Global modelling of upper tropospheric-lower stratospheric iodine: budget and implications for ozone

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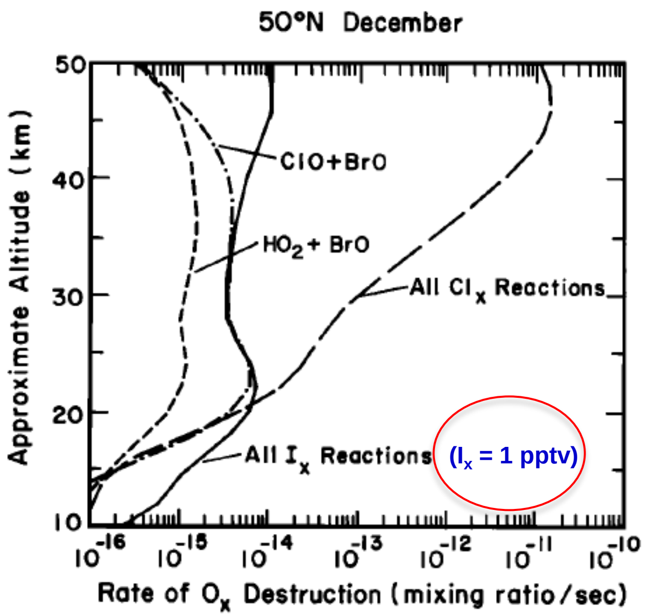
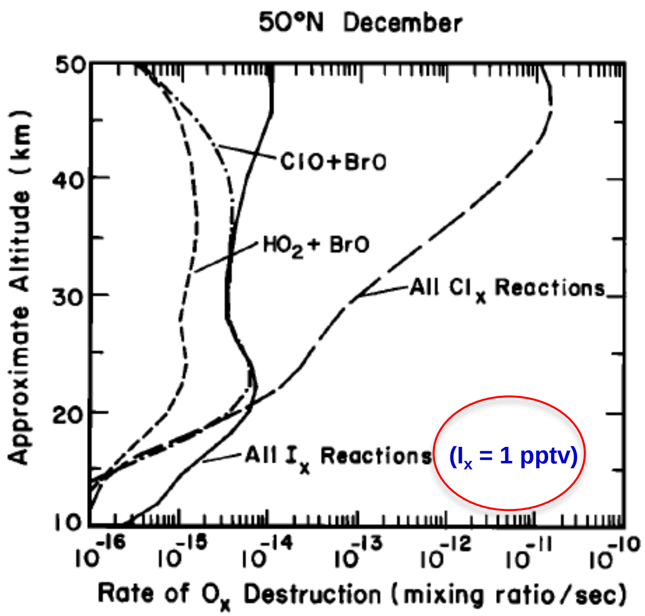
"**On the role of iodine in ozone depletion**", Solomon et al., JGR, 1994



Solomon et al., JGR, 1994

Solomon et al.,: "iodine loadings of 1 pptv and rapid inter-halogen photochemical reactions involving iodine could be of substantial importance to ozone loss in the lowermost stratosphere".

Motivation



Solomon et al., JGR, 1994

Since then:

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

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

Most recent analysis: < 0.1 pptv IO, OIO in lower stratosphere in northern high and mid-latitudes, and tropics

Estimated total inorganic iodine: ~ 0.2 pptv I_y
(Photochemical 1-D model)

1) Budget and partitioning of iodine species in the global UTLS using CCM
2) Re-evaluation of suggested role of iodine in UTLS O_3 destruction
3) Relative contribution of iodine to halogen-driven UTLS O_3 destruction

CAM-Chem (Lamarque et al., *Geosci. Model Dev*. 2012):

- Global Chemistry-Climate Model
- 1.9° (lat) x 2.5° (lon) horizontal resolution
- 26 vertical levels (surface to ~ 4 hPa)
- time step = 30 min

Tropospheric Halogen Chemistry

- Implementation of VSL (lifetime < 6 months) halogenated sources from the ocean.
- Emissions following Chl-a over tropics
- Catalytic release from sea-salt
- Photochemistry
- Dry / wet deposition
- 160 species, 427 reactions

