NCAR Atmospheric Chemistry Division

Global modelling of iodine in the troposphere and lowermost stratosphere

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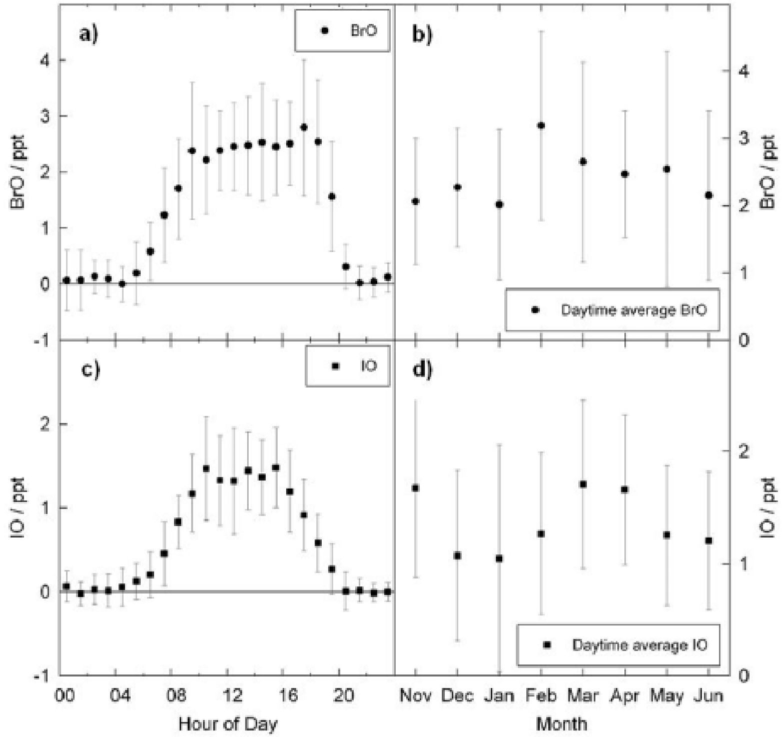
Outline

1. Motivation
2. Implementation of VSL halogenated sources in CAM-Chem
3. Model results for reactive bromine / iodine
4. Impact of bromine / iodine on O_3 (tropics)
5. Summary and ongoing work

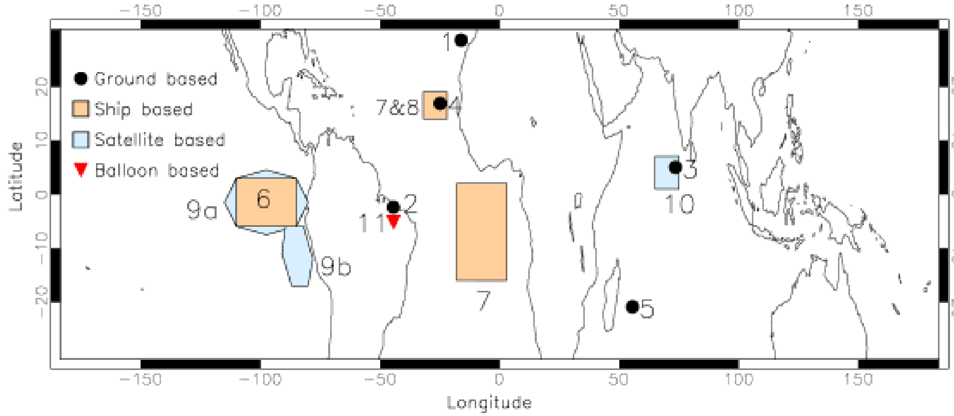
1. Motivation

1. Troposphere

- Observations of IO, BrO, etc. in polar and coastal areas
- Presence of IO and BrO confirmed over the open oceans



Halogen chemistry has a significant and extensive influence on photochemical ozone loss in the tropical Atlantic Ocean boundary layer (Read et al., Nature, 2008).



IO and BrO at ppt levels
(Saiz-Lopez et al., ACP, 2012)

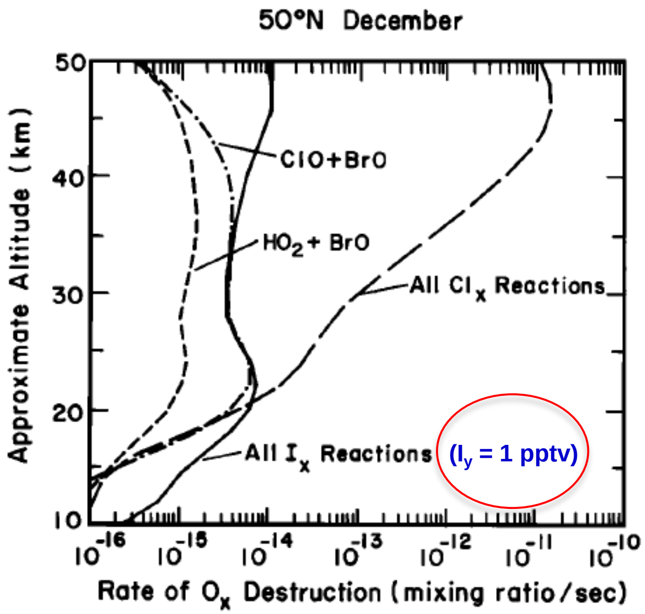
Scientific questions:

- Impact of halogens on the O_3 budget
- Impact on HO_x, NO_x, methane lifetime

1. Motivation

2. Stratosphere

"**On the role of iodine in ozone depletion**", Solomon et al., JGR, 1994



Solomon et al., JGR, 1994
Gilles et al., JPC-A, 1997

Since then:

- New kinetic information on iodine available
- Attempts to detect reactive iodine in the UTLS

Wennberg et al., JGR,1997
Wittrock et al., GRL, 2000
Bösch et al., JGR, 2003
Pundt et al., JAC, 1998
Berthet et al., JGR, 2003
Butz et al., ACP, 2009

Most recent analyses:

- **≤0.1 pptv IO, OIO** in lower stratosphere (in northern high and mid-latitudes, and tropics)
- Estimated total inorganic iodine: (Photochemical 1-D model) **I_y ~ 0.2 pptv**

Sci. Assessment of Ozone Depletion (WMO, 2011):

Unlikely that iodine plays a significant role in the photochemistry of stratospheric ozone

2. Implementation of VSL sources

CAM-Chem

- Fixed SST and ice (monthly climatology)
- 1.9° (lat) x 2.5° (lon) horizontal resolution
- 26 vertical levels (surface to ~ 4 hPa)
- Tropospheric and stratospheric chemistry

(Emmons et al., 2010; Kinnison et al., 2007)

VSL Halogen Chemistry

- Implementation of VSL (τ < 6 months) halogenated sources from the ocean

Very short-lived (VSL) halogenated sources

Source gas	Local Lifetime (WMO, 2010)	Main loss	
CH_2BrCl	137 days	OH, hv	
CH_2Br_2	123 days	OH, hv	
$CHBrCl_2$	78 days	OH, hv	
$CHBr_2Cl$	59 days	hv, OH	
$CHBr_3$	24 days	hv, OH	
CH_3I	7 days	hv, OH	(Bell et al., 2002)
CH_2ICl	~ 2–3 h	hv	
CH_2IBr	~1 h	hv	
CH_2I_2	~ 5 min	hv	
I_2	~ secs	hv	

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  (Emmons et al., 2010; Kinnison et al., 2007)

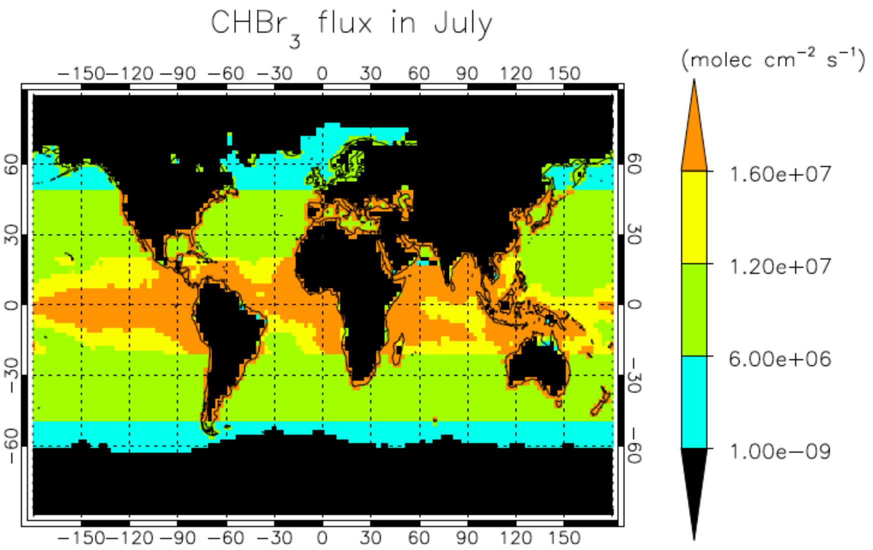
VSL Halogen Chemistry

- Implementation of VSL (τ < 6 months) halogenated sources from the ocean

- Emissions following Chl-a over tropics
- Top-down approach (following Warwick et al., JGR, 2006; Liang et al., ACP, 2010)

- Photochemistry
- Dry / wet deposition
- Catalytic release from sea-salt

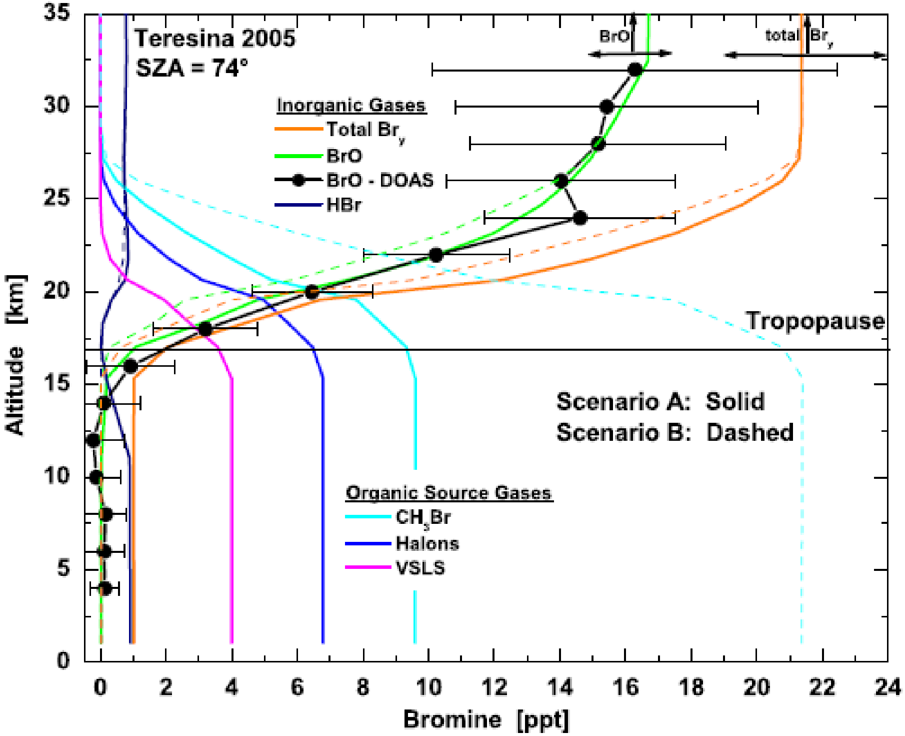
VSL halogen sources in CAM-Chem



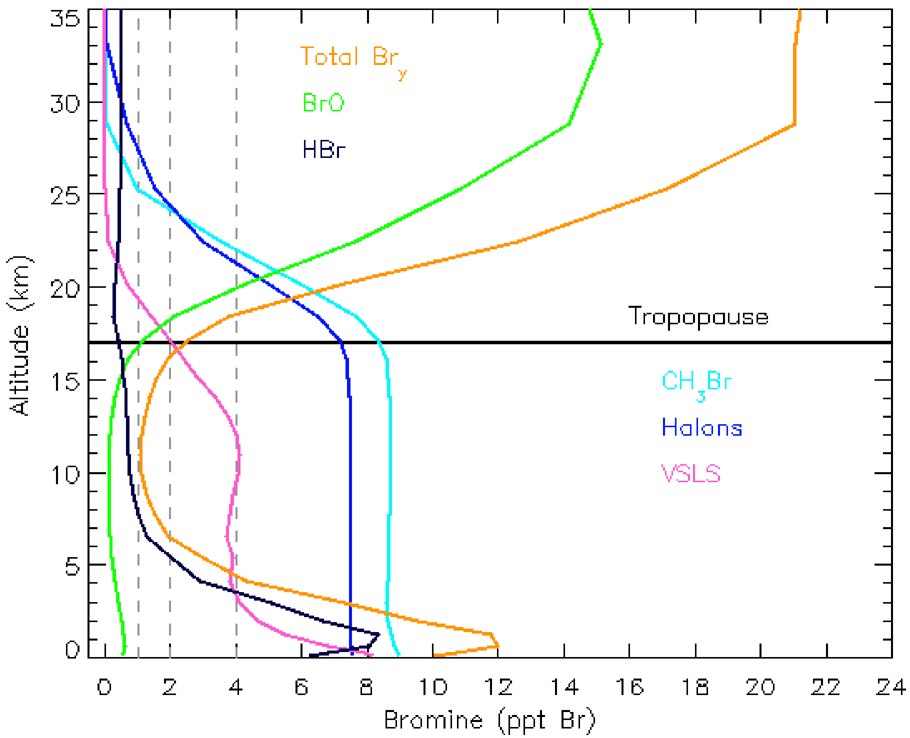
Ordóñez et al., ACP, 2012 → Description and evaluation of VSL sources

3. Results: Daytime bromine profiles over the tropical oceans

Teresina (Dorf et al., ACP, 2008)



CAM-Chem_bromine (23° N – 23° S)



Notes:

• SLIMCAT run with CH_3Br (9.6 ppt), halons (6.8 ppt), and VSLS (4 ppt as CH_2Br_2) plus PGs (1 ppt as HBr).

