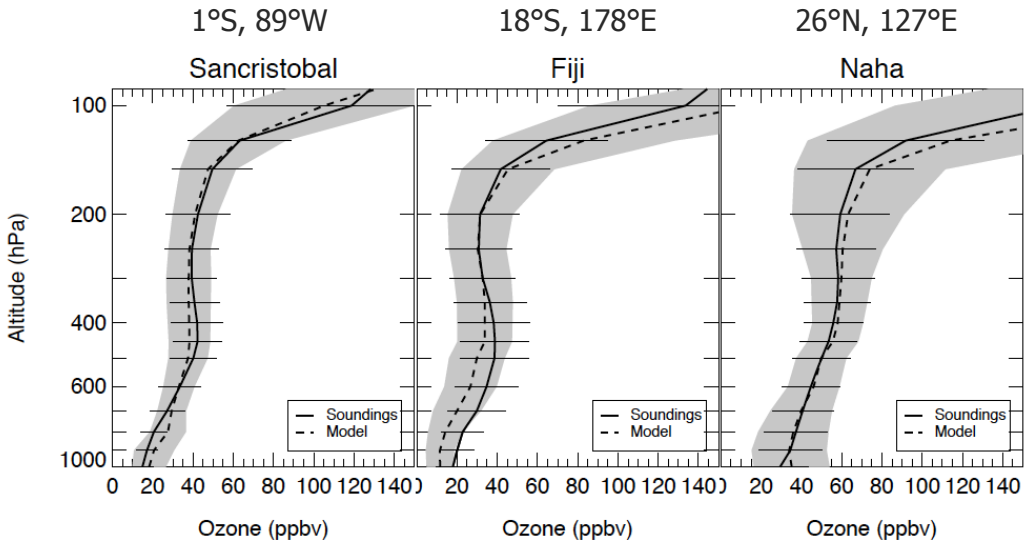
Surface Ozone *** Diurnal and Seasonal

Surface Ozone Loss (105 mol/cm3/s)**



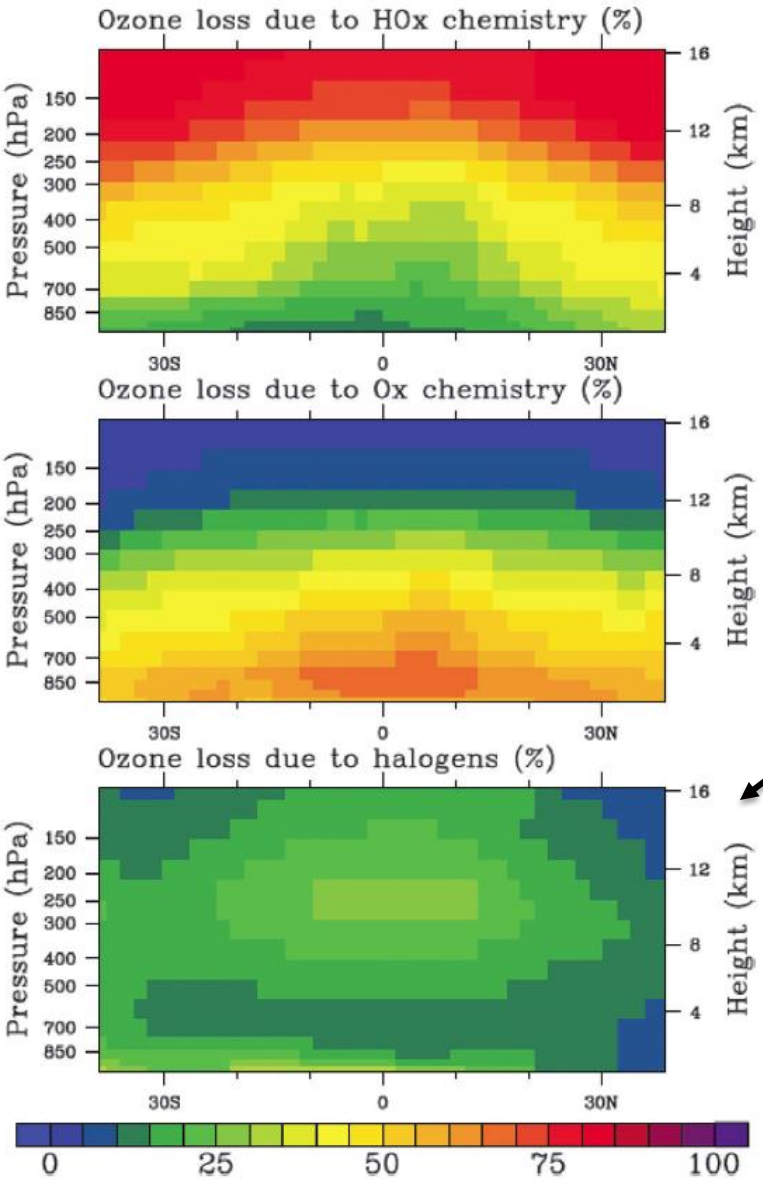






Saiz Lopez et al., ACP, 2012.

% Odd-oxygen Loss Due to Halogens



Saiz Lopez et al., ACP, 2012.

Up to ~25% in tropical UT

Iodine / Bromine Chemistry:

$I + O_3 \Rightarrow IO + O_2$
$Br + O_3 \Rightarrow BrO + O_2$
$IO + BrO \Rightarrow Br + I + O_2$

$2O_3 \Rightarrow 3O_2$

Iodine / Hydrogen Chemistry:

$I + O_3 \Rightarrow IO + O_2$
$IO + HO_2 \Rightarrow HOI + O_2$
$HOI + hv \Rightarrow I + OH$
$OH + O_3 \Rightarrow HO2 + O_2$

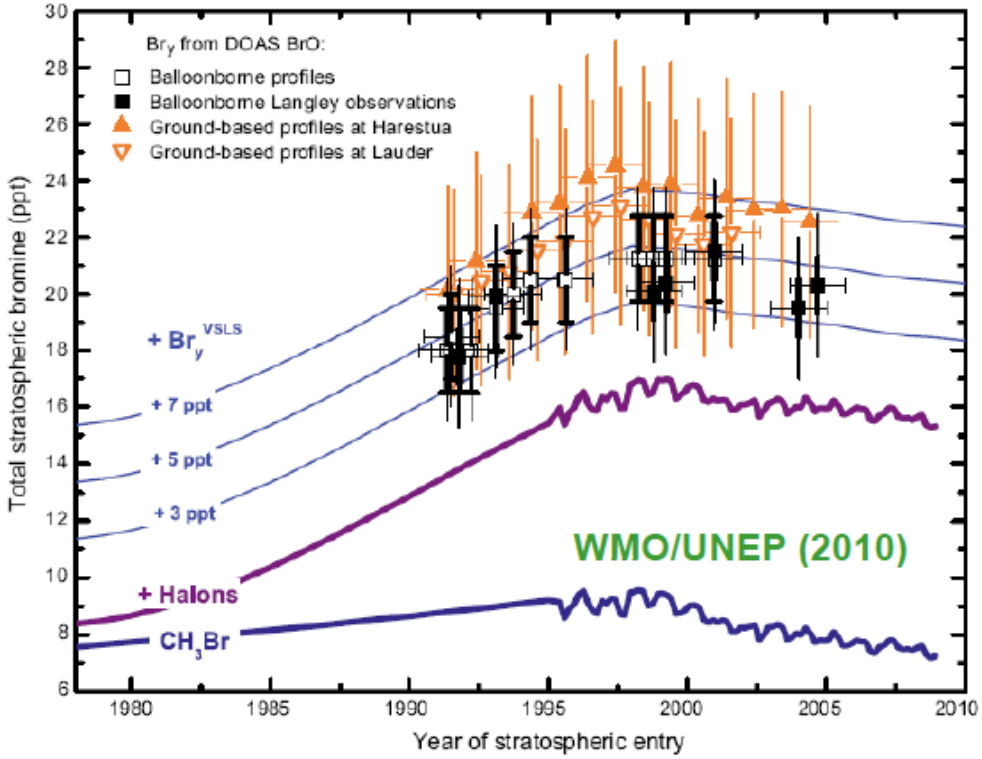
$2O_3 \Rightarrow 3O_2$

Iodine Only Chemistry:

$2(I + O_3 \Rightarrow IO + O_2)$
$IO + IO \Rightarrow OIO + I$
$OIO + hv \Rightarrow I + O_2$

$2O_3 \Rightarrow 3O_2$

Stratospheric Bromine Loading



- Total bromine necessary to explain BrO:
  Br_y ~ 21 to 24 pptv
- Sum of Halons + CH_3Br insufficient
  Br_y ~ 15 to 16 pptv
  - VSL halogens