VSL halogen sources in CAM-Chem

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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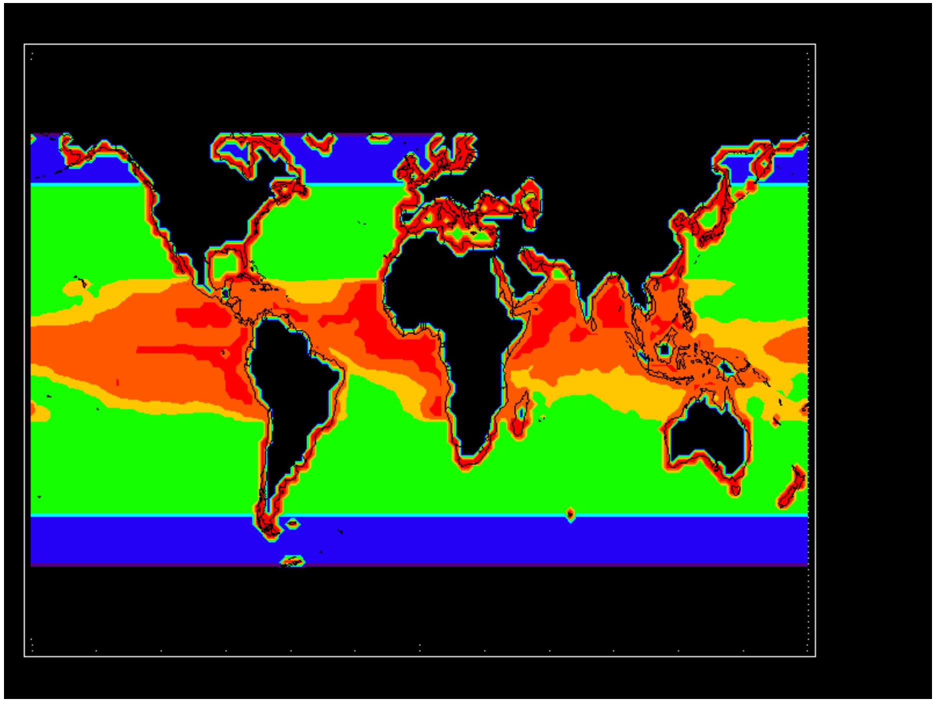
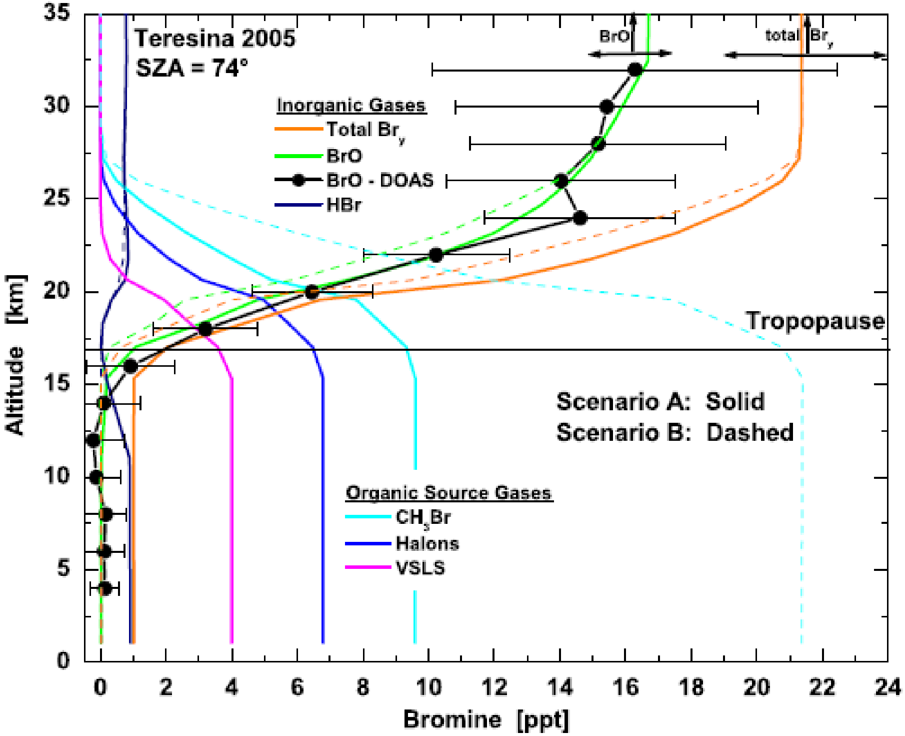
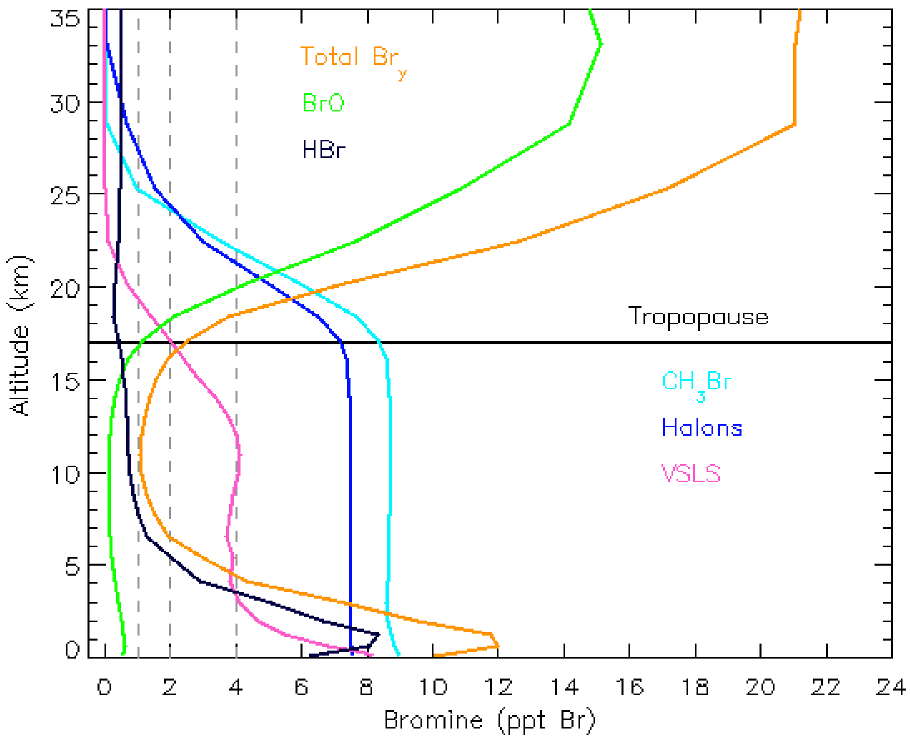