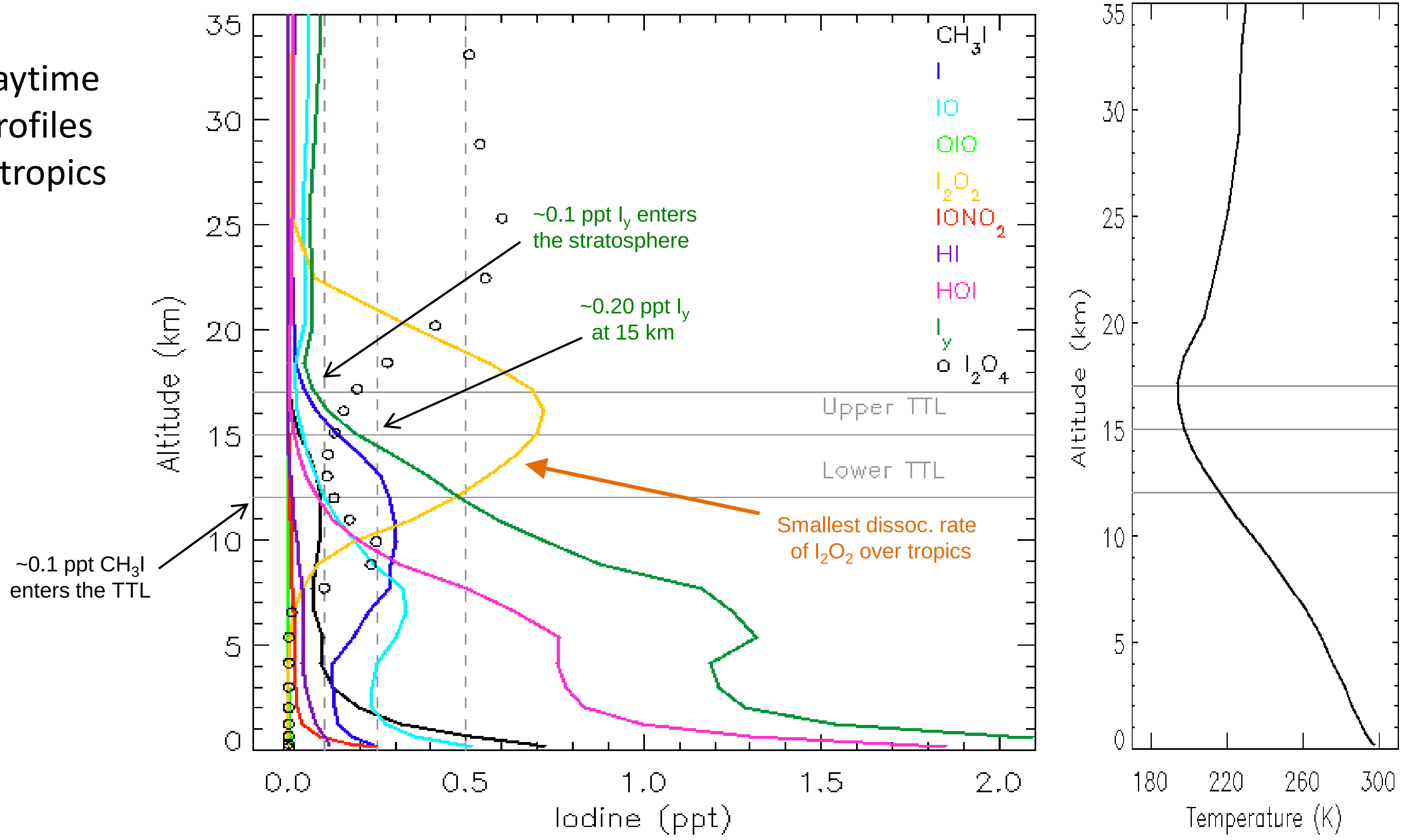
• Photochemical breakdown only in stratosphere.

Notes CAM-Chem:

- Halons = H-1211 + H-1301 (i.e. $CF_2ClBr + CF_3Br$)
- VSLS = $3\ CHBr_3 + 2\ CH_2Br_2 + CH_2BrCl + 2\ CHBr_2Cl + CHBrCl_2$
- Total Br_y = $Br + BrO + HBr + BrONO_2 + BrCl + HOBr$

Iodine profiles over tropical oceans (no photolysis of I_2O_y)

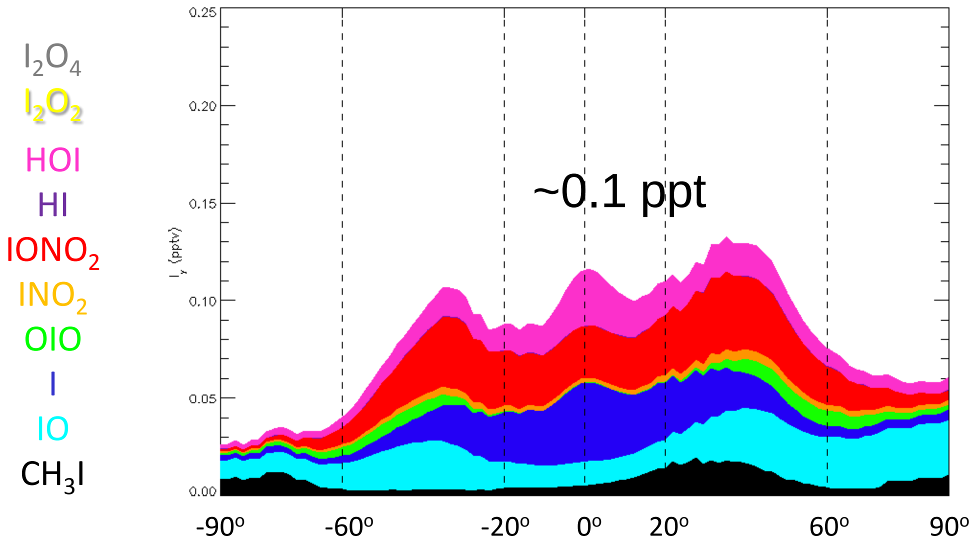
Daytime profiles in tropics

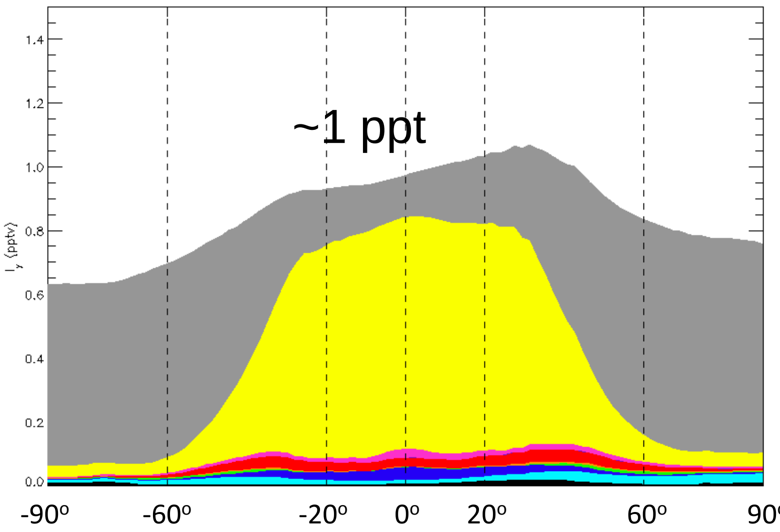


$I_y = I + IO + OIO + IONO_2 + HI + HOI$

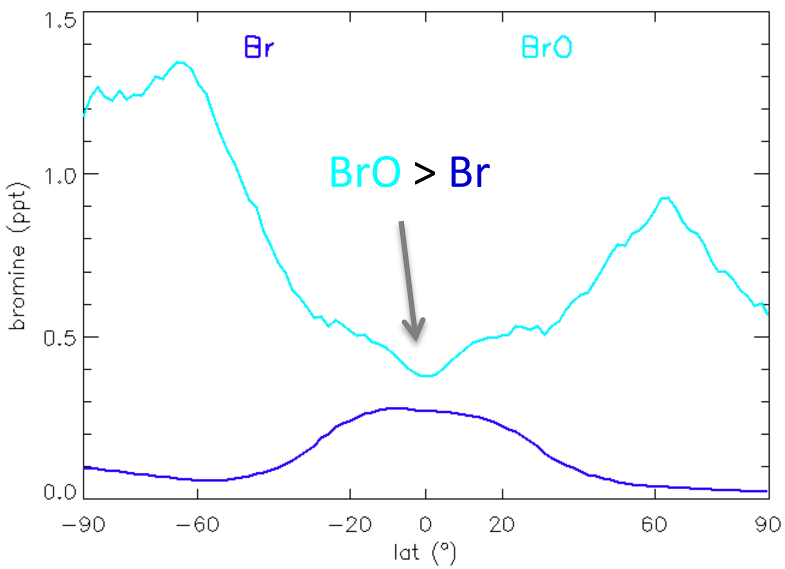
Butz et al. (2009): Upper limits of IO, OIO ~ 0.1 ppt

Iodine partitioning in LMS (thermal tropopause – 400 K isentrope)

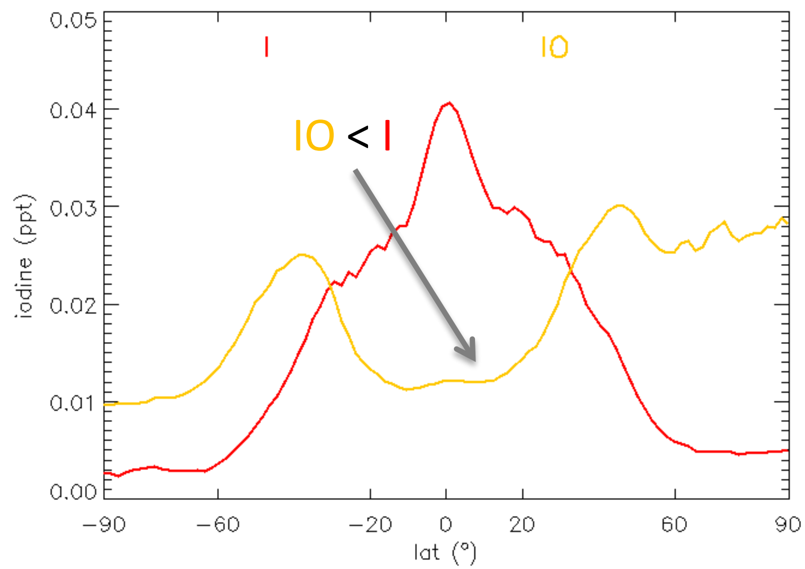




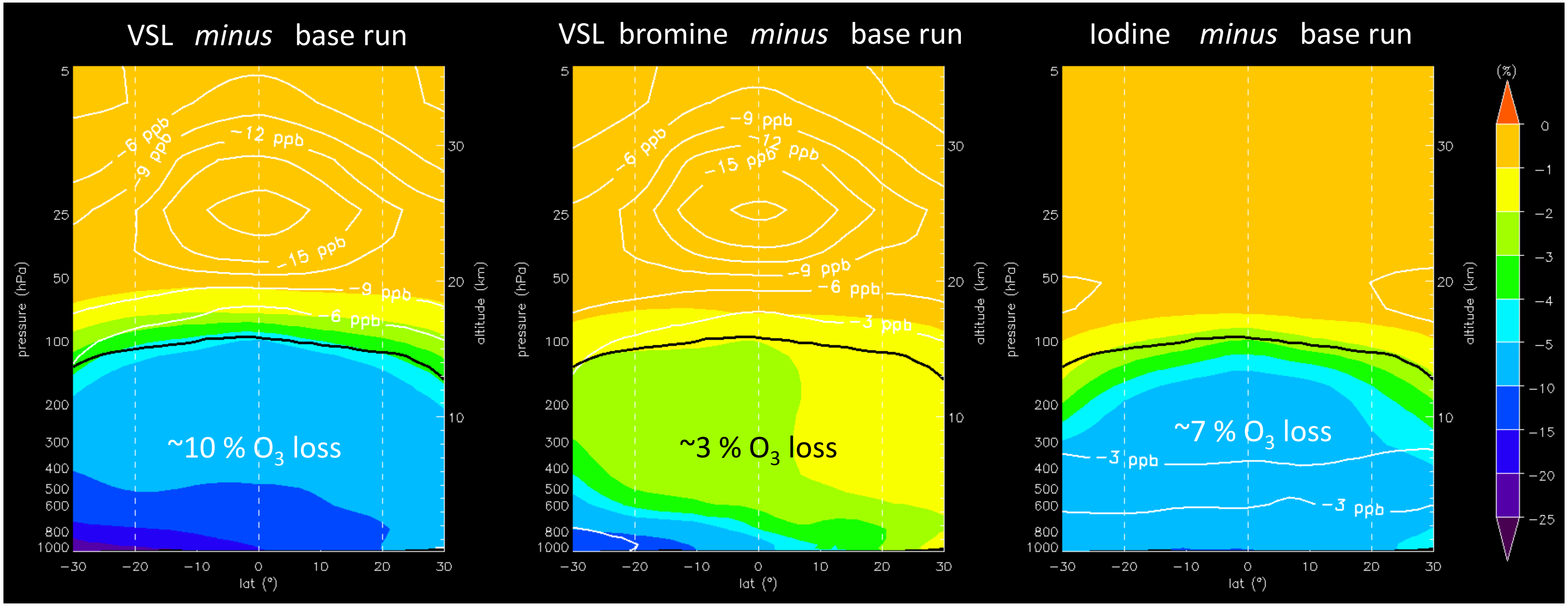
BrO_x



IO_x



4. Halogen-driven ozone loss in the tropics (VSL *minus* no VSL)



Change in tropical tropospheric ozone column:

ΔO_3 = - 2.6 DU (10.5 %) ΔO_3 = - 0.8 DU (3.2%) ΔO_3 = -1.8 DU (7.3%)

Yang et al., JGR, 2005:
4-6% trop. O_3 loss
(due to bromine)

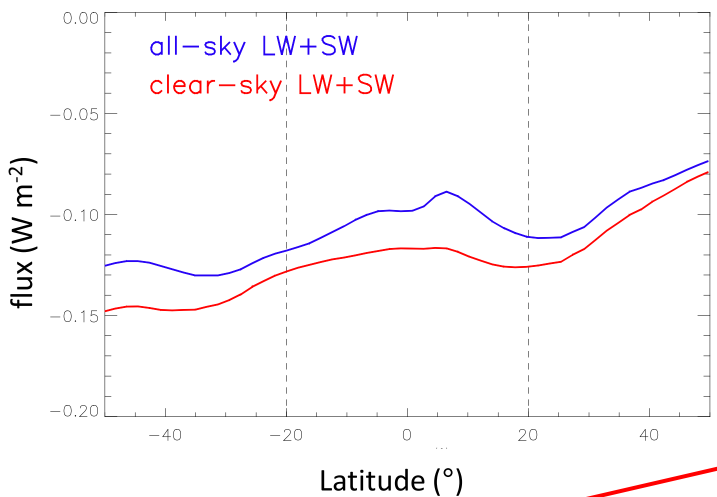
Parrella et al., ACPD, 2012:
6.5 % trop. O_3 loss
(due to bromine)

Annual average difference in radiation fluxes at tropopause

Saiz-Lopez et al., ACP, 2012

Lower O_3 → Lower IR absorp.

VSL - base run



Average for tropics (20° S – 20° N)

	Longwave flux (W m^{-2})	Net flux (W m^{-2})
All-sky	-0.104	-0.103
Clear-sky	-0.138	-0.122

1/3

Sensitivity under all-sky conditions:

0.10 W m^{-2} / 2.5 DU = 0.04 W m^{-2} / DU ≈ 0.042 W m^{-2} / DU

(Ramaswamy et al., IPCC, 2001)

Is our -0.100 Wm^{-2} significant?