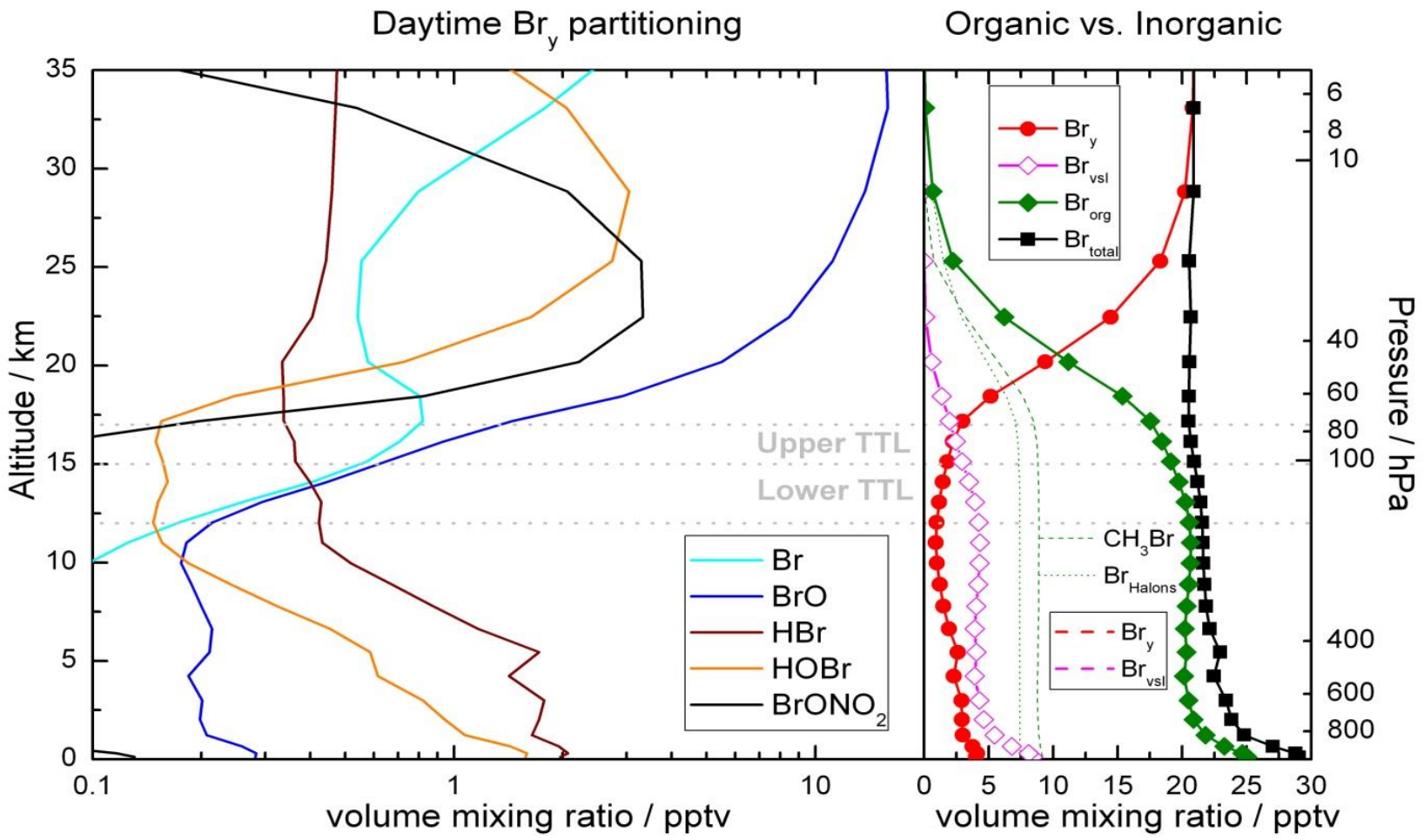
  Br_y^{VSLS} 6 (3 to 8 pptv) (WMO 2010)

VSL Bromocarbons

$CHBr_3$
CH_2Br_2
$CHBrCl_2$
$CHBr_2Cl$
CH_2BrCl

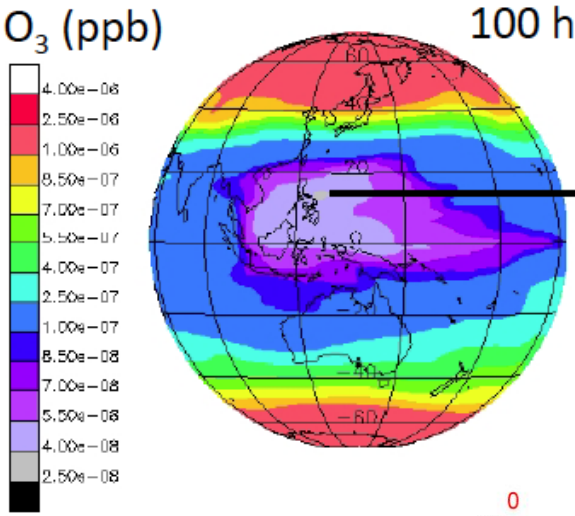
Several model studies have highlighted the relevance of bromocarbons for carrying bromine to the stratosphere (literature):
e.g. *Dvortsov et al., 1999; Sinnhuber et al., 2002; Salawitch et al., 2005; Warwick, et al., 2006 Dorf et al., 2008; Kerkweg et al., 2008; Aschmann et al., 2009, 2011; Brioude et al., 2010; Hossaini et al., 2010, 2012; Liang et al., 2010; Schofield et al., 2011; Ordoñez et al., 2012; Aschmann and Sinnhuber, 2013*

Tropical Bromine in CAM-Chem, ZM, Annual Average



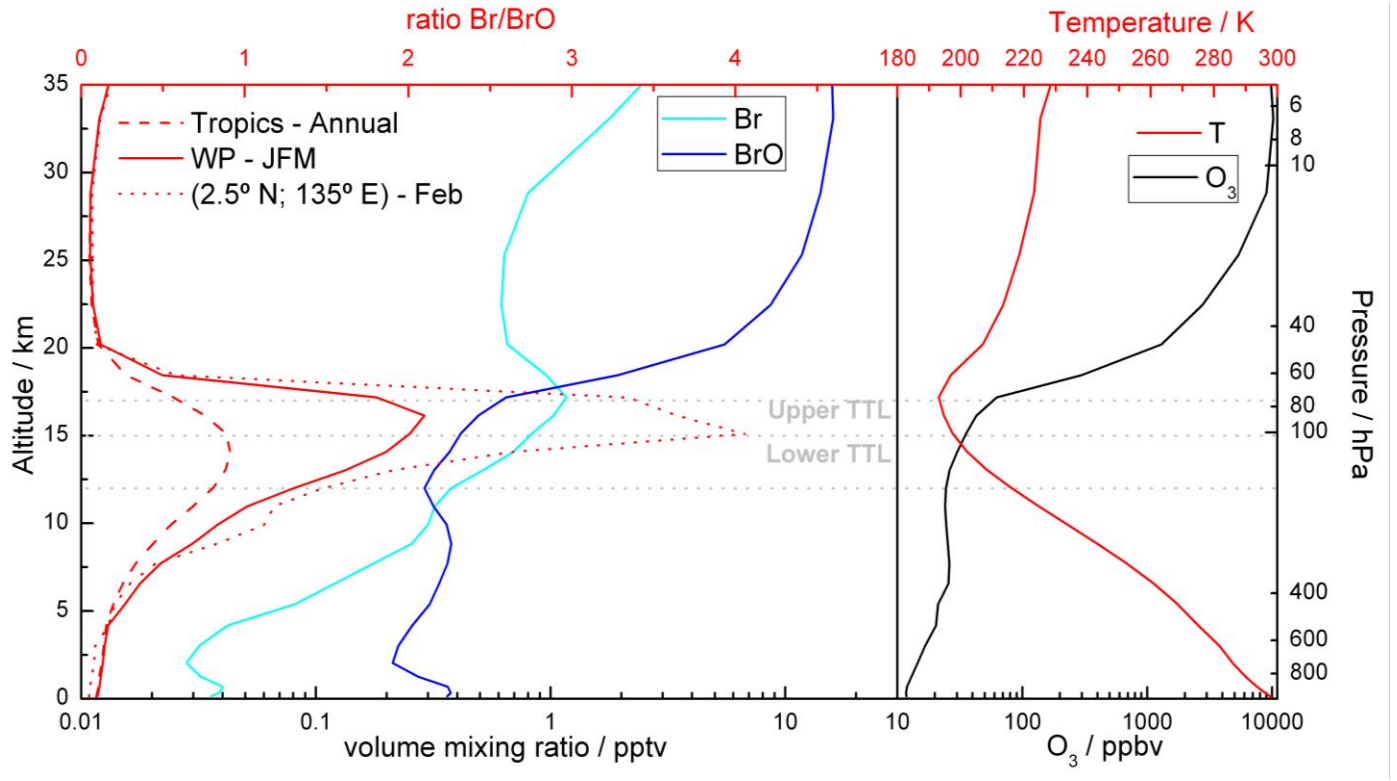
Total inorganic bromine (Br_Y) in the stratosphere is ~21 pptv; ~5 pptv comes from VSL species (chemical lifetimes < 6-months).