Ordoñez et al., ACP, 2012
Saiz-Lopez et al., ACP, 2012

Teresina (Dorf et al., ACP, 2008)



CAM-Chem_bromine (23° N – 23° S)



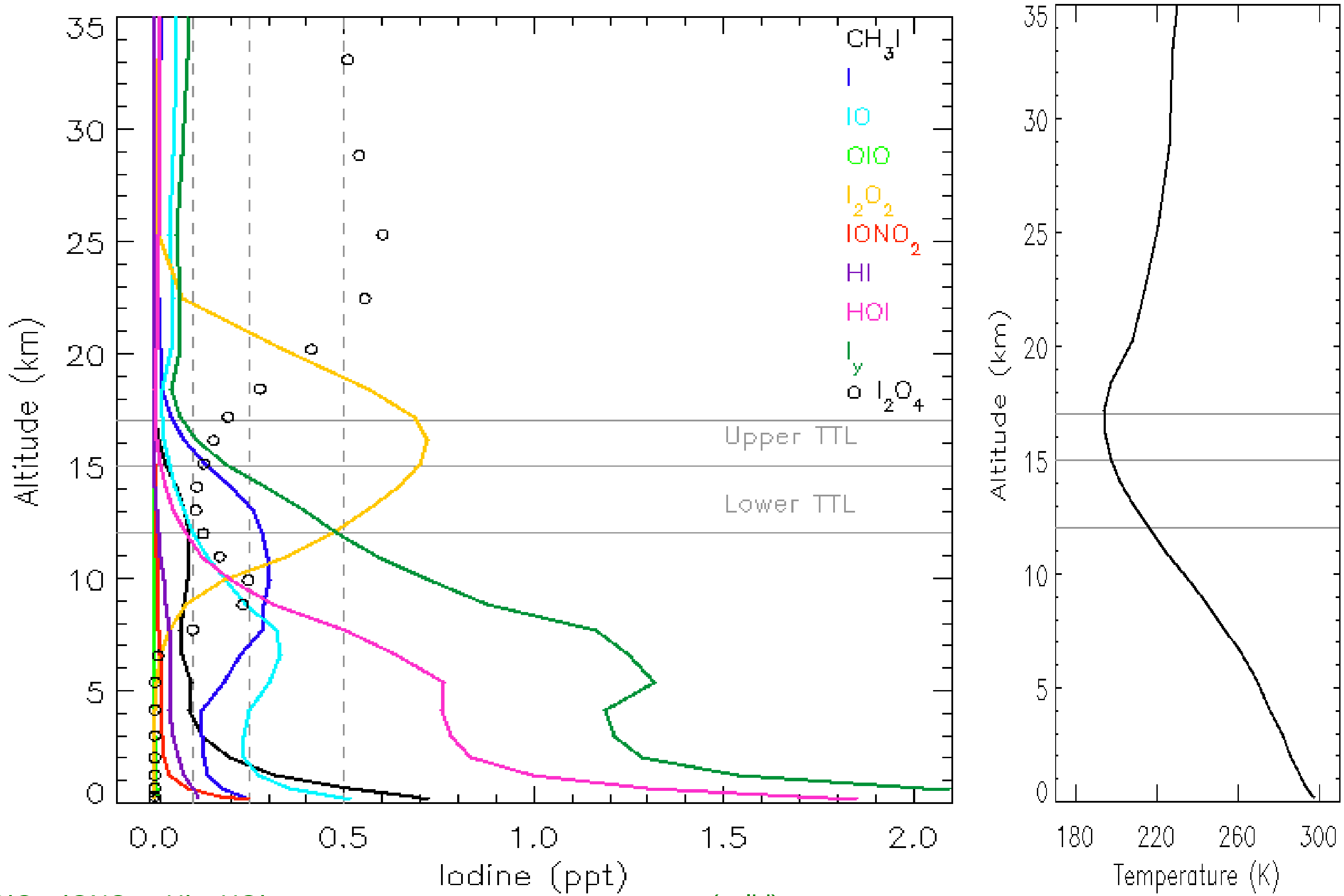
Notes:

- 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

Daytime profiles in tropics



$I_y = I + IO + OIO + IONO_2 + HI + HOI$ (solid)