LWRE from tropospheric ozone: ~ 0.33 W m^{-2} (all-sky)

~ 0.50 W m^{-2} (clear-sky)

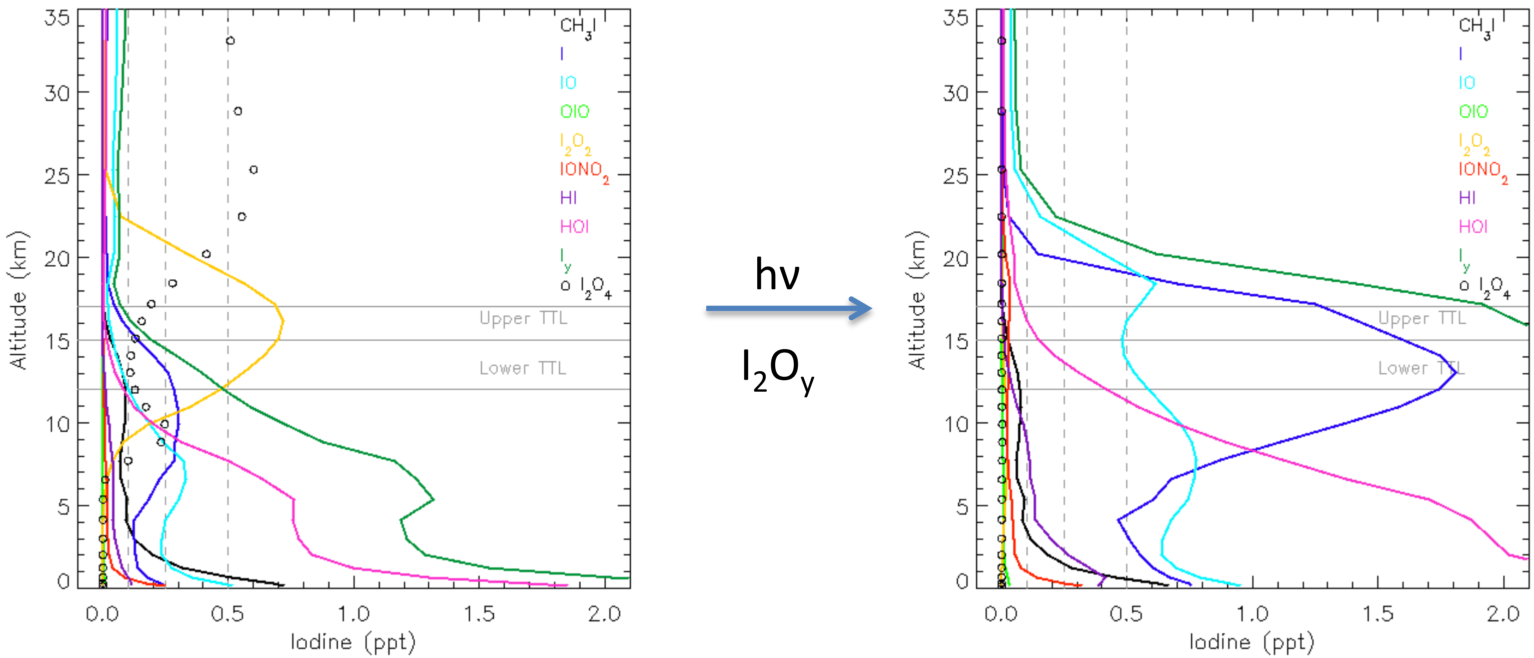
(Worden et al., 2010)

This negative contribution is ~ 30% of the positive contribution to the TOA radiation flux associated with infrared ozone absorption

Sensitivity runs: photolysis of I_2O_y

Tropical profiles

High levels of I_2O_2, I_2O_3, I_2O_4



Ozone depletion efficiency by iodine enhanced if I_2O_y photolysis is included.

However significant uncertainties:

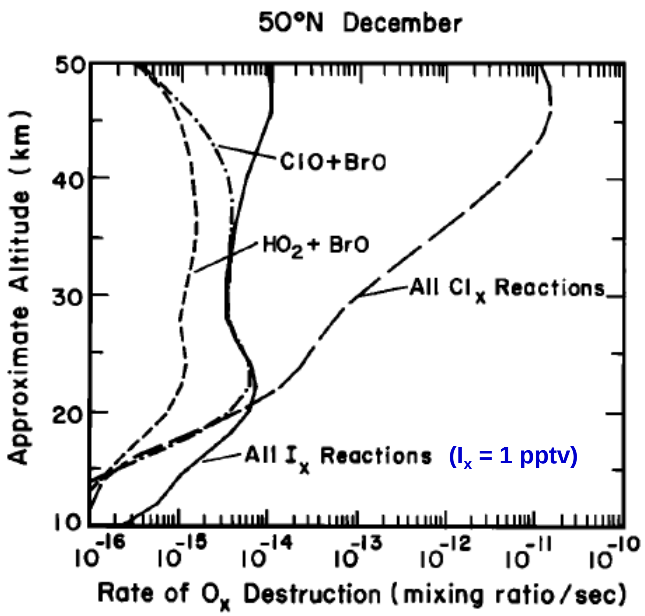
- I_2O_y absorption cross sections
- Possible mechanism for iodine loss (e.g. uptake by stratospheric aerosols)

5. Summary & ongoing work

- **VSL** oceanic sources and chemistry of bromine/iodine implemented in **CAM-Chem 3.6.x** → Current work: Implementation in **CESM 1.1**
- **Iodine partitioning**: high I/IO ratio in tropical UTLS
- **Iodine-mediated ozone depletion**, compared to bromine, dominates throughout the **tropical troposphere** (impact on TOA radiation flux), but small in **tropical LMS**.
- Experimental work on I_2O_y (and other iodine species) is key to further determine the **role of iodine in ozone depletion in the UTLS**

2. Motivation to include VSLS

2. Stratosphere



Solomon et al., JGR, 1994

Since then:

- New kinetic information on iodine available
- Attempts to detect reactive iodine in the UTLS

Sci. Assessment of Ozone Depletion (WMO, 2011):

- Unlikely that iodine plays a significant role in the photochem. of stratospheric ozone
- VSLS contribute to stratospheric bromine ~1–8 ppt.
- Uncertainties in quantifying the impact of Cl- and Br-containing VSLS on stratospheric ozone
- Contribution of VSLS to stratosphere could be altered under a changed climate

3. CESM framework

Feedbacks among the different elements in the climate system

1. Motivation. Why to include VSL halogens in a CCM?

Very short-lived halogens
(τ < 6 months, WMO)

Source gas	Local Lifetime (WMO, 2010)	Main loss
CH_2BrCl	137 days	OH, hv
CH_2Br_2	123 days	OH, hv
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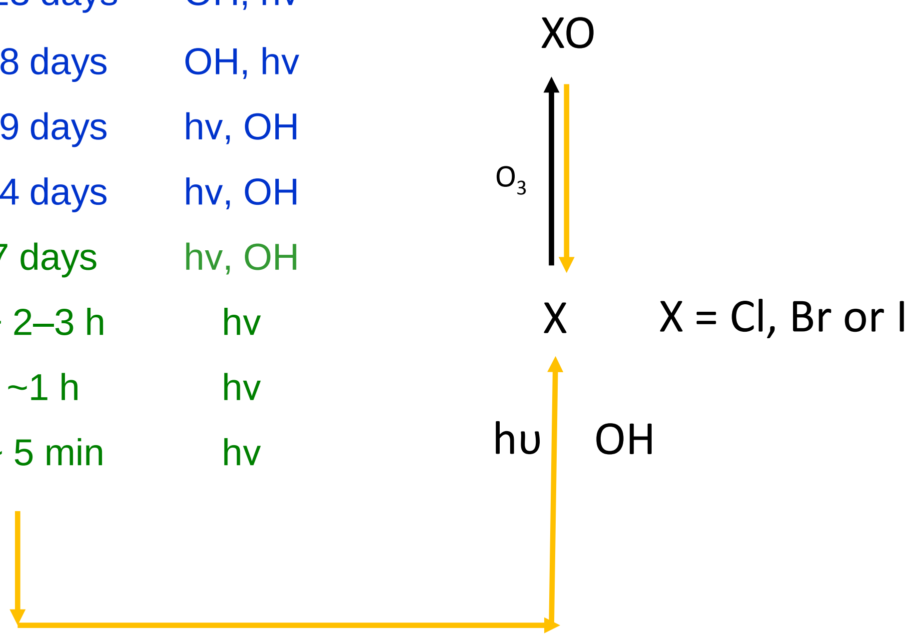

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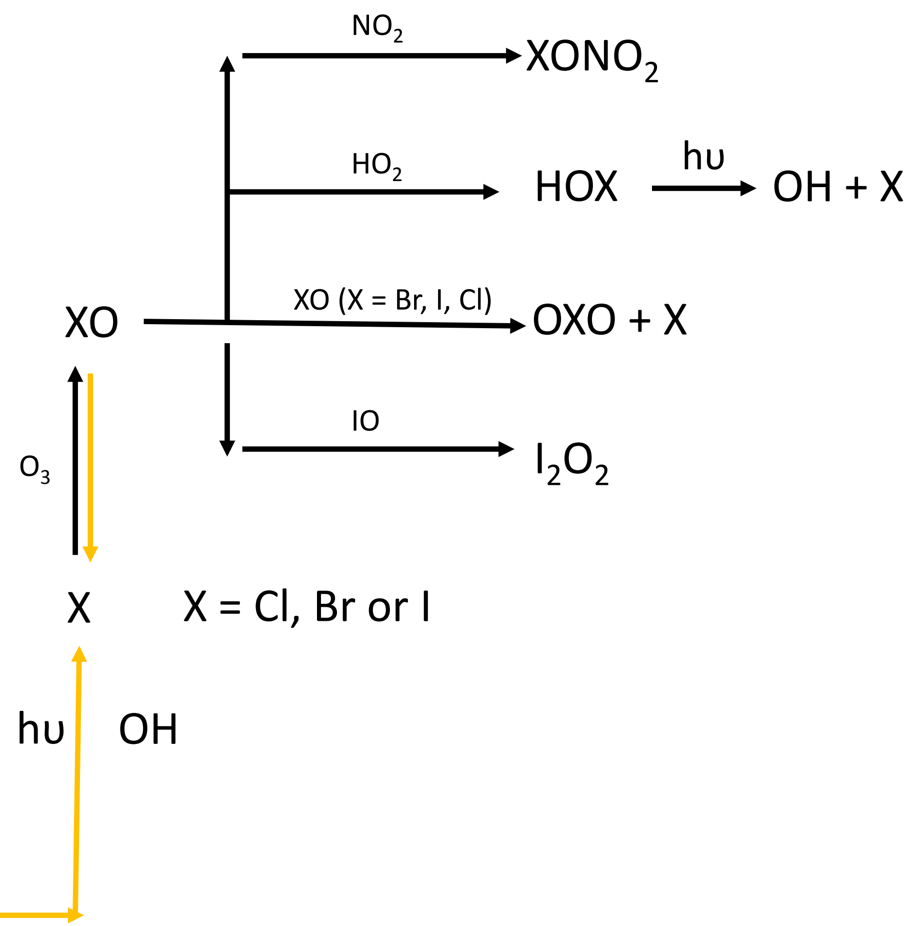

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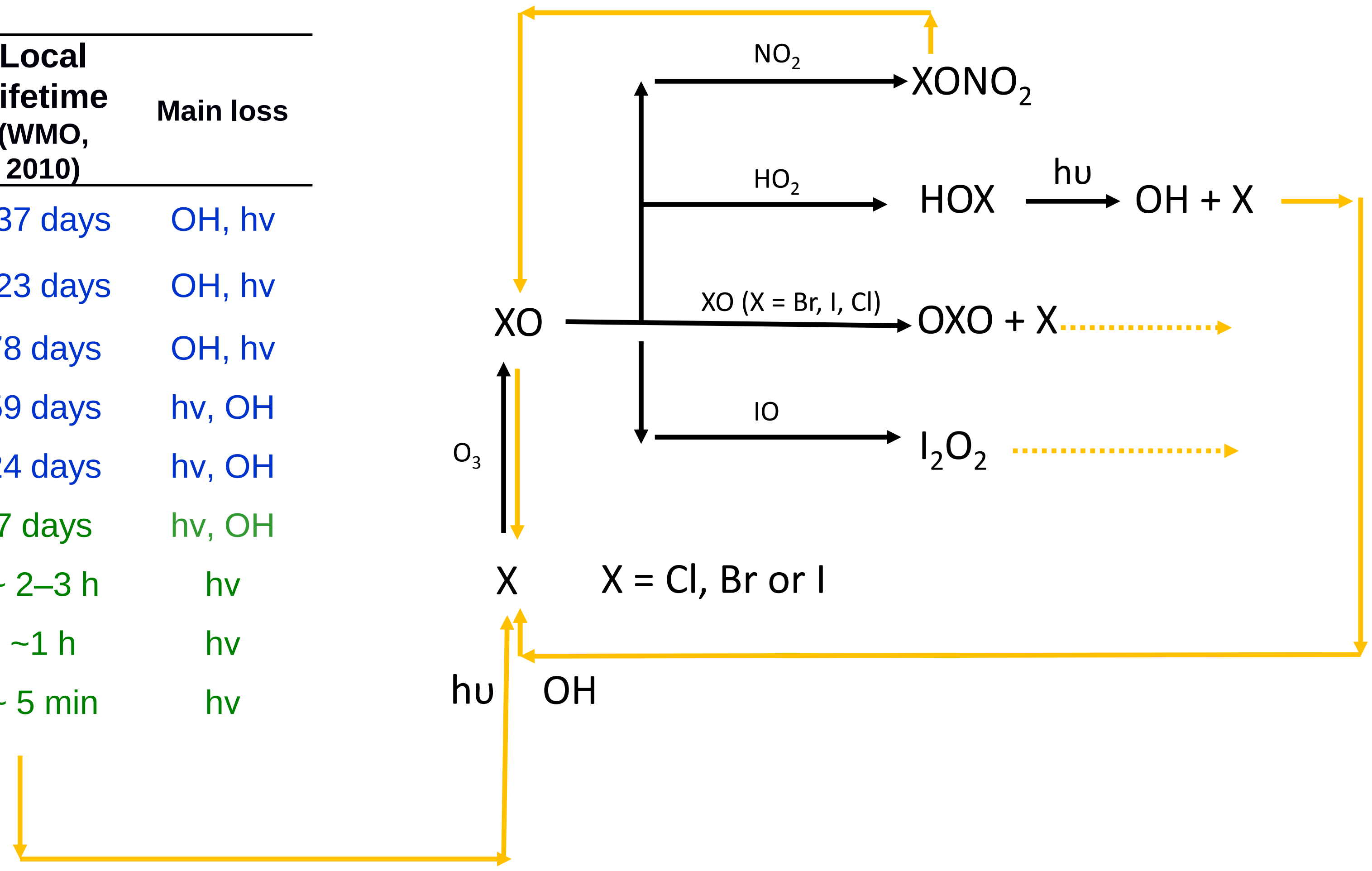