Br/BrO ratio at the Tropopause over the Western Pacific



For the range of Temp in the TTL:

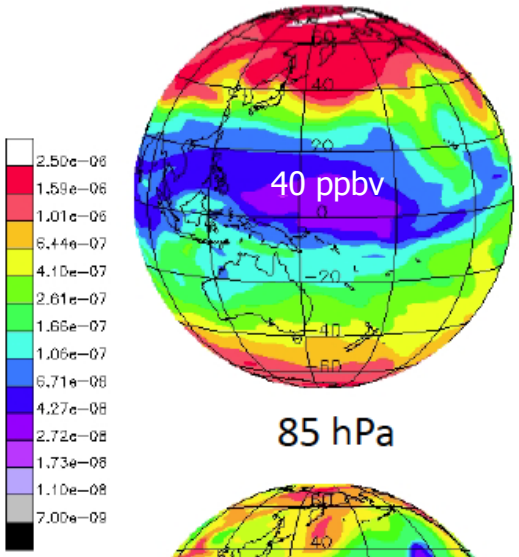
O_3 threshold below which Br>BrO is ~60 ppbv



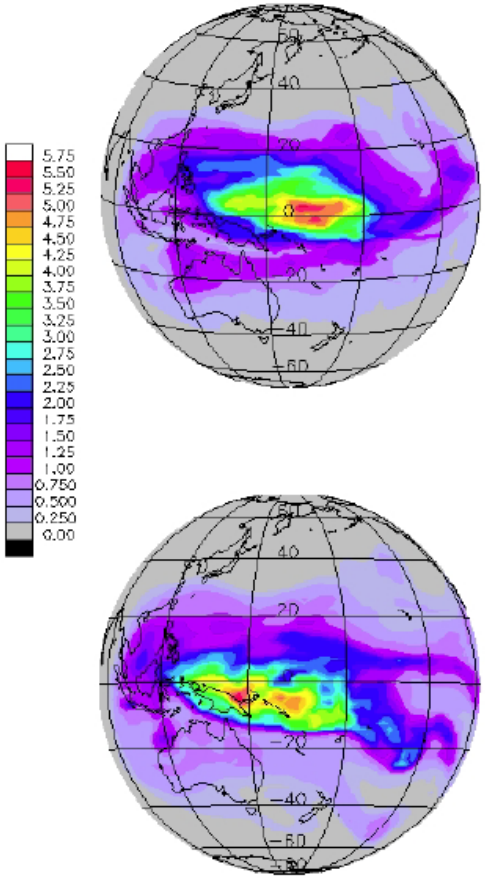
Sensitivity of Br/BrO to [O_3], T, jBrO

DJF

Ozone (ppbv)



Br/BrO



Daytime Br/BrO in TTL is primarly controlled by:

[O_3] → Br + O_3 > BrO

T → (E/R) = 780

*j*BrO → BrO + hv > Br + O

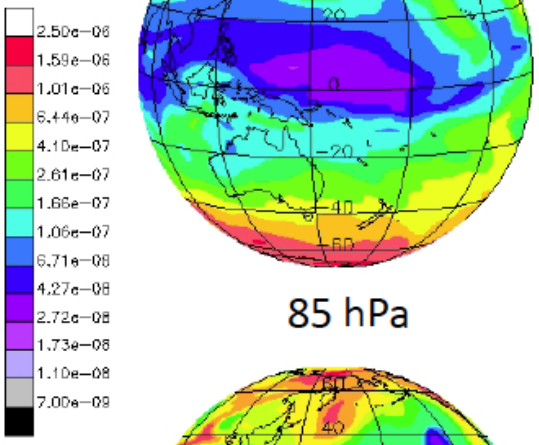
Daytime % of Br_y:
Br: 58 %
BrO : 12 %

Nighttime % of Br_y:
HBr : 40 %
BrCl : 50 %

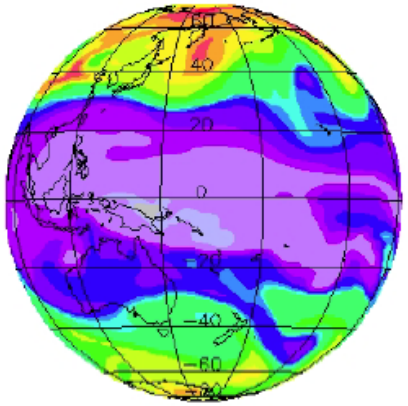
Sensitivity of I/IO to [O_3], T, jIO

DJF

Ozone (ppbv)

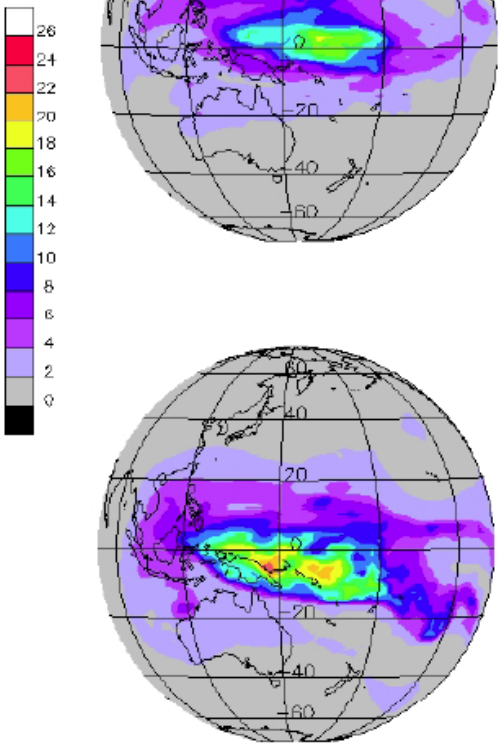


85 hPa



165 hPa

I/IO



Daytime I/IO in TTL is primarly controlled by:

[O_3] → $I + O_3 > IO$

T → (E/R) = 870

*j*IO → $IO + h\nu > I + O$

***j*IO > *j*BrO**

***j*HI > *j*HBr**

I/IO > Br/BrO

Daytime % of I_y:

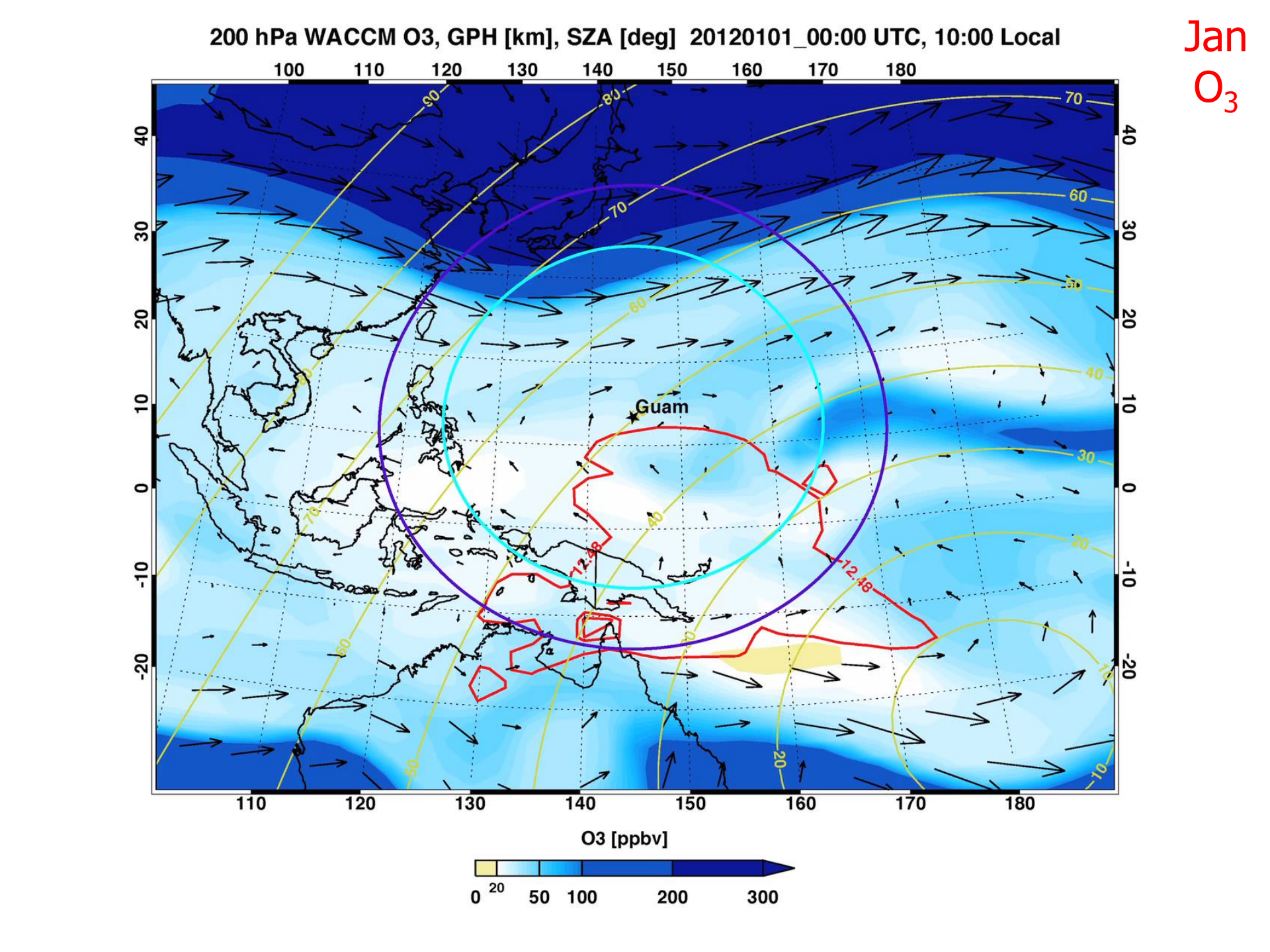
I: 90 %

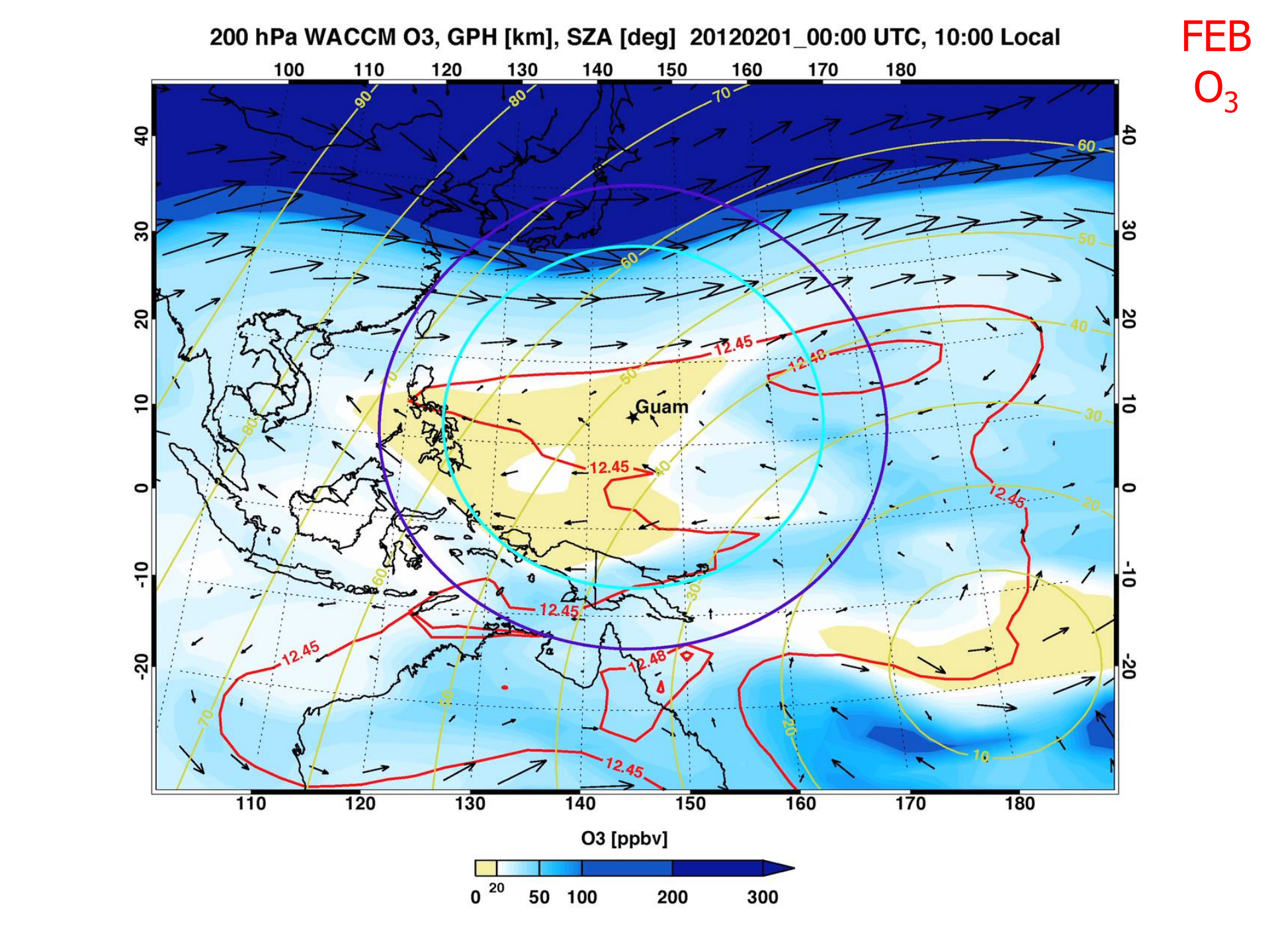
Western Pacific Conditions in Jan/Feb 2012

- Min O_3: Compare Early January and Early February.
- Halogens: BrO, Br/BrO, and $CHBr_3$
- SE Asia Influence: CO

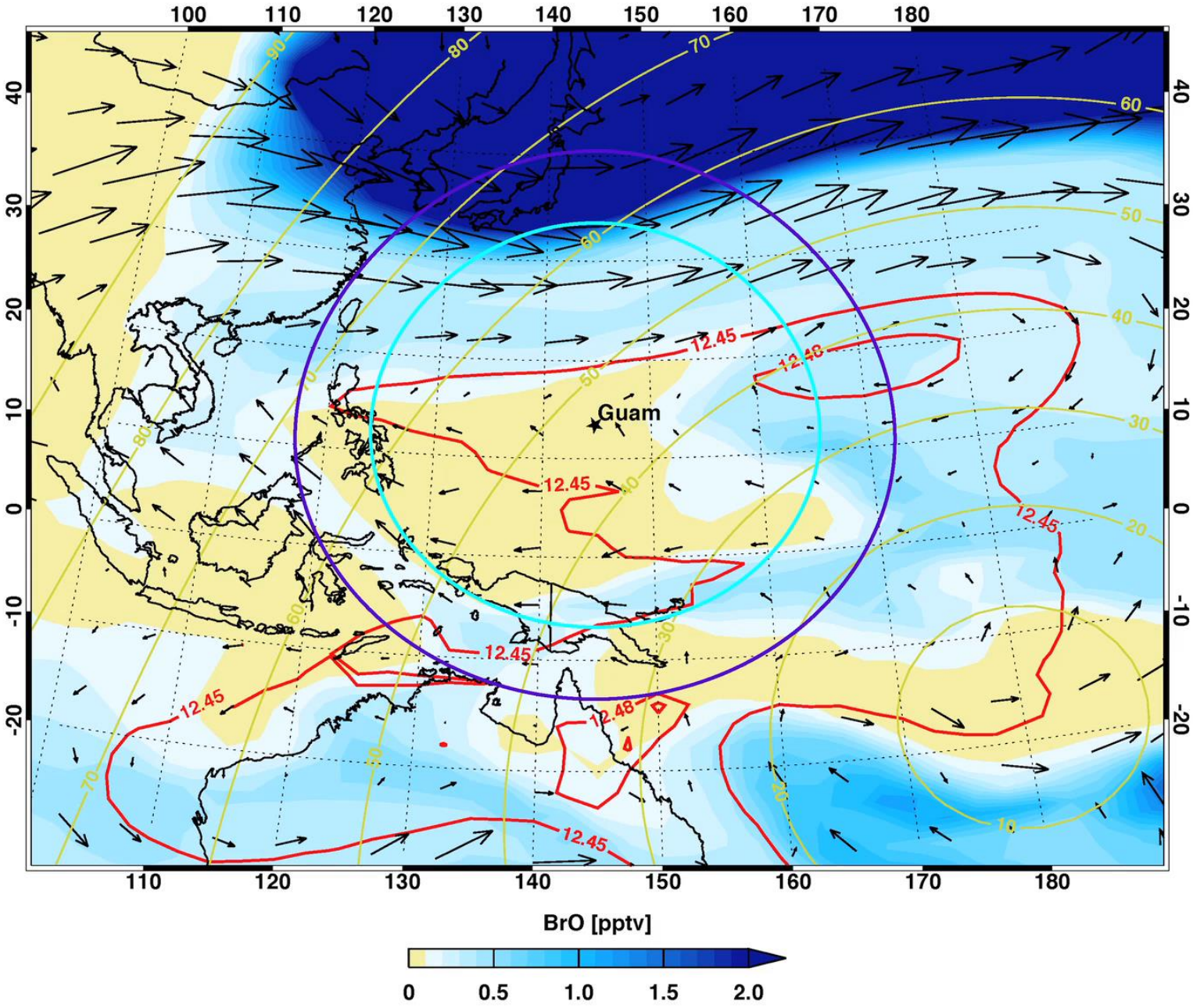
NOTE: These results are from a CCMI SD-WACCM / MERRA simulation. This version does not include all the VSL chemistry. However, it does include $CHBr_3$ and CH_2Br_2 set globally to 1.2 pptv.