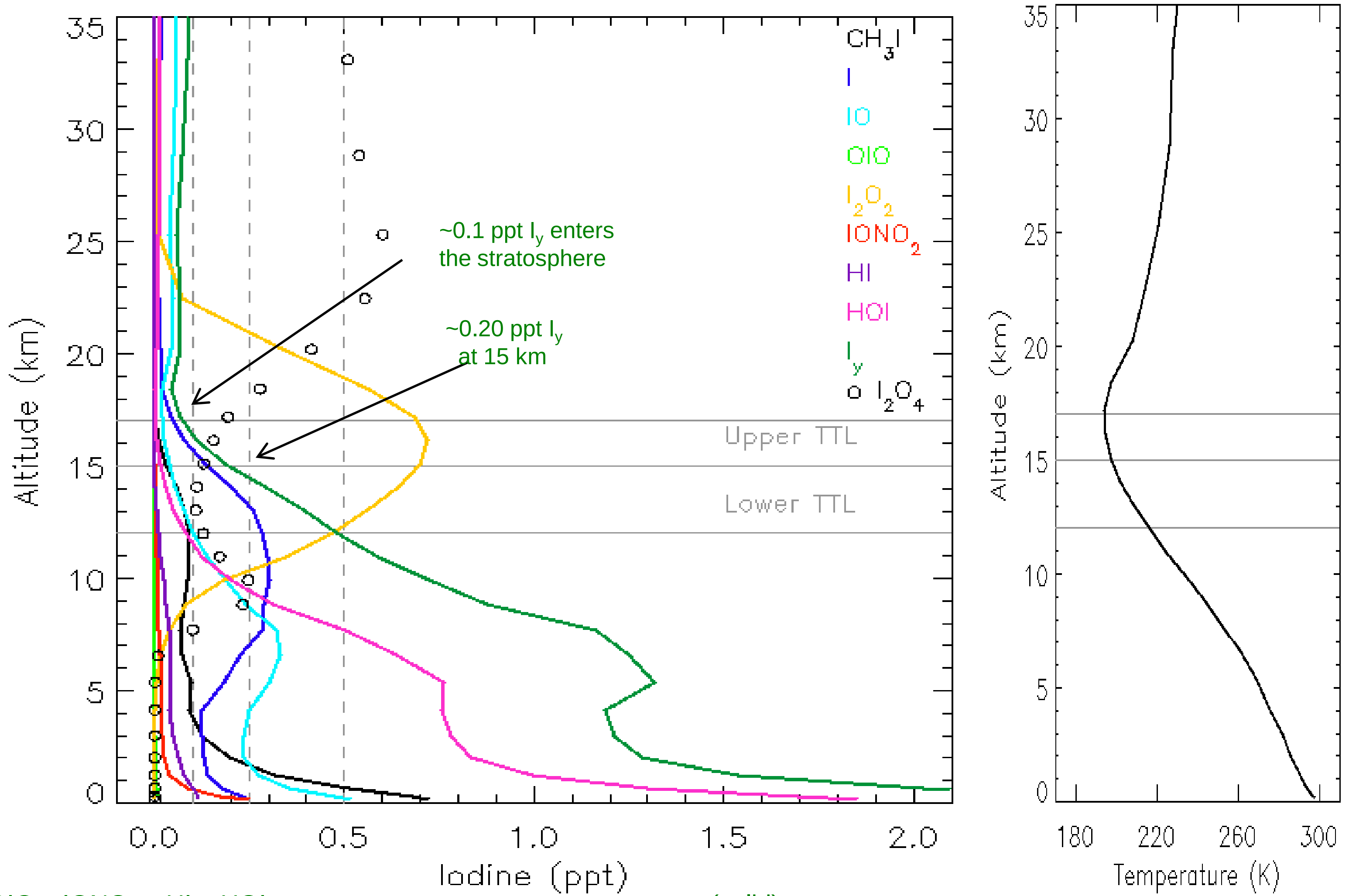
Measured TTL to CPT abundances (Table 1-9 of WMO, 2011): :

IO, OIO PG < 0.1 ppt (Upper limits reported by Butz et al., 2009)

Table 1-7 indicates a mean of 0.12 ppt (range 0.00-0.23 ppt) CH_3I for the lower TTL (12-14 km)

Iodine species: profiles and I_y (no photolysis of I_2O_y)