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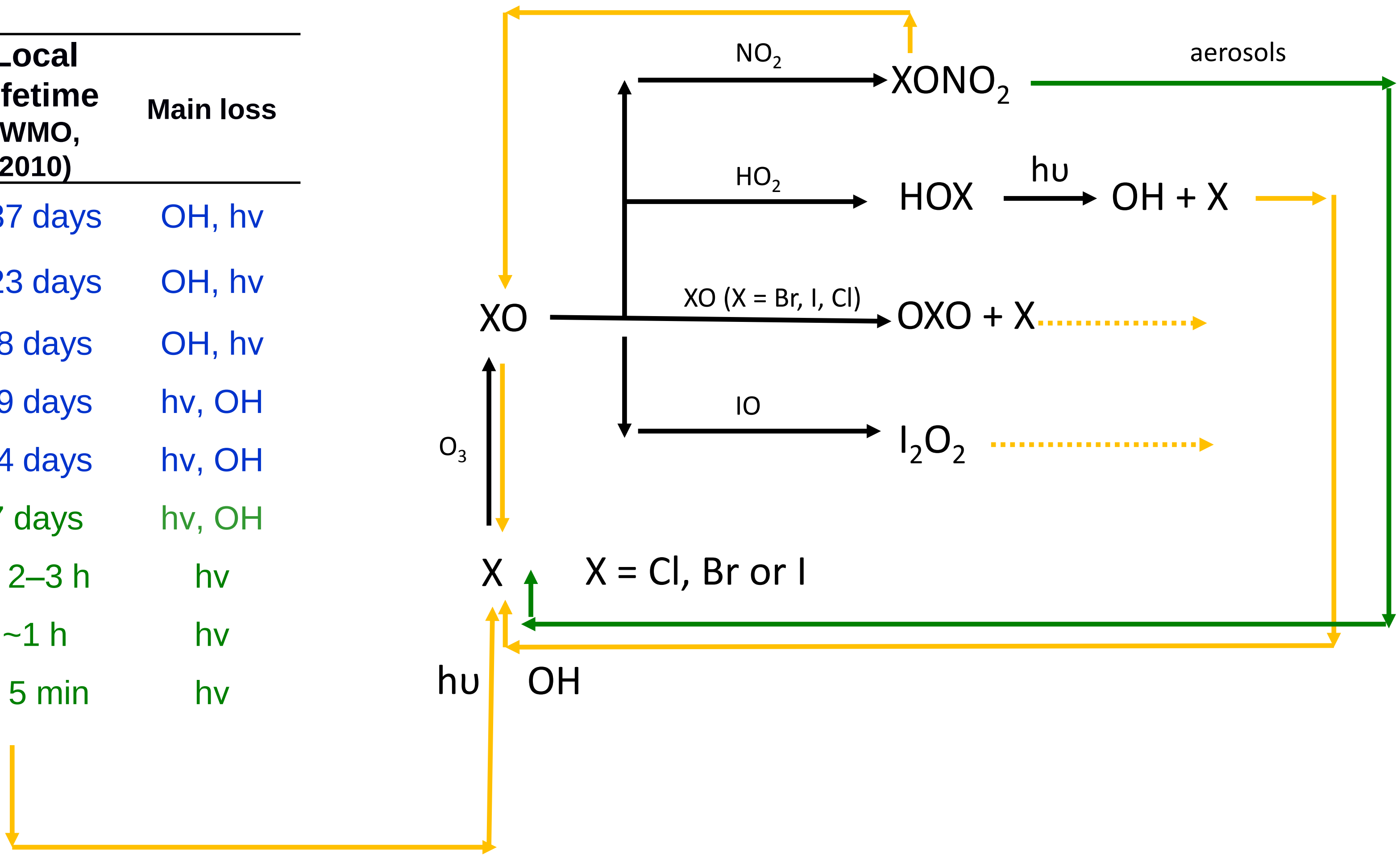

1. Motivation. Why to include VSL halogens in a CCM?

Introductory conclusion: Oxidizing capacity and O_3 radiative impact

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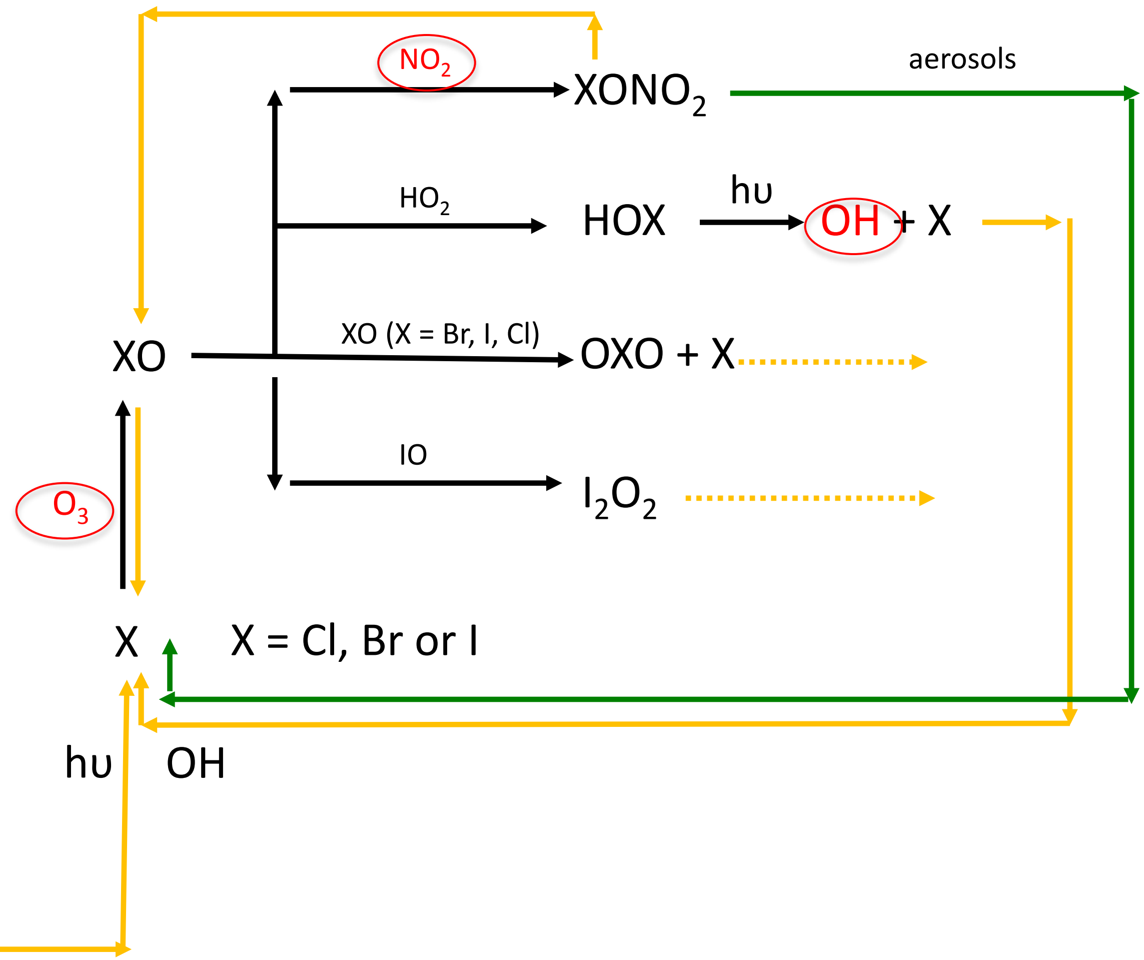
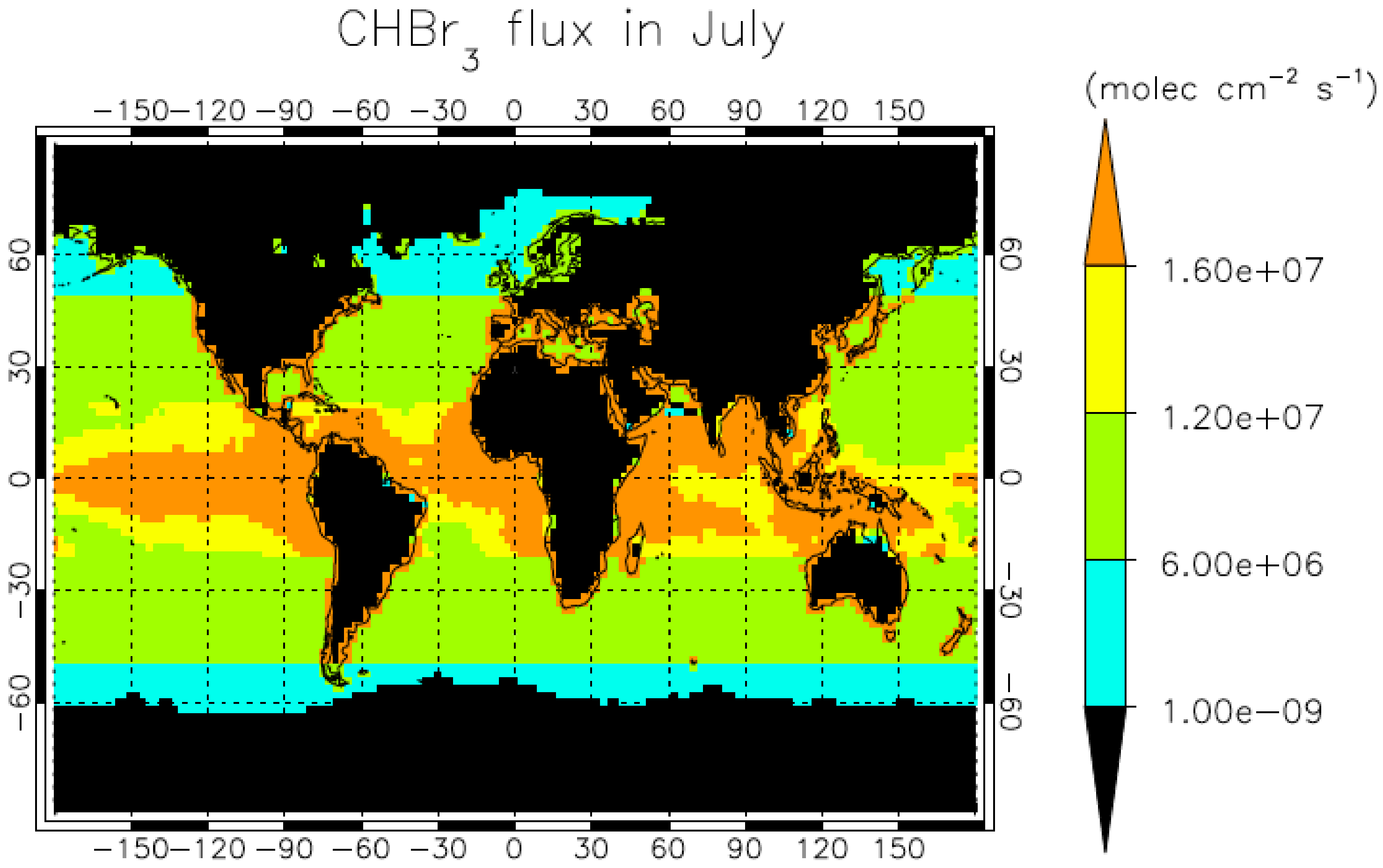
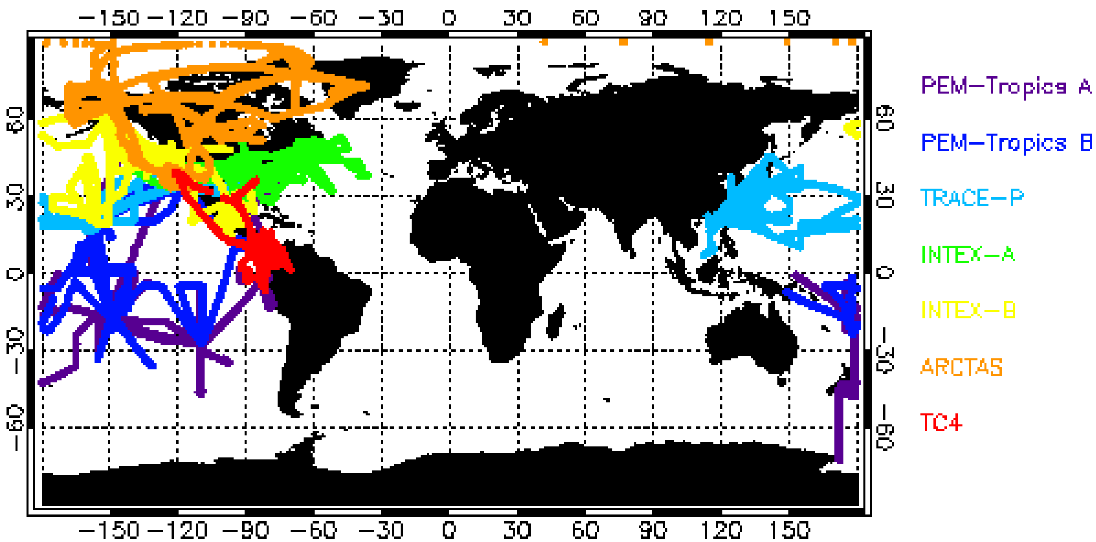


Example: $CHBr_3$ emissions

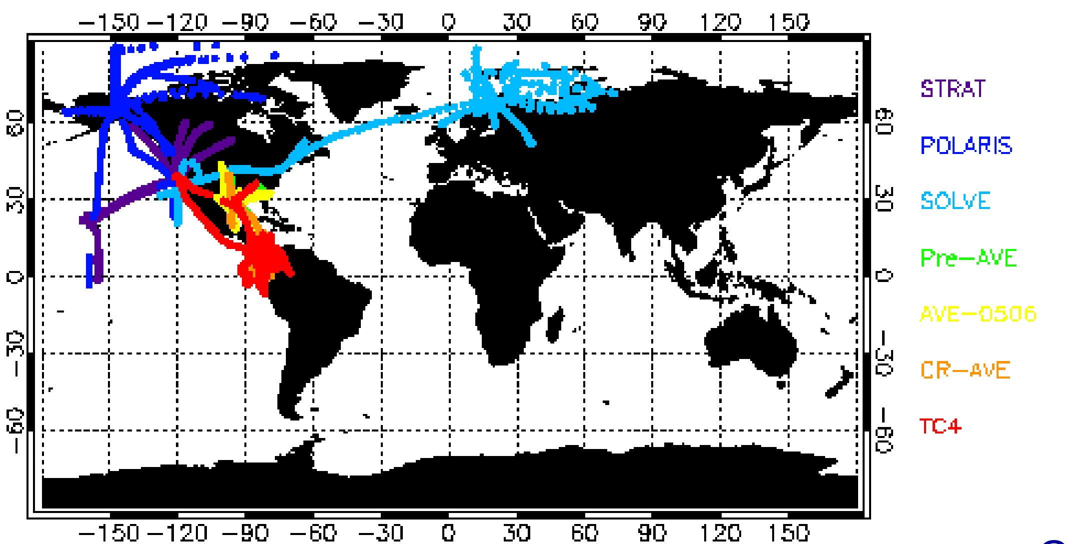


Ordóñez et al., ACP, 2012

Comparison with aircraft observations (1996 – 2008)