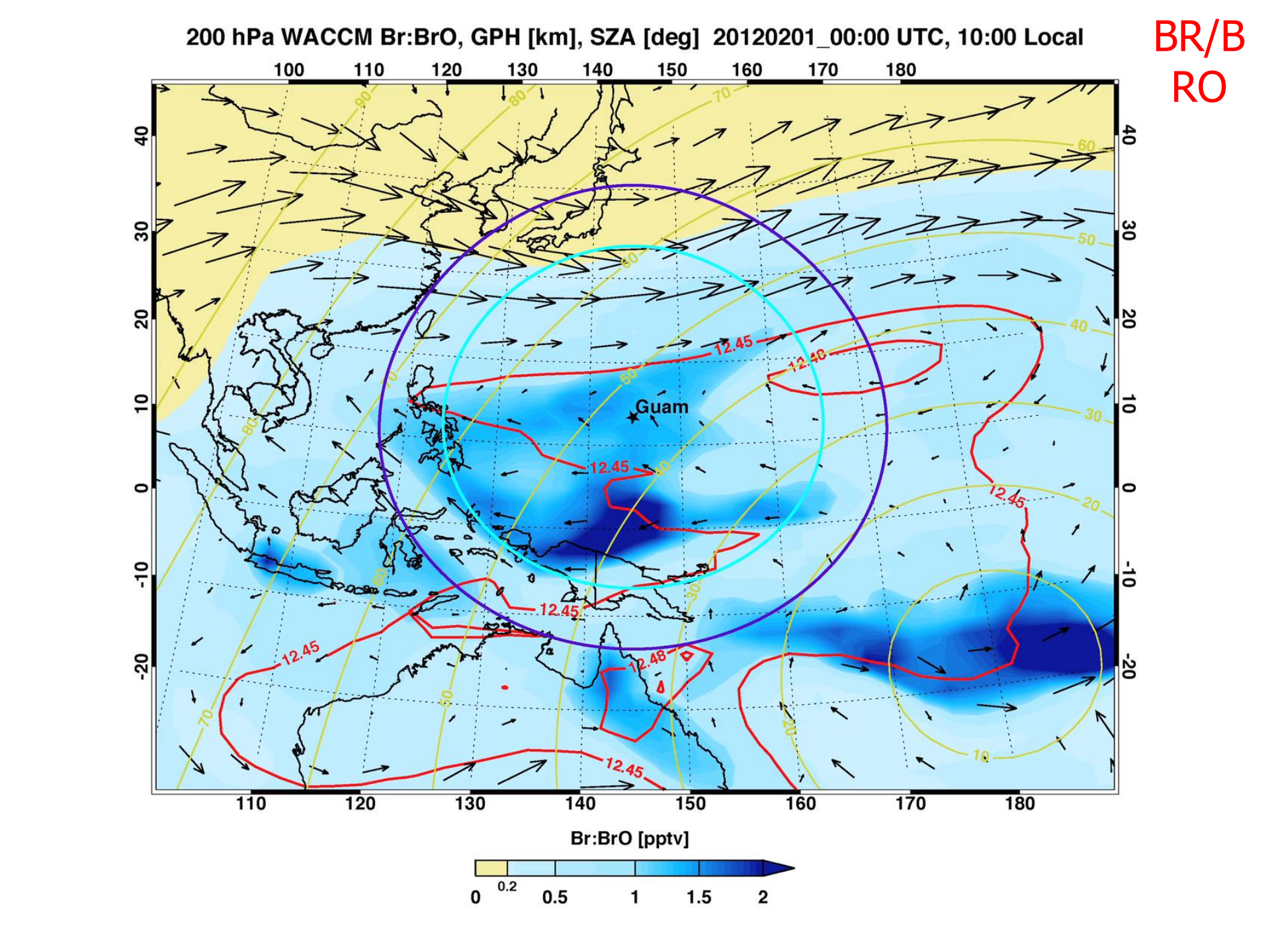
Movies Courtesy of Shawn Honomichl and Laura Pan

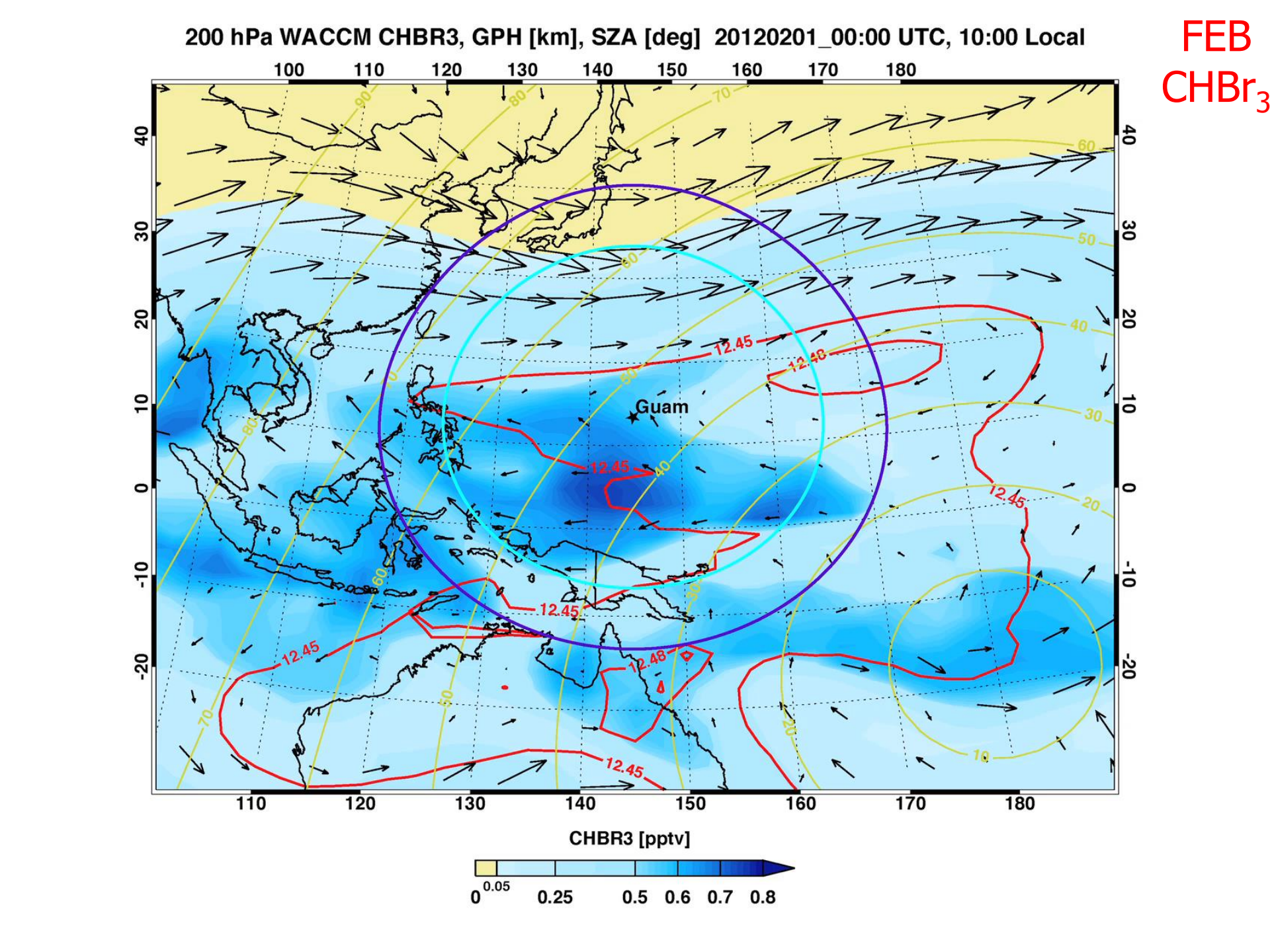

200 hPa WACCM O3, GPH [km], SZA [deg] 20120101_00:00 UTC, 10:00 Local
Jan
O3
Guam
O3 [ppbv]
0
20
50
100
200
300