Daytime profiles in tropics



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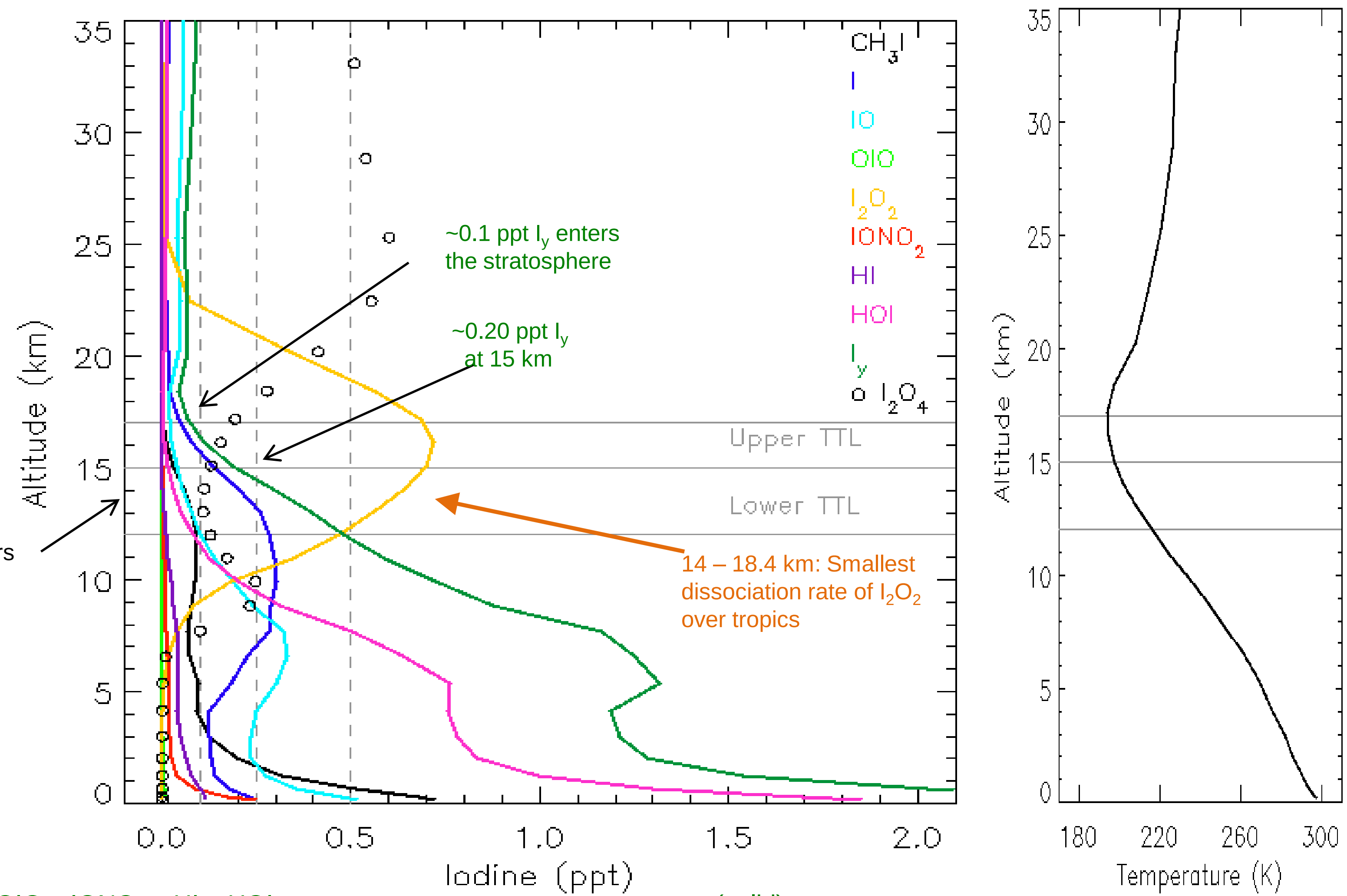
Daytime profiles in tropics

Only ~0.05 ppt CH_3I enters the TTL, while some obs. suggest ~0.10 ppt CH_3I



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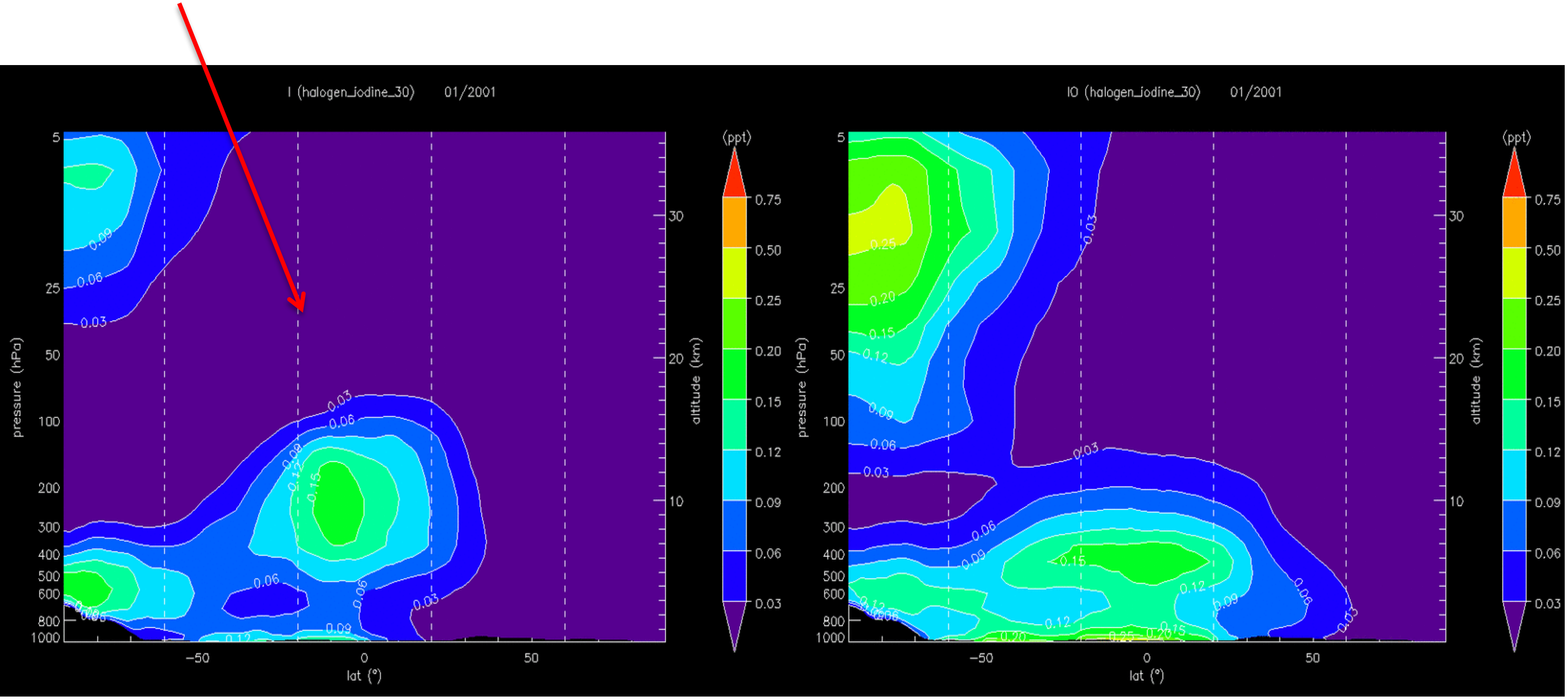
Iodine species: IO/I zonal averages