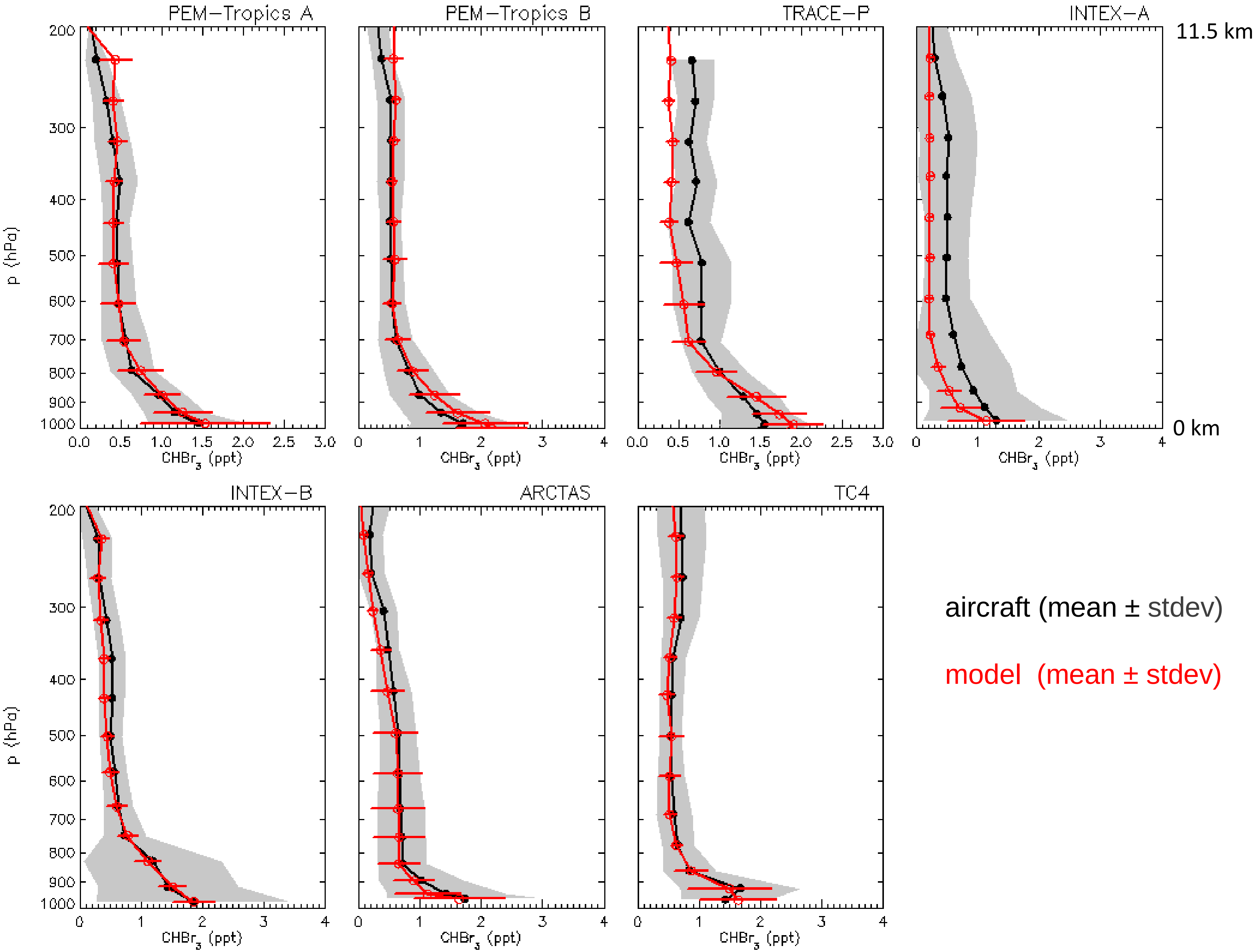
Troposphere
(1000 – 200 hPa)



UTLS (300 – 50 hPa)

Comparison with monthly output
from the latest year of a model simulation

Bromoform ($CHBr_3$)



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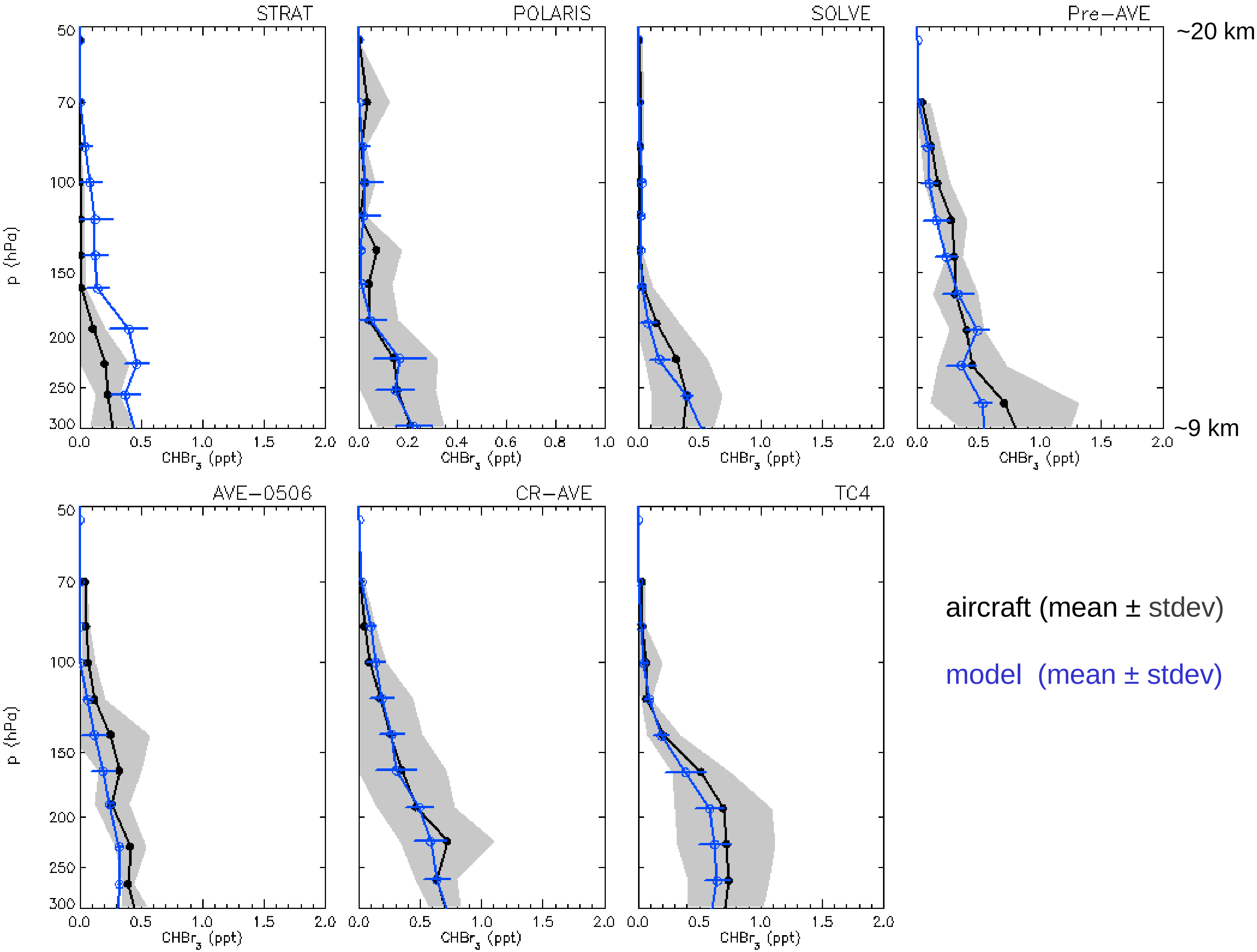
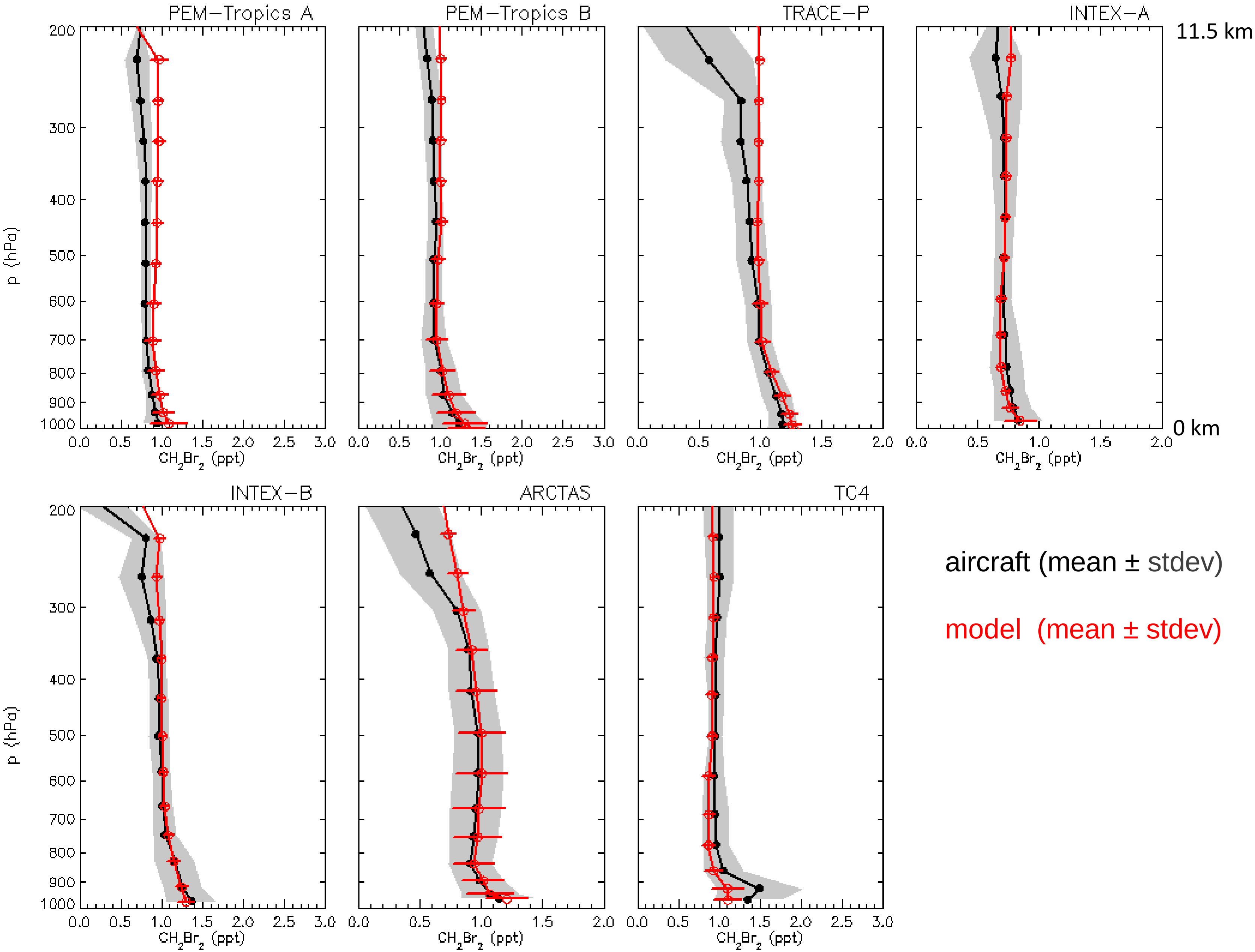


aircraft (mean ± stdev)

model (mean ± stdev)

Dibromomethane (CH_2Br_2)



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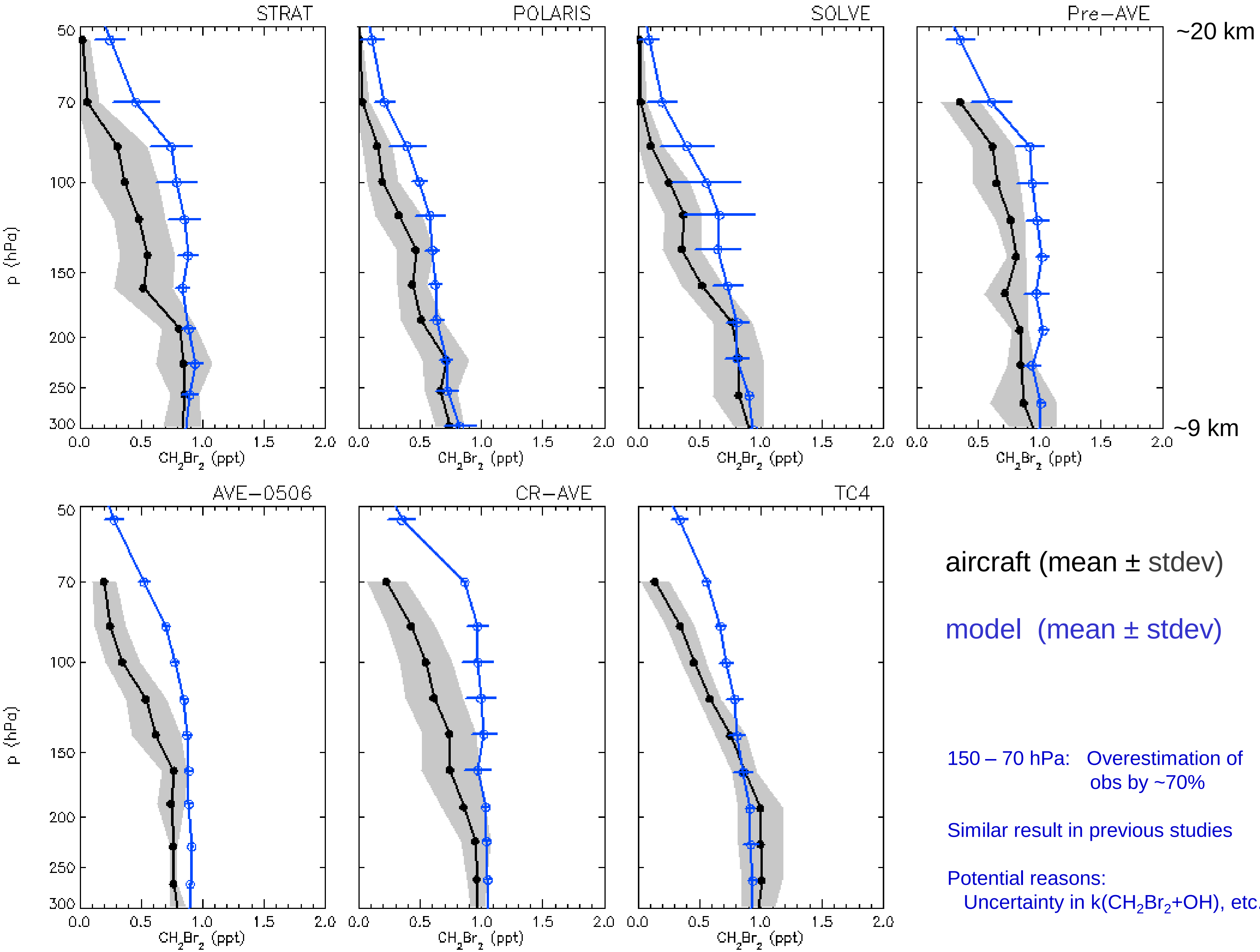


aircraft (mean ± stdev)