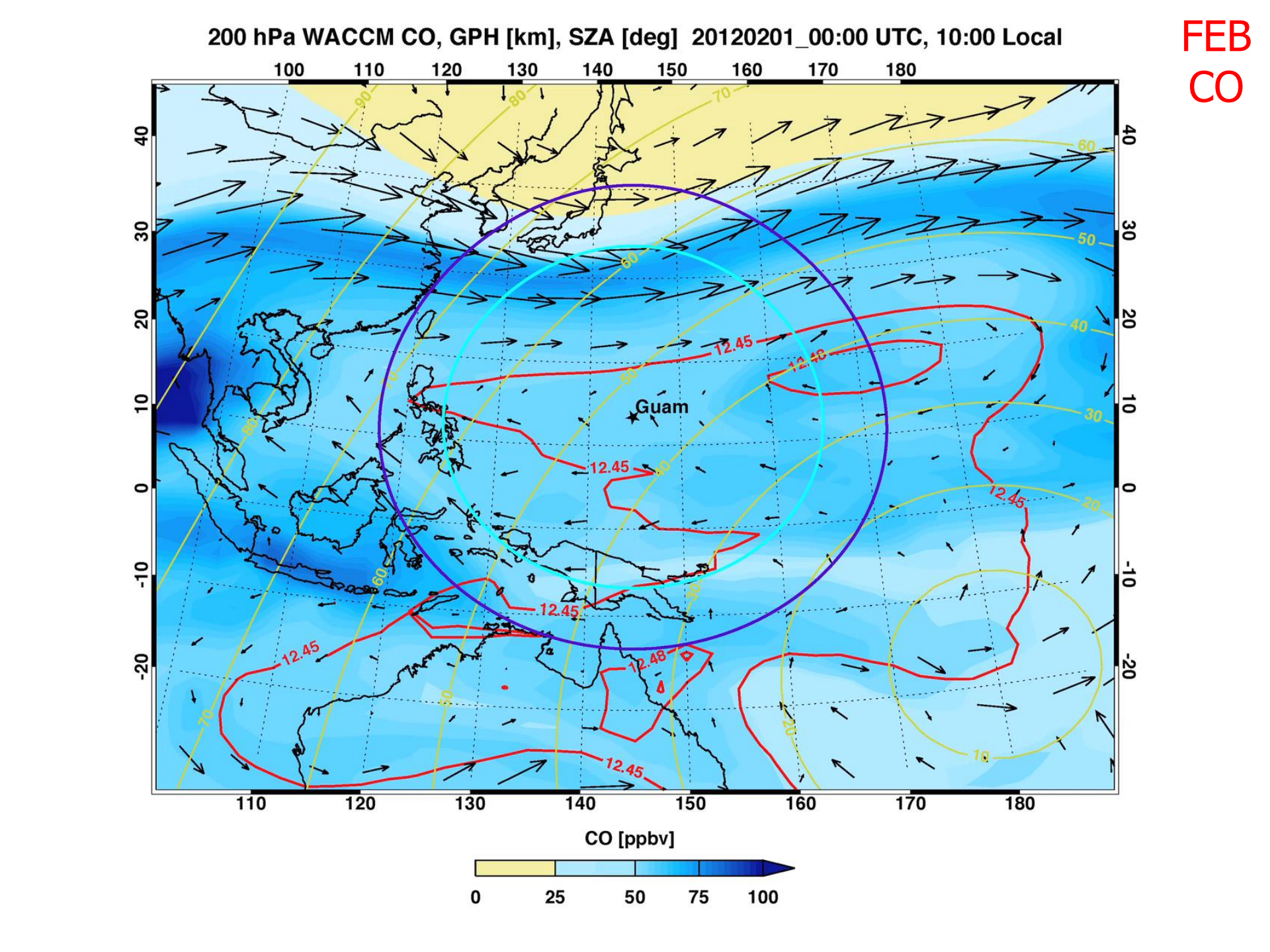

200 hPa WACCM O3, GPH [km], SZA [deg] 20120201_00:00 UTC, 10:00 Local
FEB
O3
Guam
O3 [ppbv]
0 20 50 100 200 300

BRO


200 hPa WACCM BrO, GPH [km], SZA [deg] 20120201_00:00 UTC, 10:00 Local
Guam
12.45
12.48
BrO [pptv]
0
0.5
1.0
1.5
2.0


200 hPa WACCM Br:BrO, GPH [km], SZA [deg] 20120201_00:00 UTC, 10:00 Local
BR/BRO
Guam
12.45
12.48
Br:BrO [pptv]
0
0.2
0.5
1
1.5
2


200 hPa WACCM CHBR3, GPH [km], SZA [deg] 20120201_00:00 UTC, 10:00 Local
FEB
CHBr3
Guam
CHBR3 [pptv]
0
0.05
0.25
0.5
0.6
0.7
0.8


200 hPa WACCM CO, GPH [km], SZA [deg] 20120201_00:00 UTC, 10:00 Local
FEB
CO
Guam
12.45
12.48
CO [ppbv]
0
25
50
75
100

Summary / Conclusions

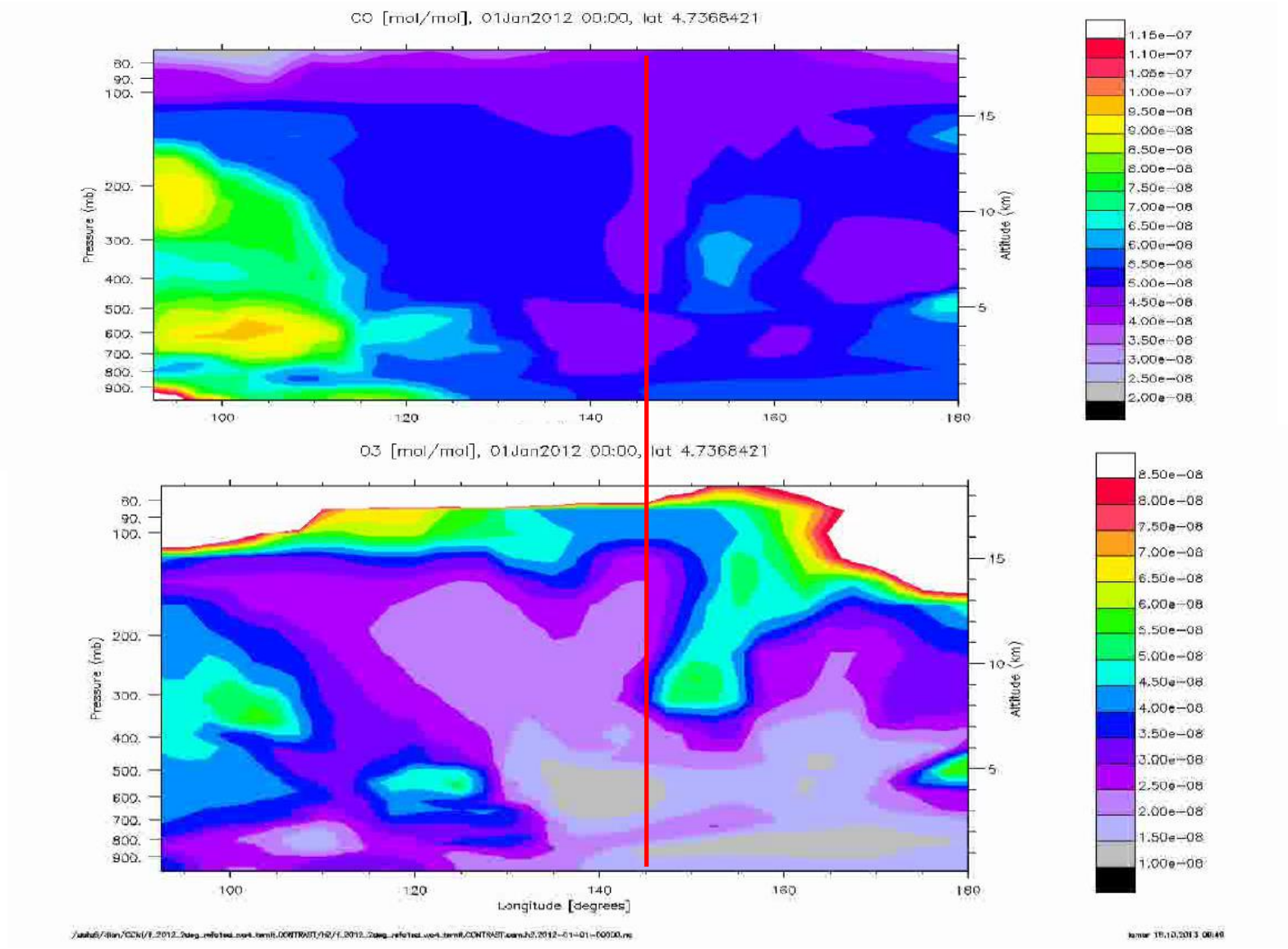
- The CAM-Chem model includes a detailed representation of VSL Bromine, Chlorine, and Iodine species. A description of this model can be found in Ordoñez et al., ACP, 2012.