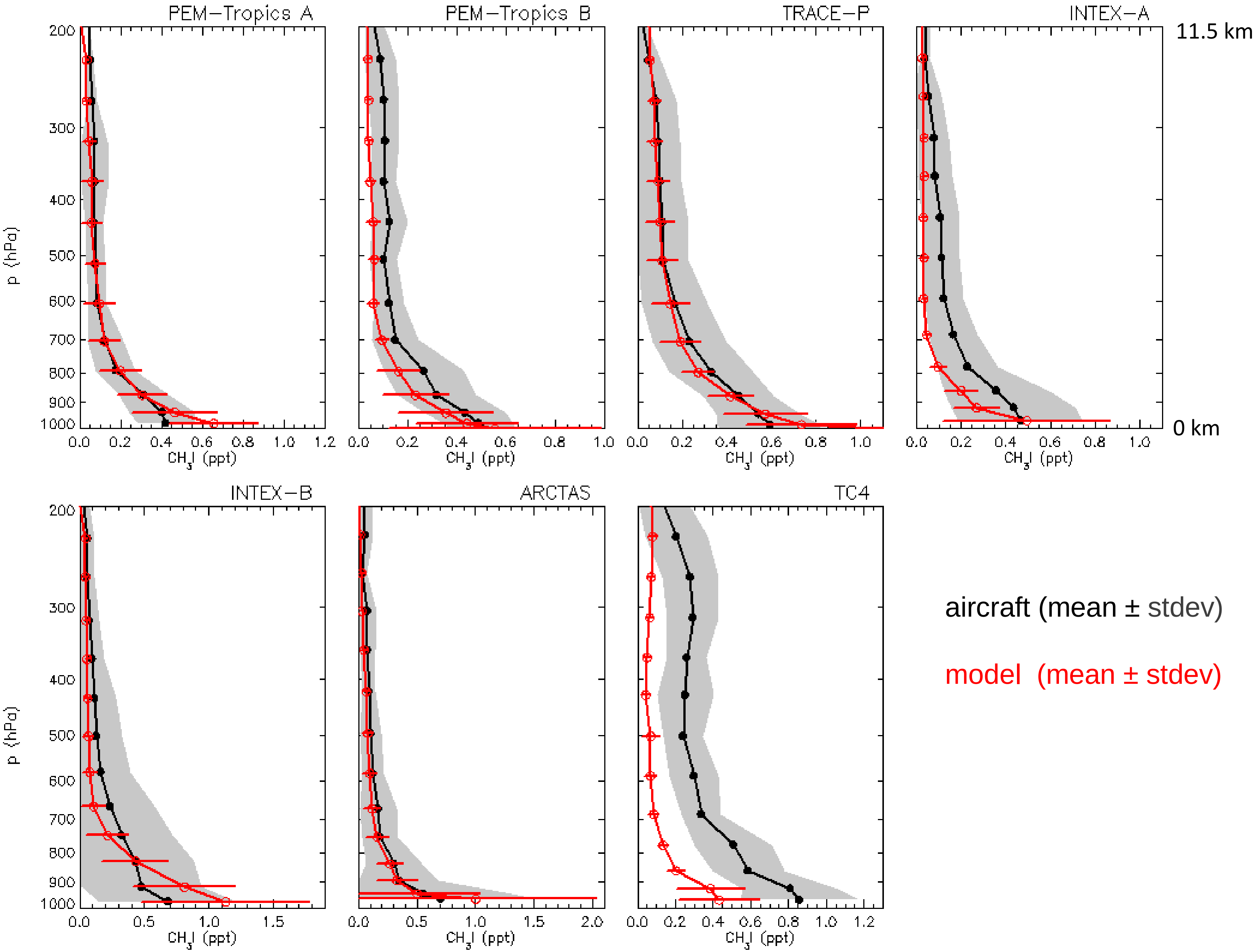
model (mean ± stdev)

150 – 70 hPa: Overestimation of obs by ~70%

Similar result in previous studies

Potential reasons:
Uncertainty in k(CH_2Br_2+OH), etc.

Methyl iodide (CH_3I)



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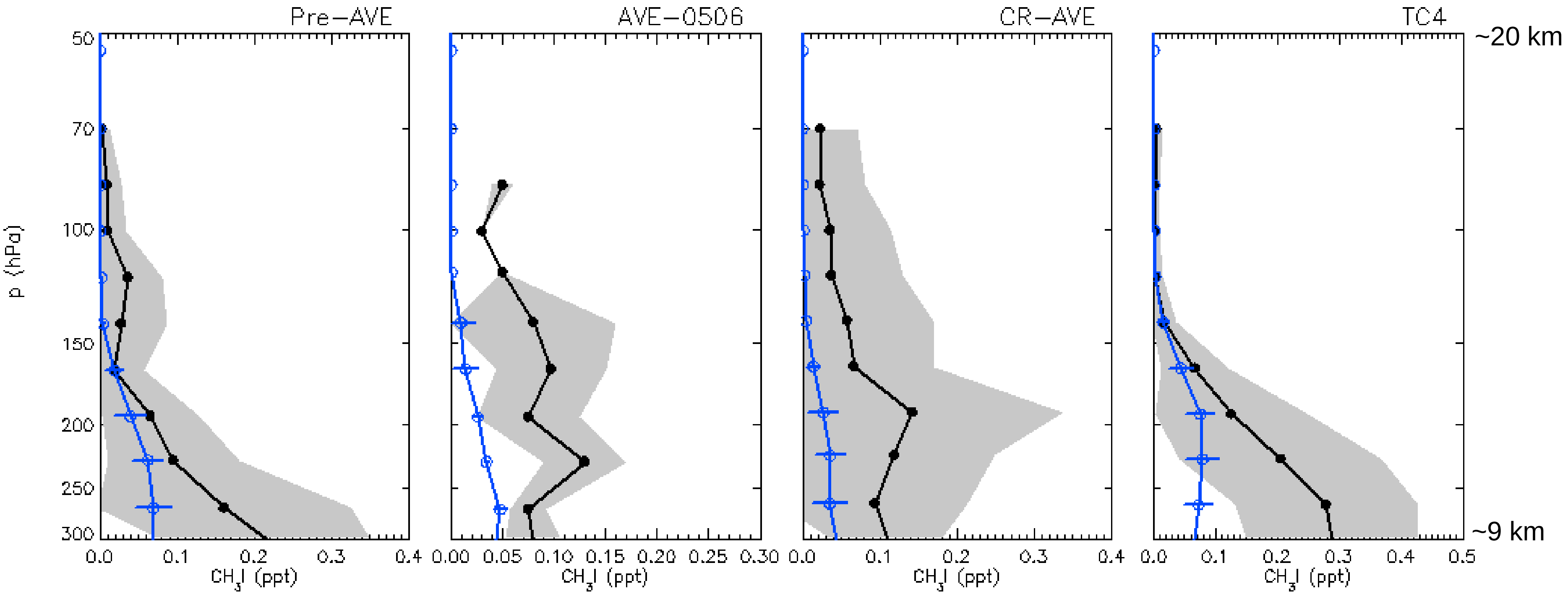

Underestimation of CH_3I, and possibly of O_3 loss by iodine chemistry in the UTLS

aircraft (mean ± stdev)

model (mean ± stdev)

For more on:

- Evaluation of VSLS (Ordóñez et al., ACP, 2012)
- Impact of VSLS on the Earth's radiative balance through their effect on tropospheric O3 (Saiz-Lopez et al., ACP, 2012)

4. Halogen-driven ozone loss in troposphere (VSL *minus* no VSL)

Yang et al., JGR, 2005:
4-6% trop. O_3 loss
(due to bromine)

Parrella et al., ACPD, 2012:
6.5 % trop. O_3 loss
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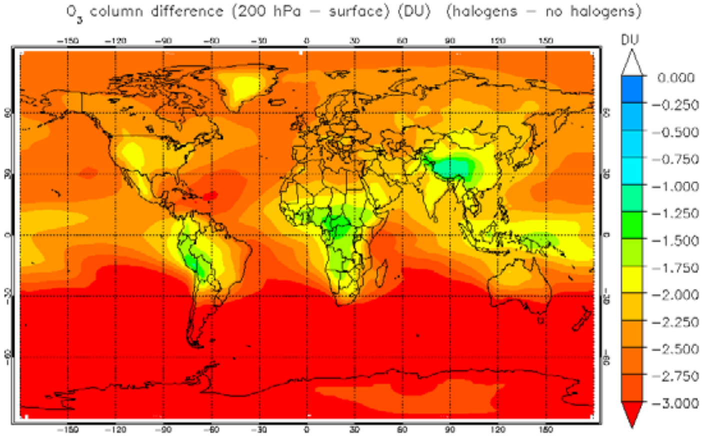

Troposphere (200 hPa – surface):

max	mean	min	
-5.0	-3.0	-1.0	DU

~ 9% of trop. column

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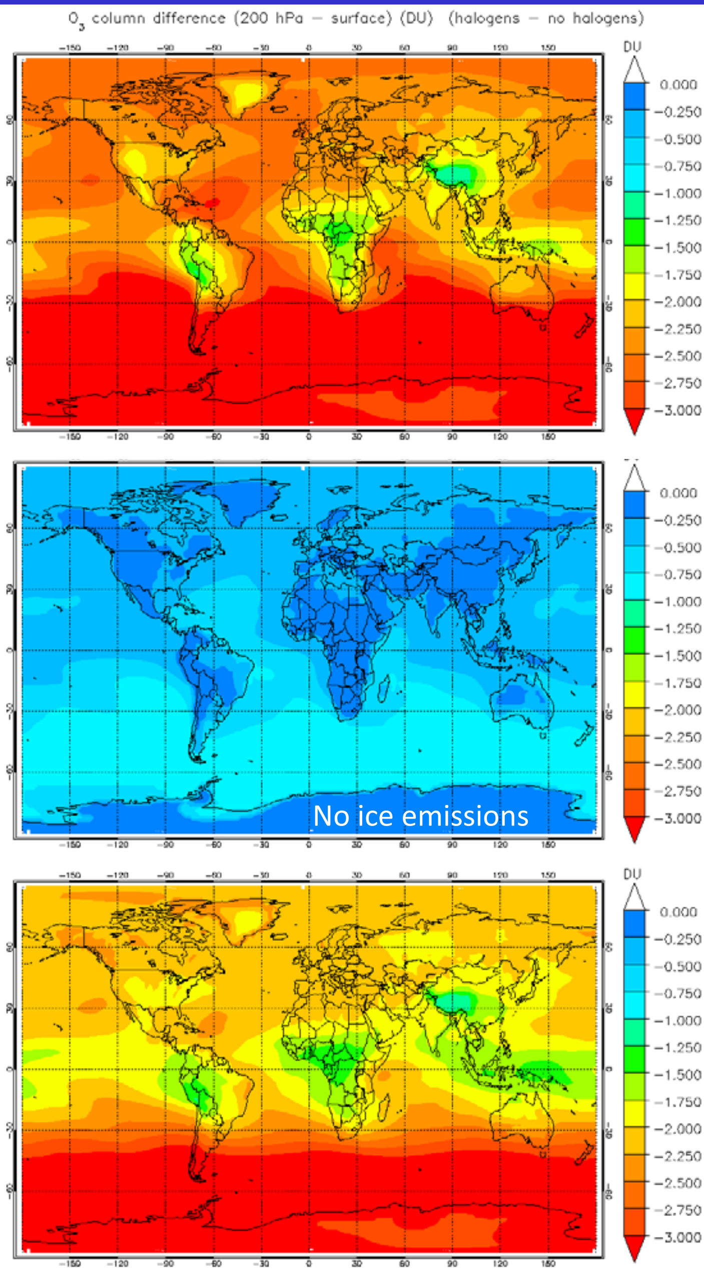


Troposphere (200 hPa – surface):

max	mean	min	
-5.0	-3.0	-1.0	DU

~ 9% of trop. column

LT (surface – 850 hPa):

max	mean	min
-1.0	-0.5	-0.0

17%

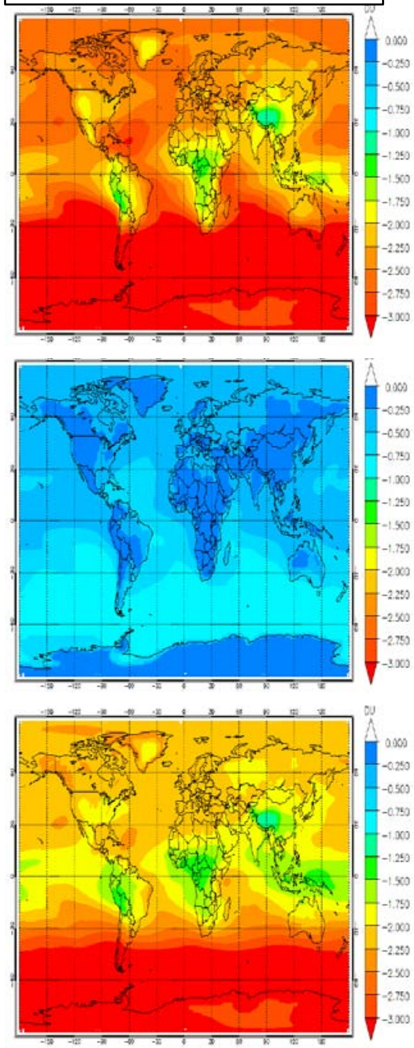
FT (850 hPa – 200 hPa):

max	mean	min
-4.6	-2.5	-1.0

83%

Ozone loss: Br / I contribution to trop. column - Global

Cl + Br + I



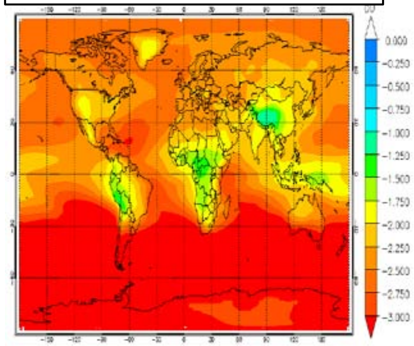
Tot

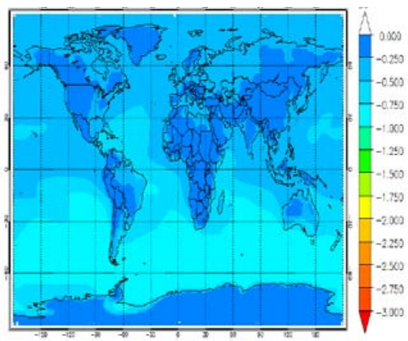
LT

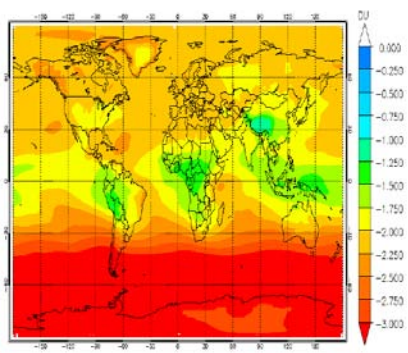
FT

Ozone loss: Br / I contribution to trop. column - Global

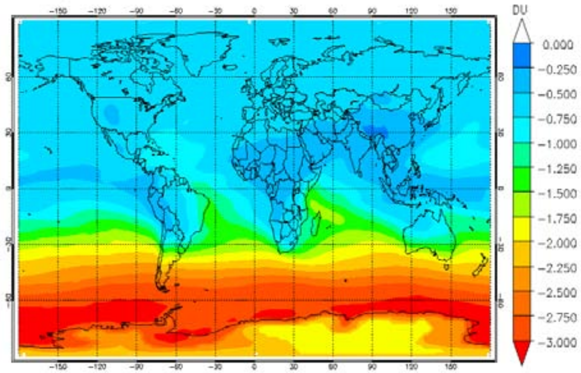
Cl + Br + I







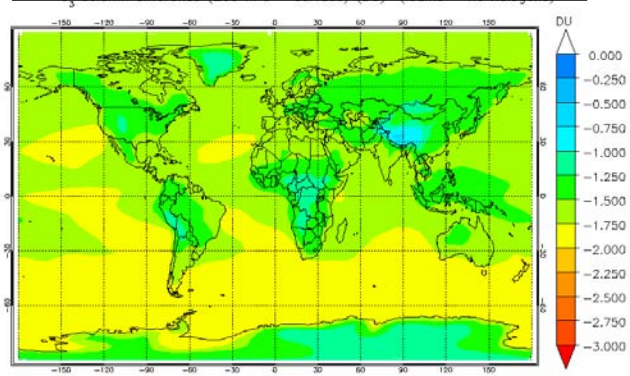
Bromine



Tot

44%

Iodine



Tot

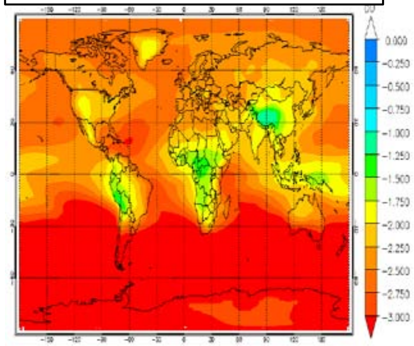
56%

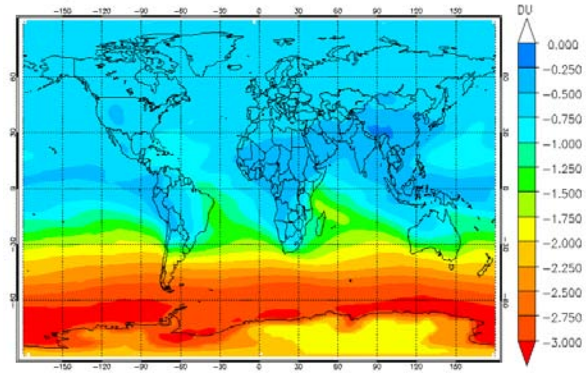
LT

FT

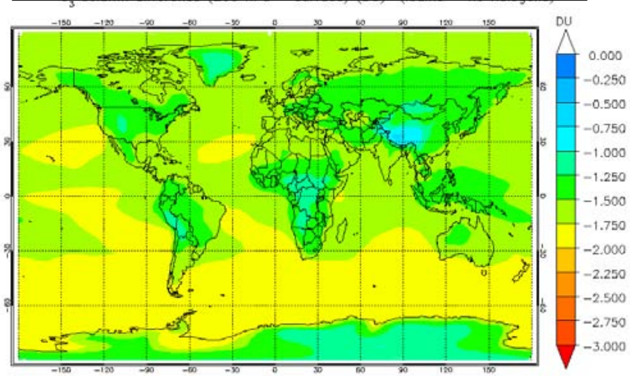
Ozone loss: Br / I contribution to trop. column - Global