- This model has been used to examine bromine partitioning and VSL bromine loading in the TTL.

- Daytime Br_y partitioning in the tropical UTLS within/near convective outflow is dominated by Br atoms (up to 60% of the Br_y) due to low O_3 and cold conditions. Experiments designed to measure the bromine budget in this region should therefore include measurements of atomic bromine.

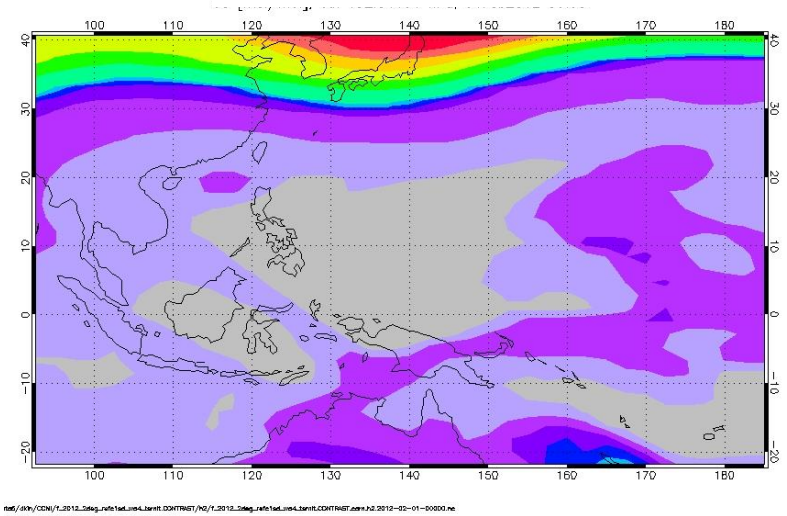
- The model is being configured to run with 3-day forecast meteorological fields (GEOS5) in support of CONTRAST.