Cl + Br + I	Bromine		Iodine	

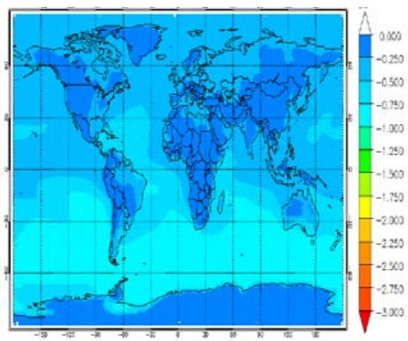


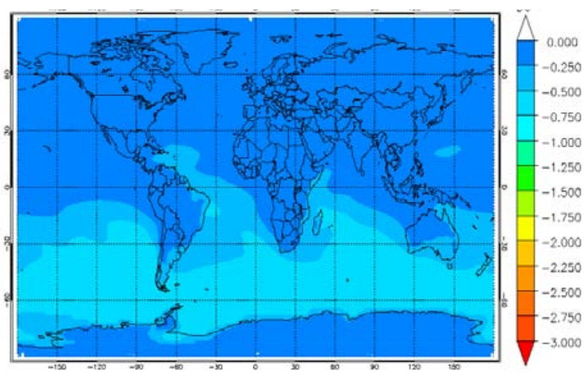


Tot
44%



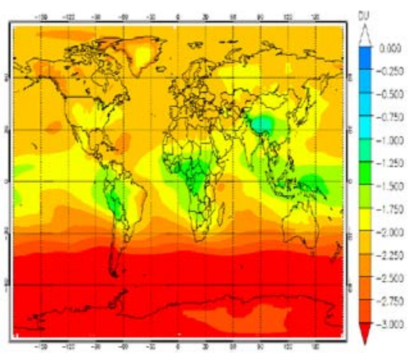
Tot
56%

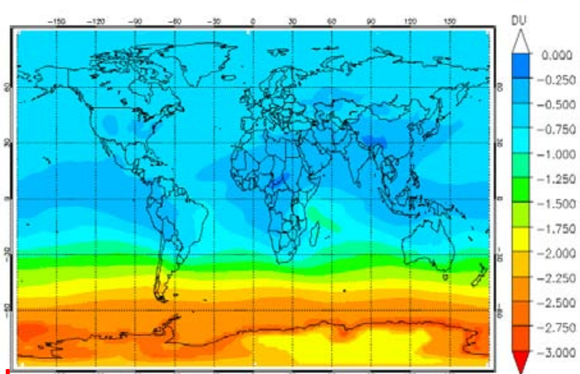




LT
7%

LT



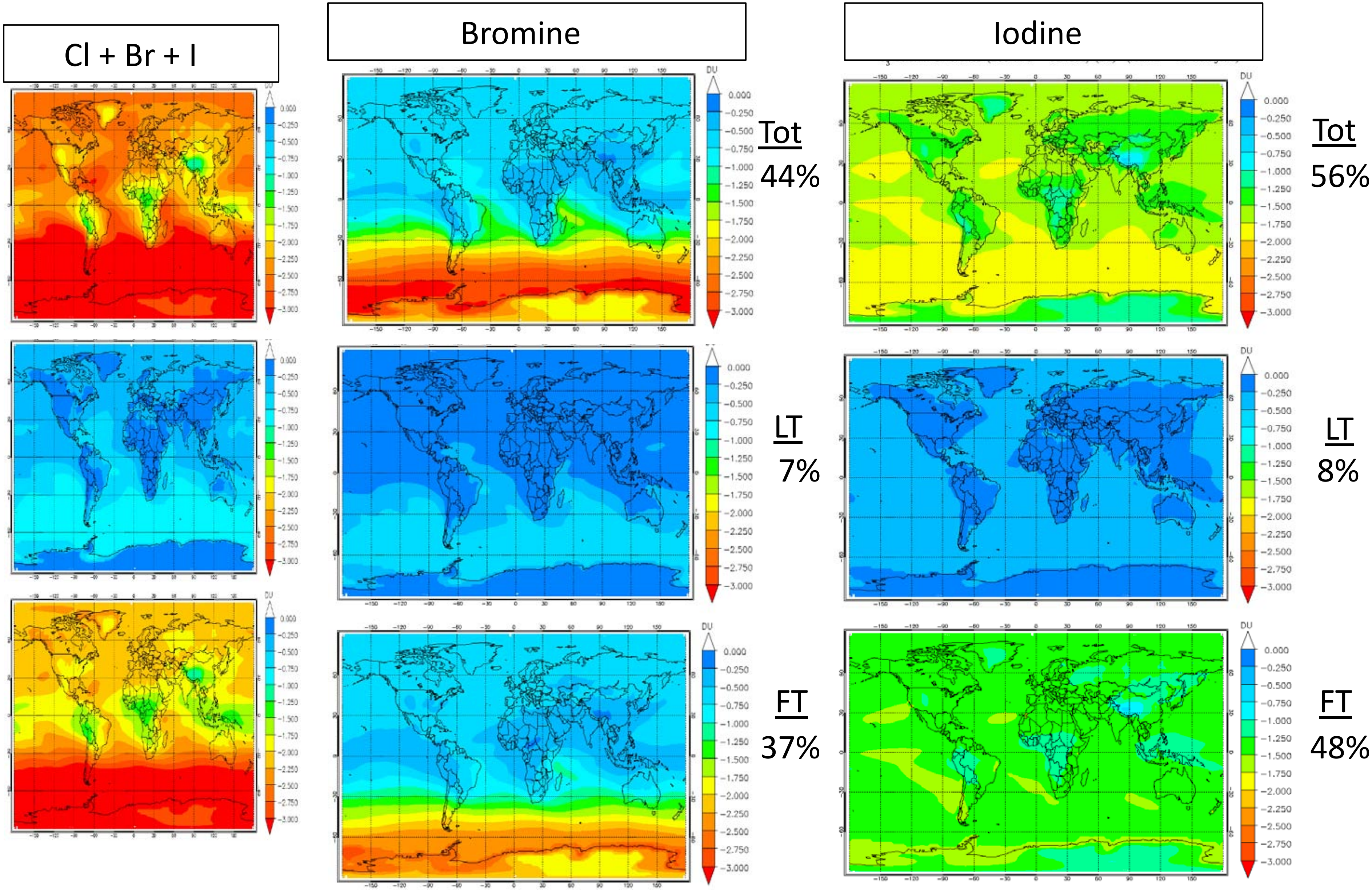


FT
37%

FT

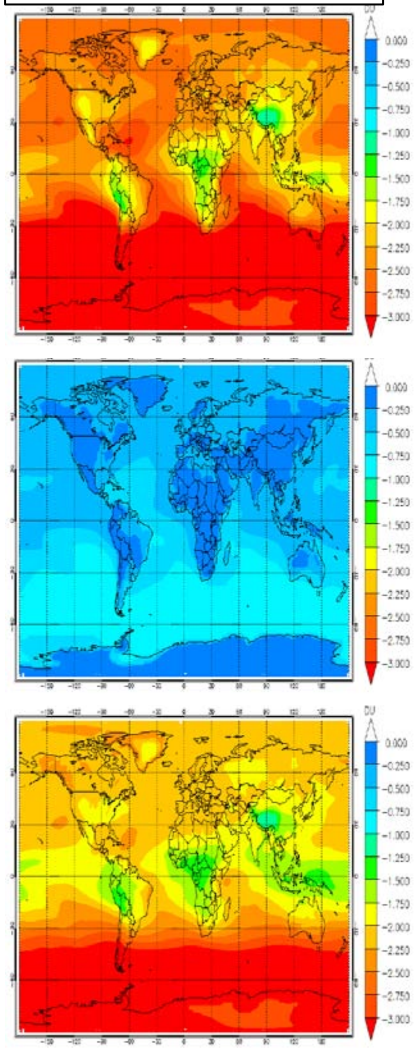
Check TROPAUSE LEVEL

Ozone loss: Br / I contribution to trop. column - Global

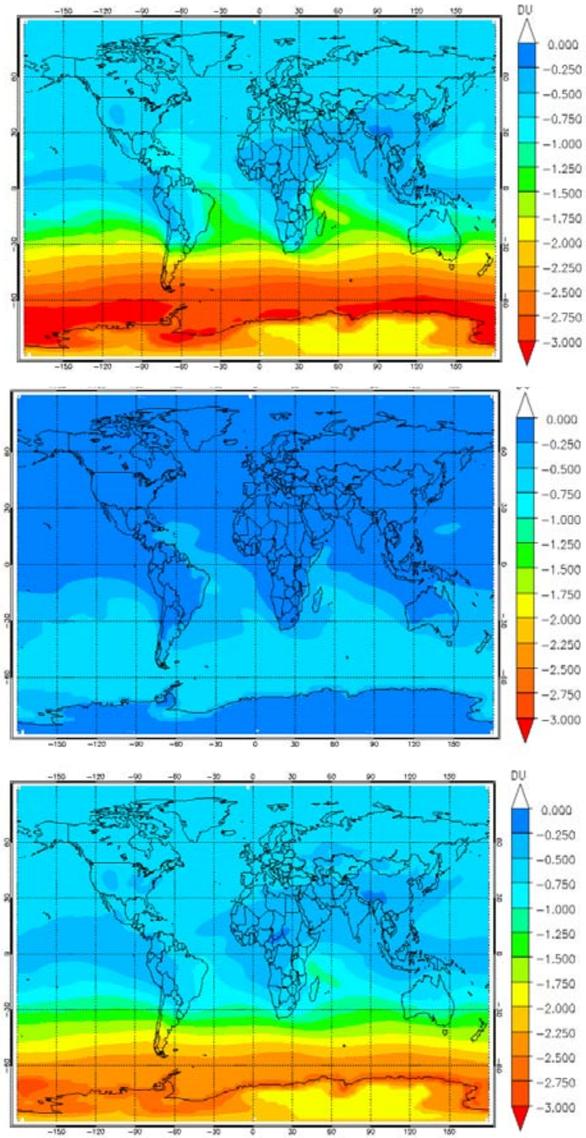


Ozone loss: Br / I contribution to trop. column - Tropics

Cl + Br + I



Bromine

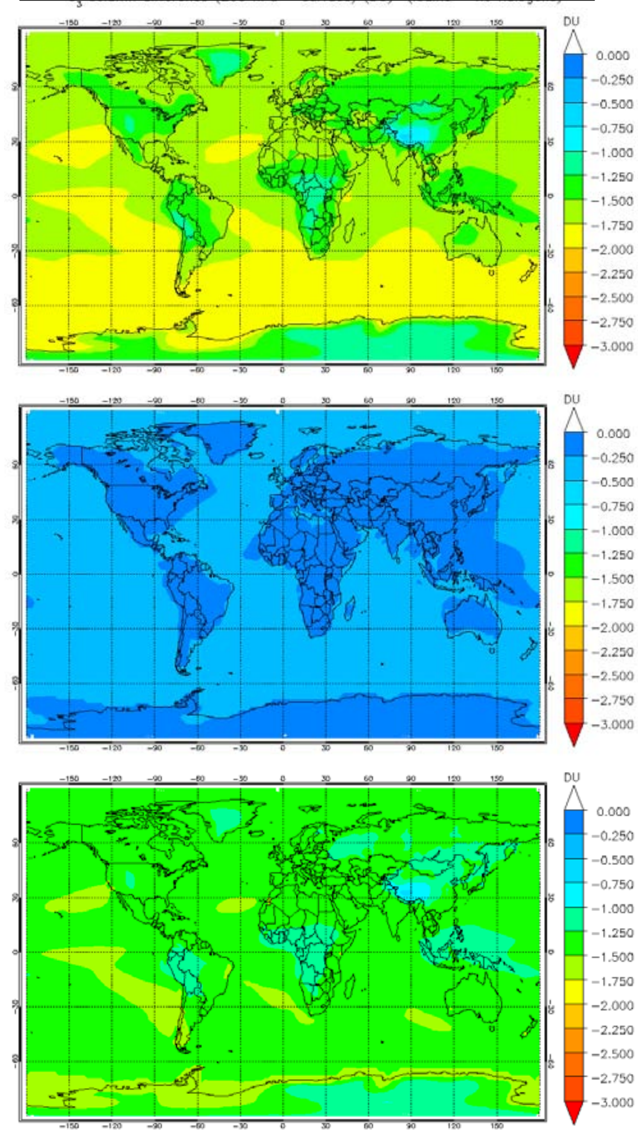


Tot
44%
30%

BL
7%
8%

FT
37%
22%

Iodine



Tot
56%
70%

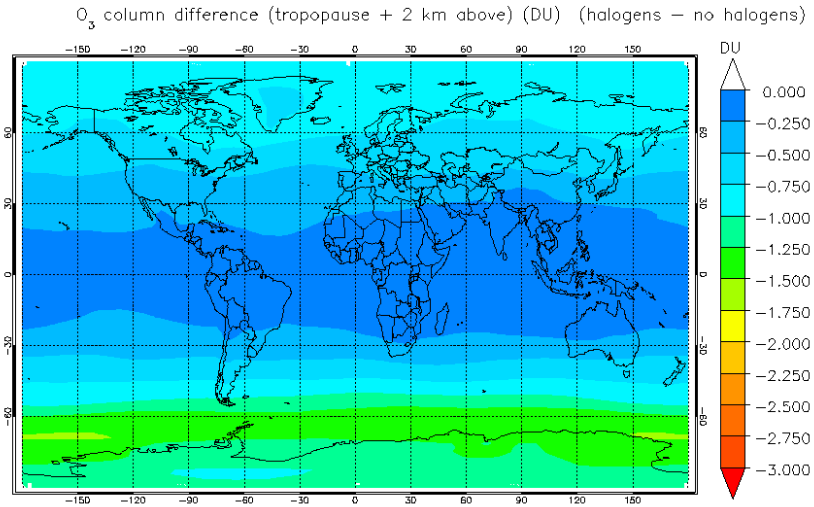
BL
8%
10%

FT
48%
60%

Ozone loss: Br / I contribution to LMS

Annually-globally integrated O_3 column difference (tropopause + 2 km above)

VSL *minus* no VSL



Up to ~1.7 DU O_3 loss

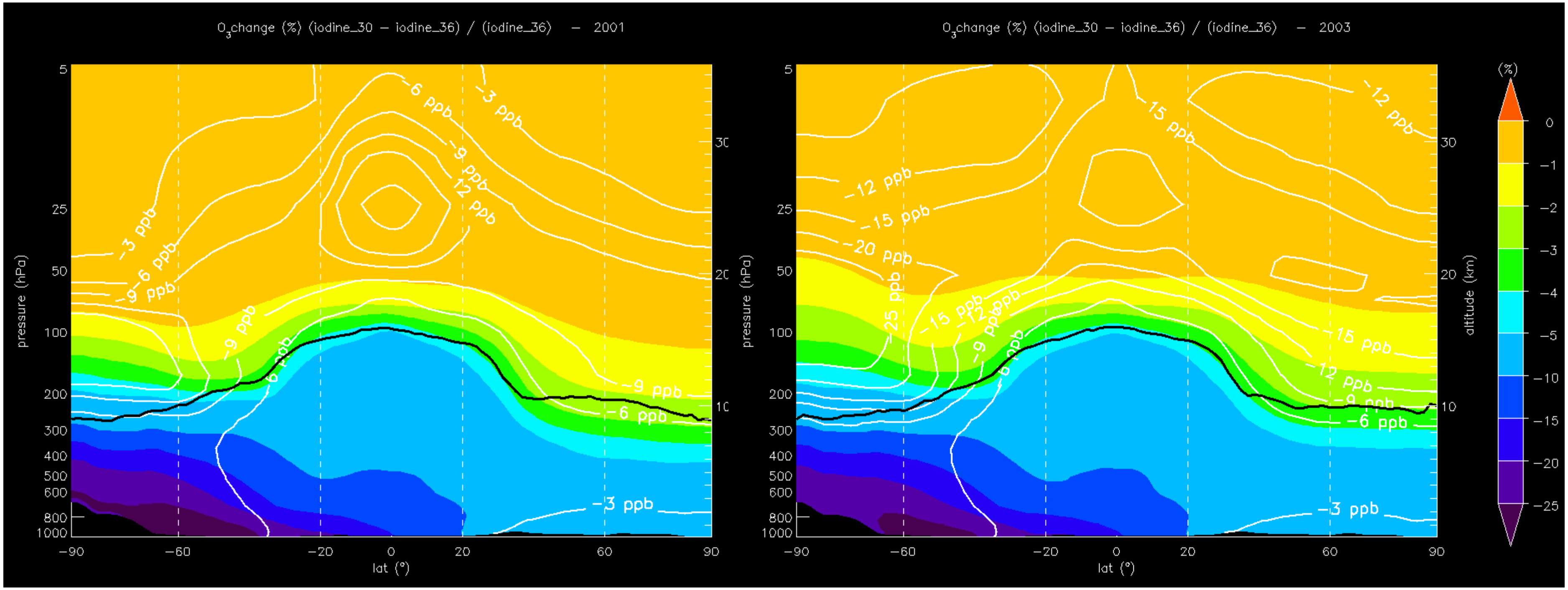
Avg. O_3 loss by VSLS: 3.5% (range 2-8 %)

- Globally, additional O3 loss from Br and I:

  VSL Br contrib. to O_3 loss: ~65%

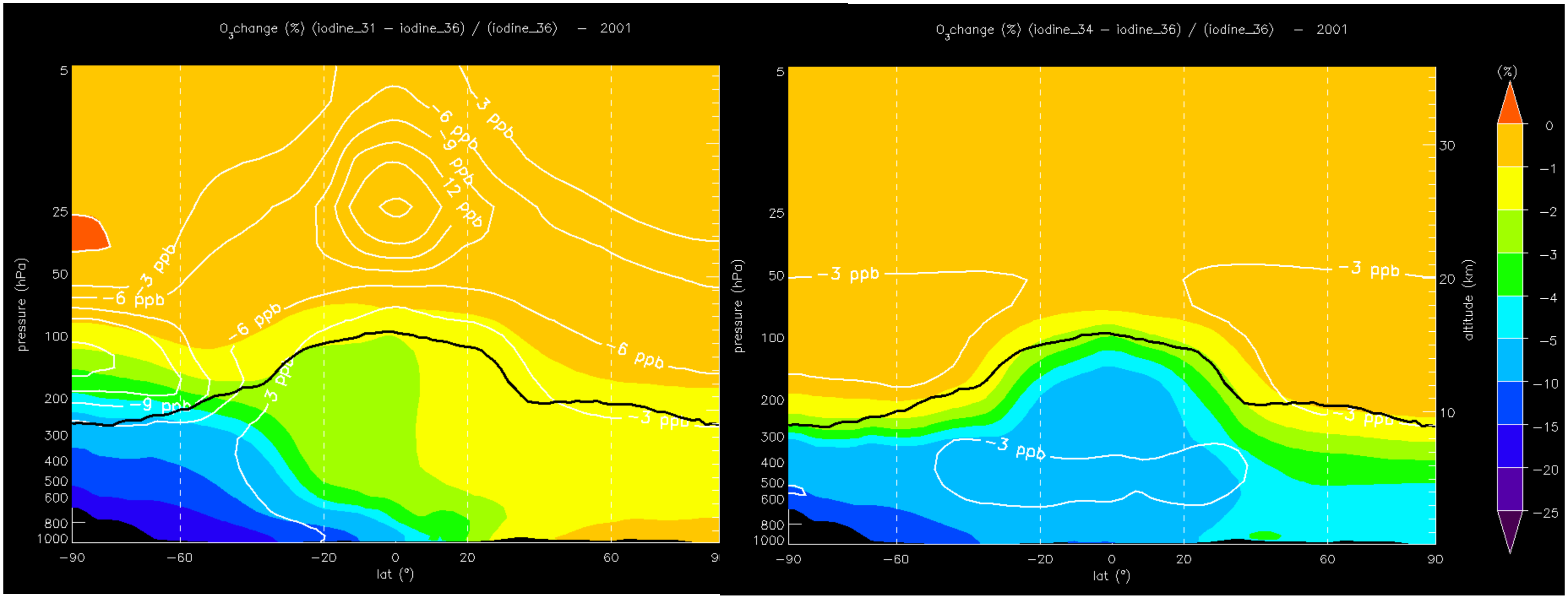
  I contrib. to O_3 loss: ~34% (but I contributes more than Br over the tropics)

VSL *minus* base run

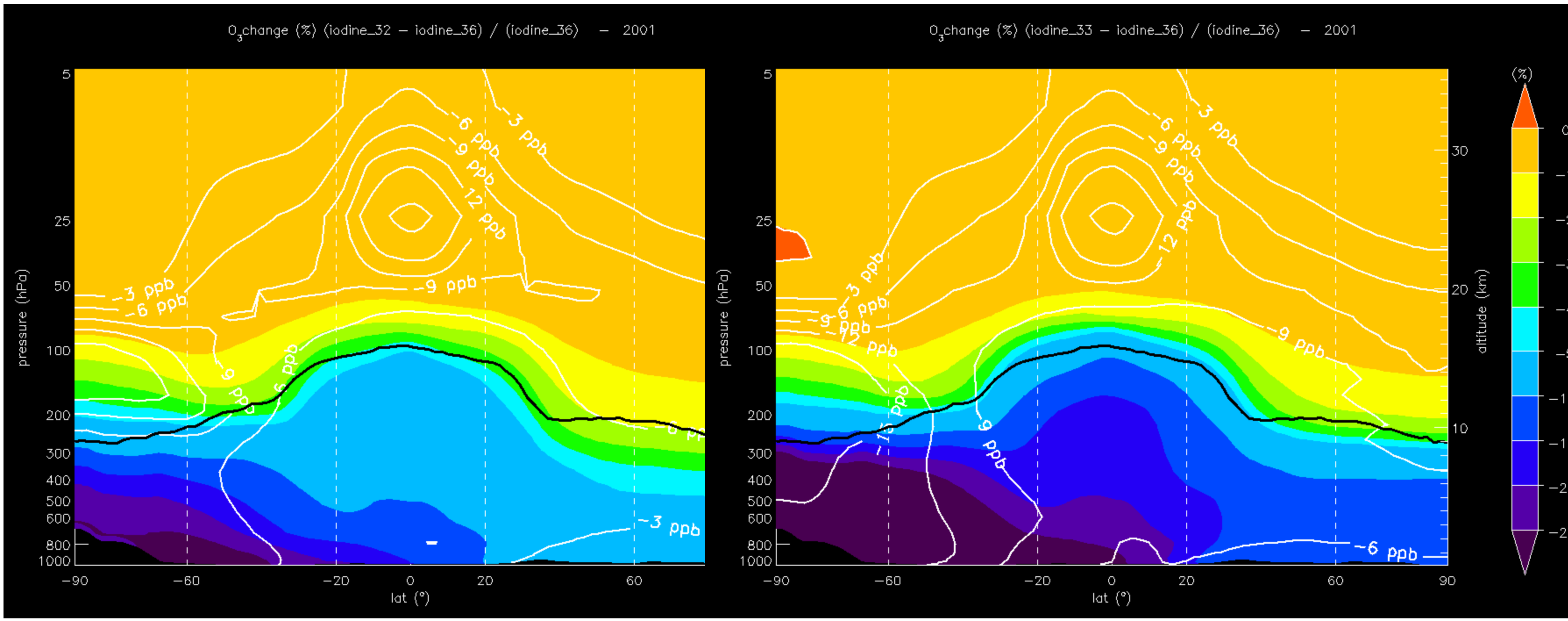


VSL bromine *minus* base run

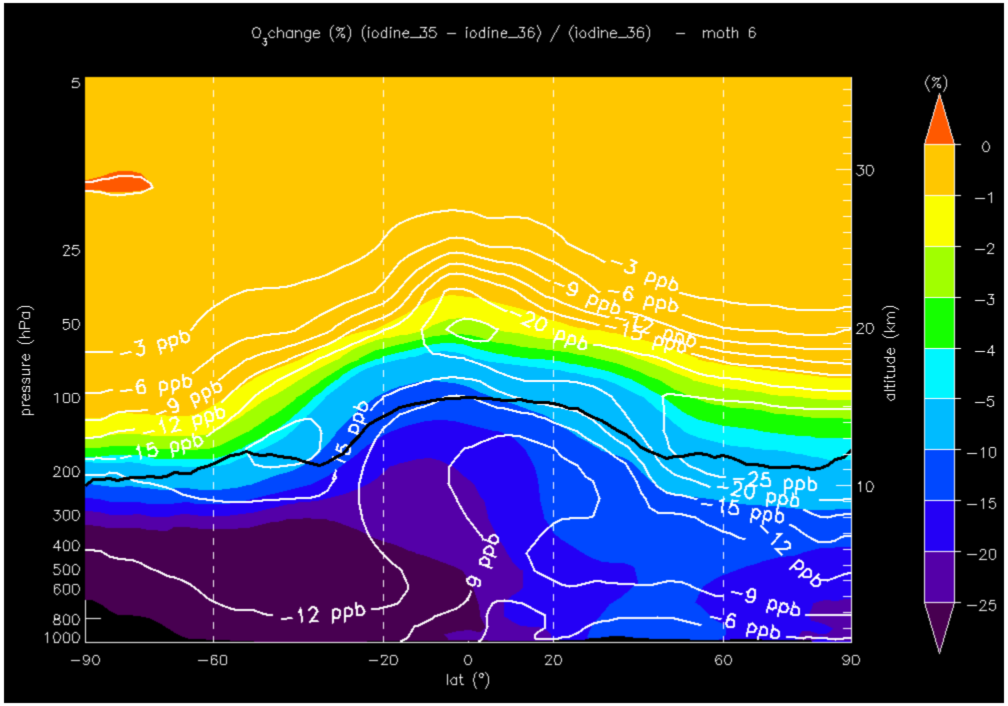
Iodine *minus* base run



(VSL + IONO2 uptake) *minus* base run (VSL + IONO2 uptake + I2Oy photol)



I2Oy photol



O_3 change (%) (iodine_35 – iodine_36) / (iodine_36) – moth 6
pressure (hPa)
altitude (km)
lat (°)
(%)
-3 ppb
-6 ppb
-9 ppb
-12 ppb
-15 ppb
-20 ppb
-25 ppb
-12 ppb
-9 ppb
-6 ppb