CO and O_3 Cross Sections *** 5° N *** Jan 2012

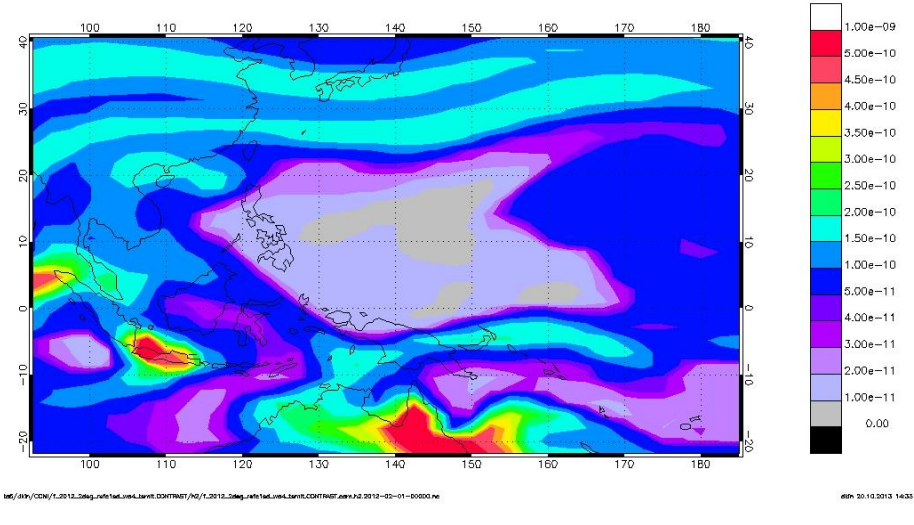


O_3, NOx, $CHBr_3$, CH_2Br_2 *** WP *** 1 Feb 2012

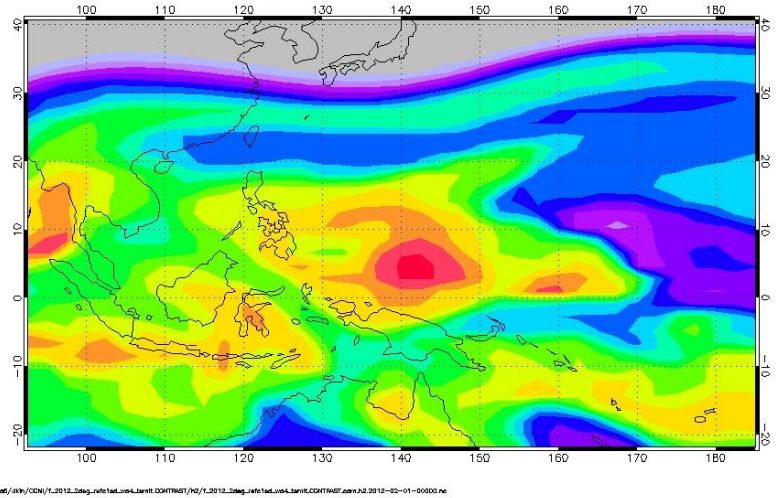
Ozone



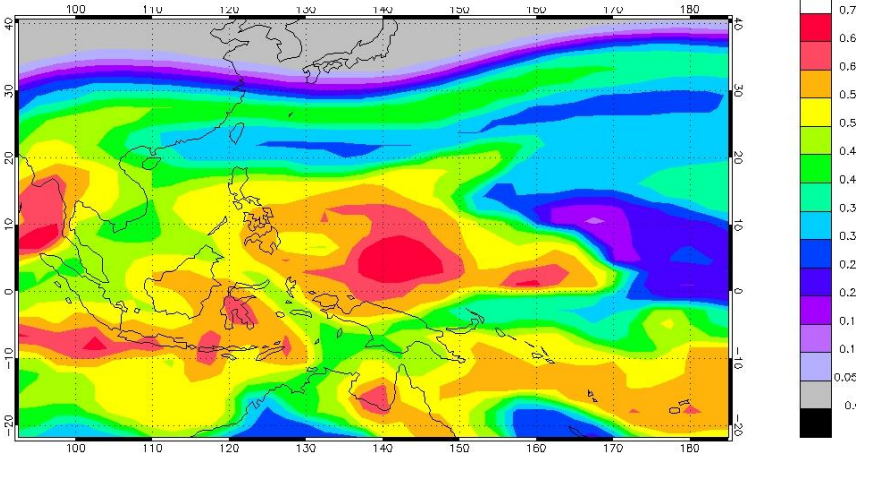
NOx



$CHBr_3$

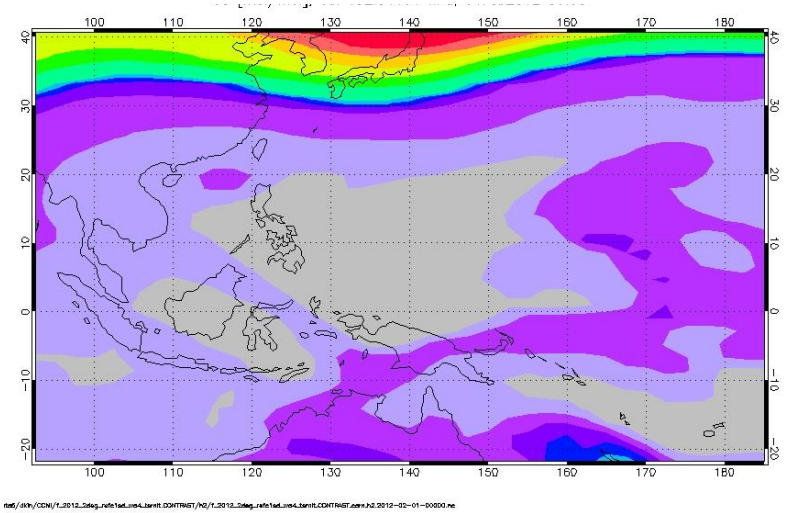


$CHBr_3$ / CH_2Br_2

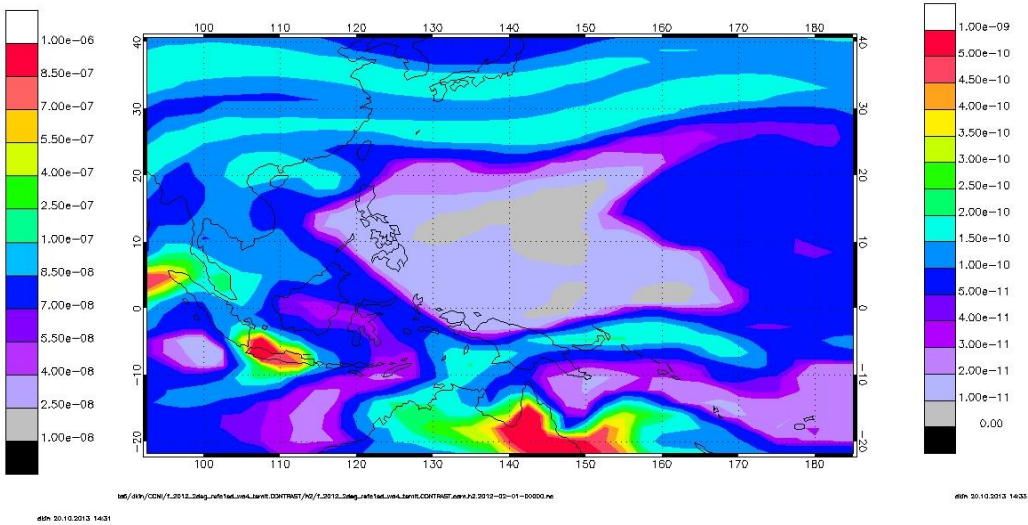


O_3, NOx, $CHBr_3$, CH_2Br_2 *** WP *** 1 Feb 2012

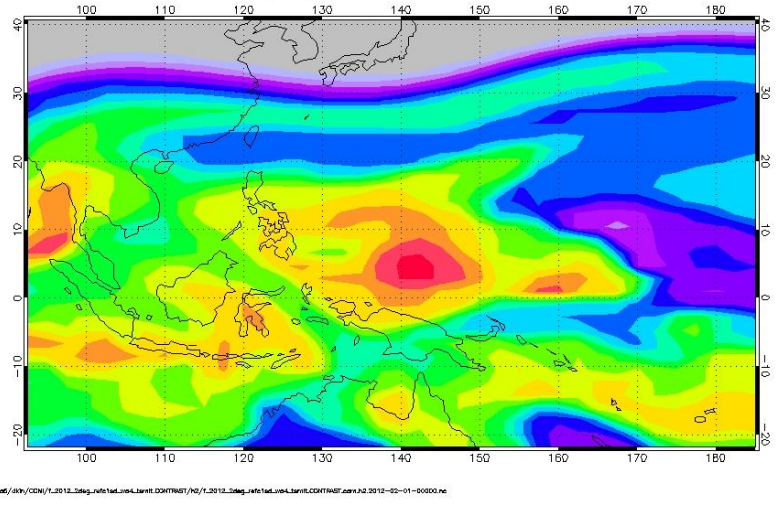
Ozone



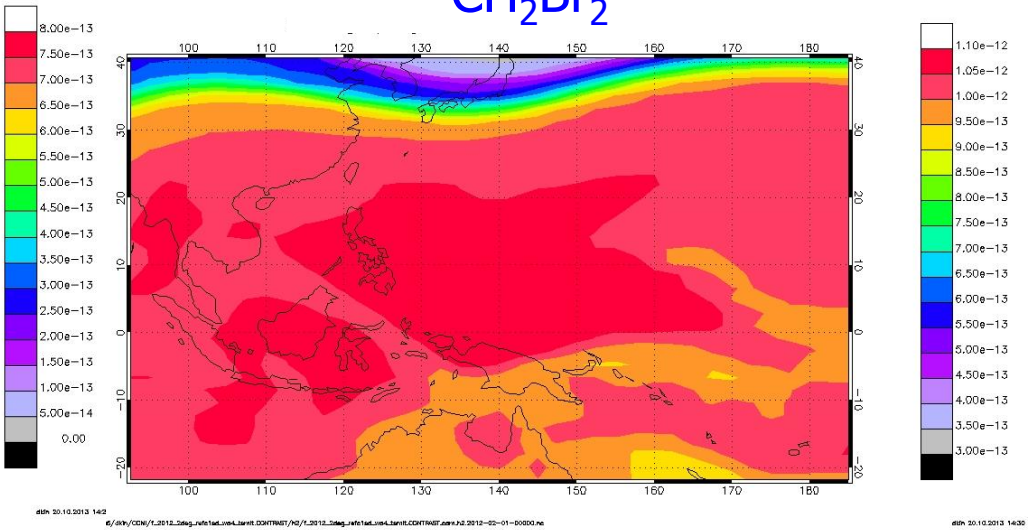
NOx

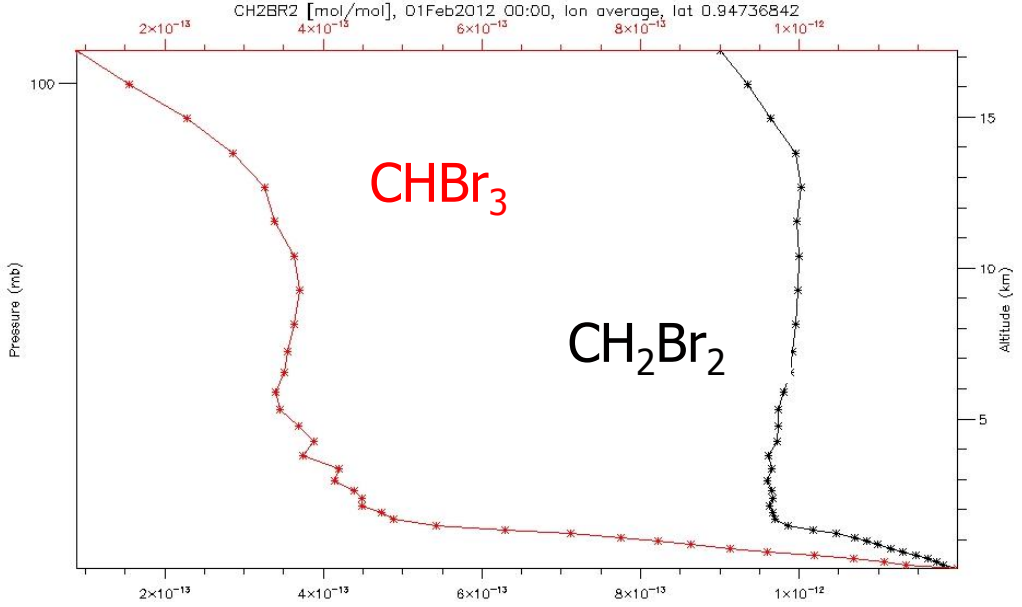


$CHBr_3$

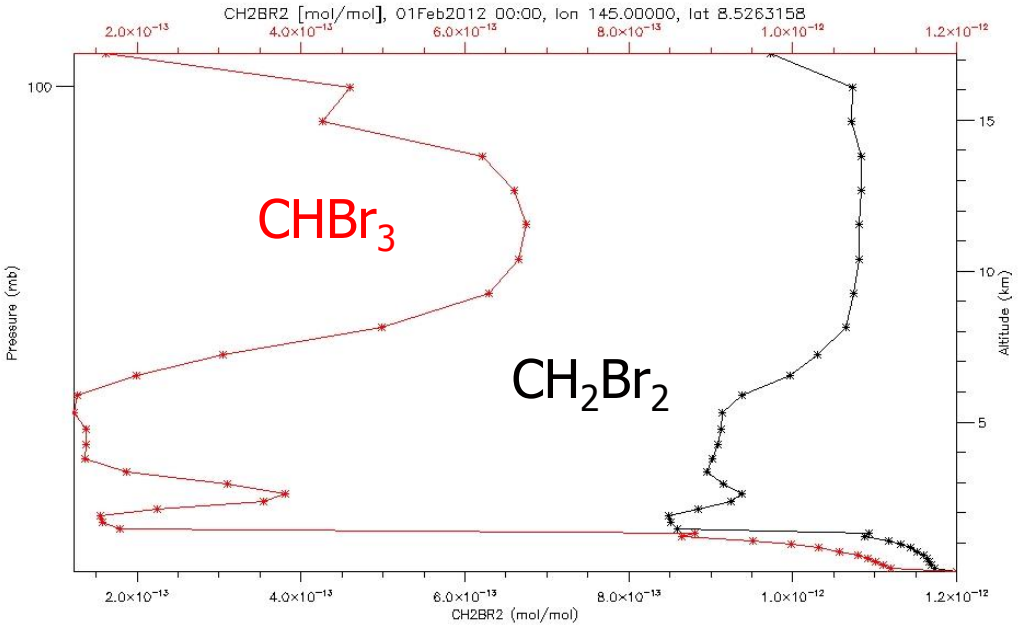


CH_2Br_2





<=EQ, Zonal Average



<=Near Guam