Zonal averages of atomic iodine and IO:

- Largest loading of IO_x is not in the MBL
- Height shift in the I and IO concentration peaks

Tropical "iodine mushroom cloud"

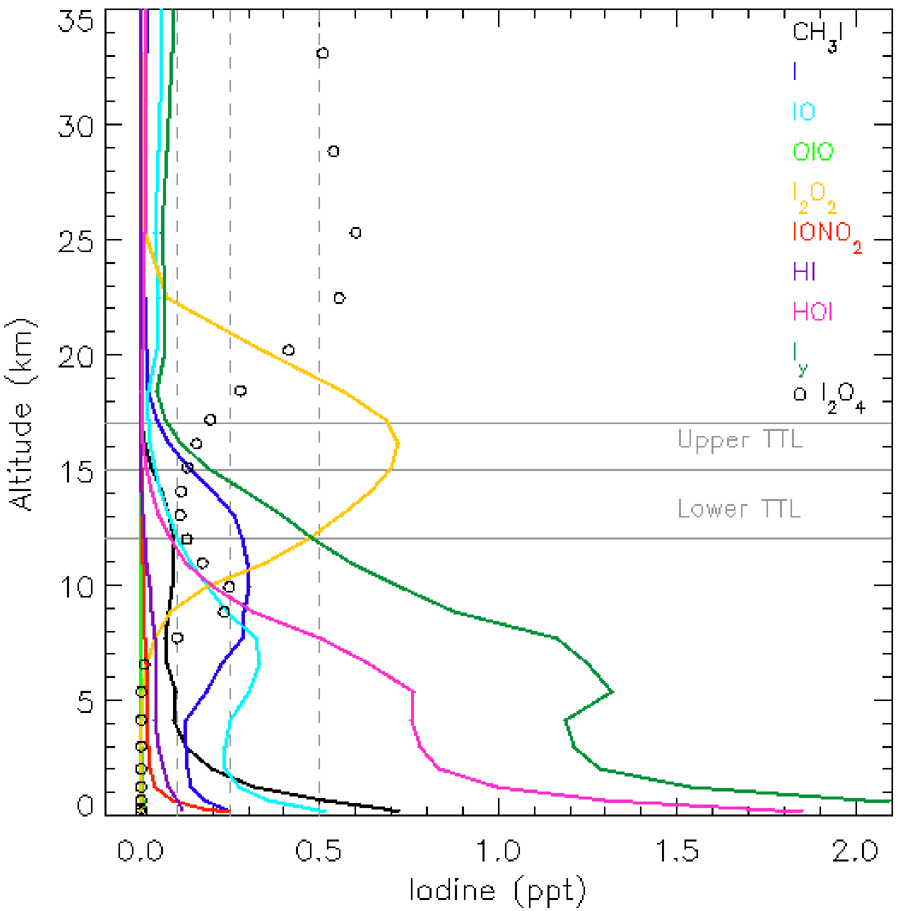


Peak I height: 10-12 km

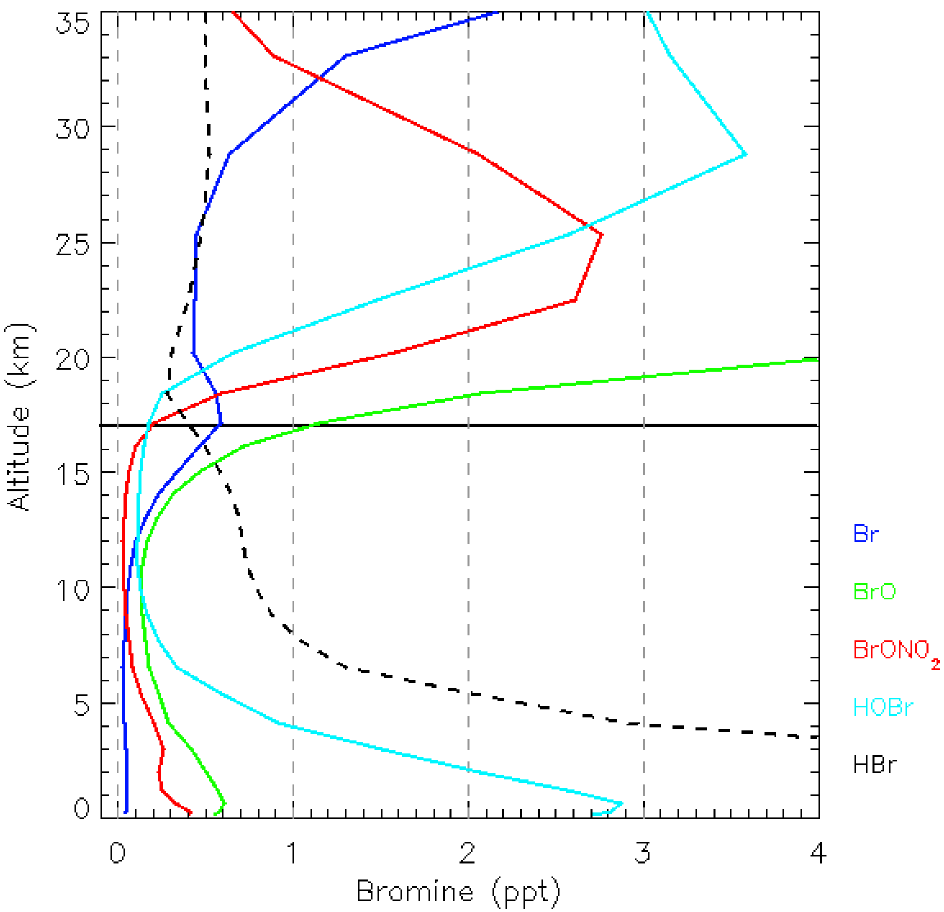
Peak I height: 5-8 km

Annually average profiles in tropics:

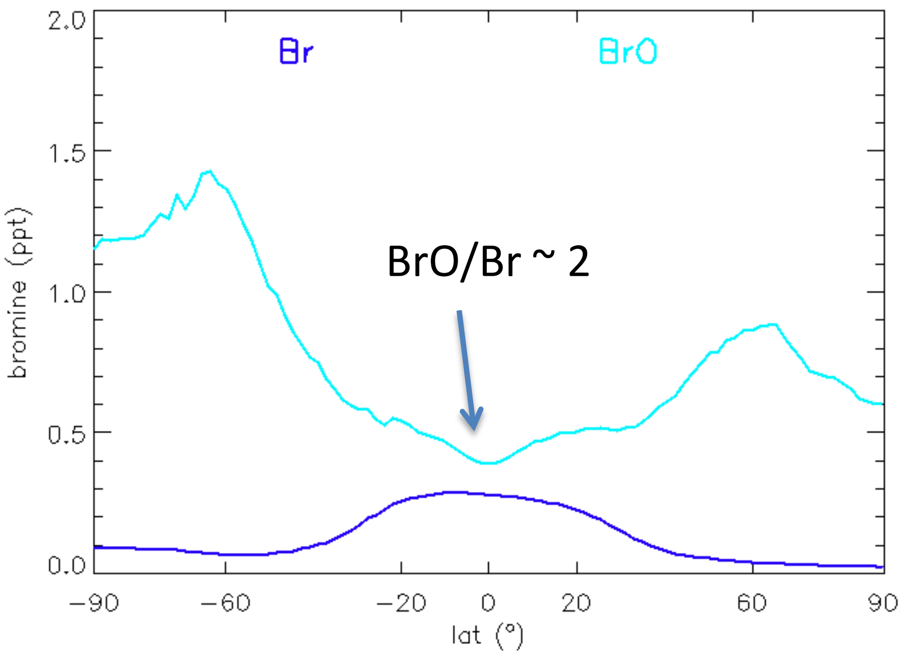
Iodine species

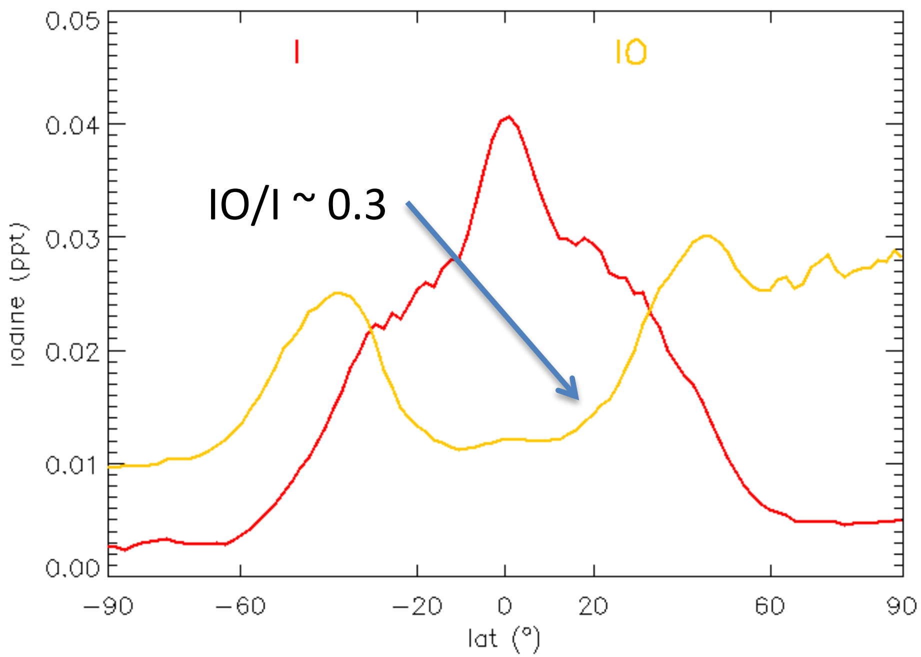


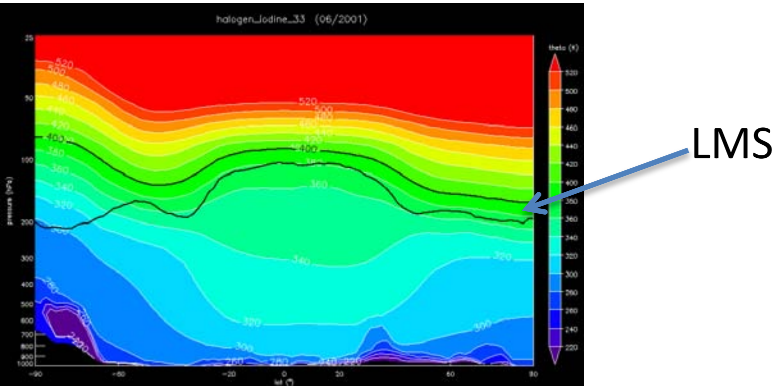
Bromine species



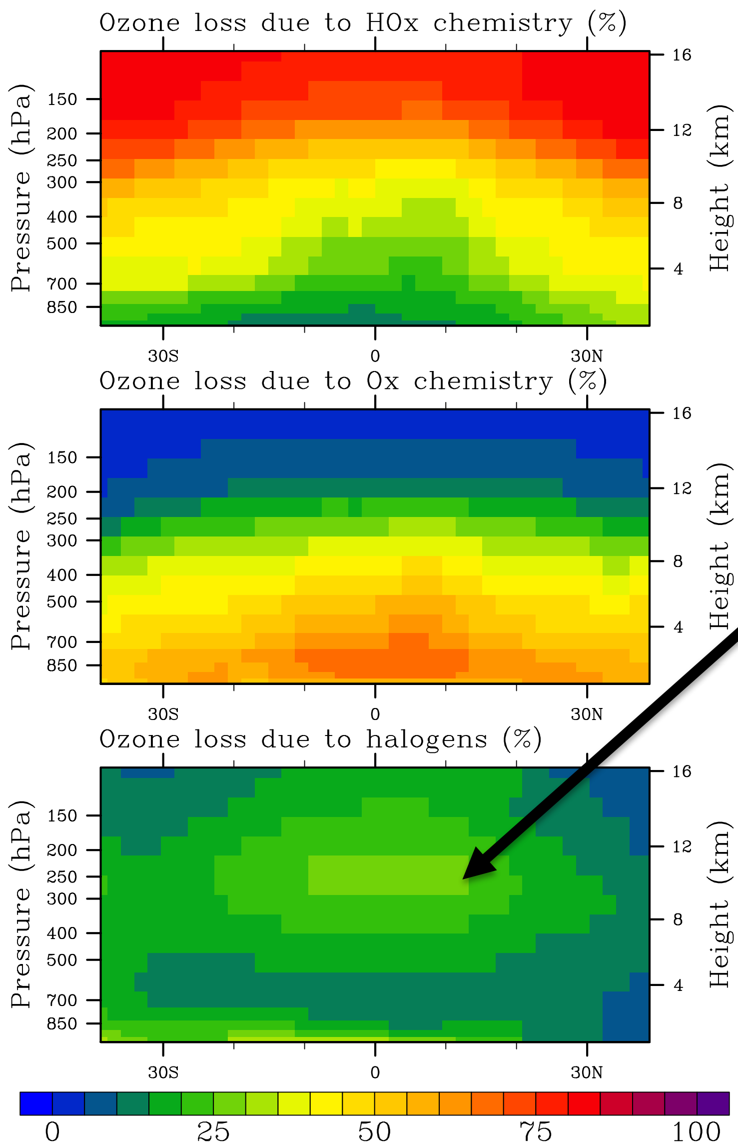
Annually average of latitudinal dependence of X/XO in LMS:







Halogen-driven tropospheric O_3 loss (Saiz-Lopez et al., 2012)



Zonal annual mean ozone loss fraction (due to chemistry)

Up to ~30% in tropical UT

Iodine Chemistry:

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

$2O_3 \Rightarrow 3O_2$

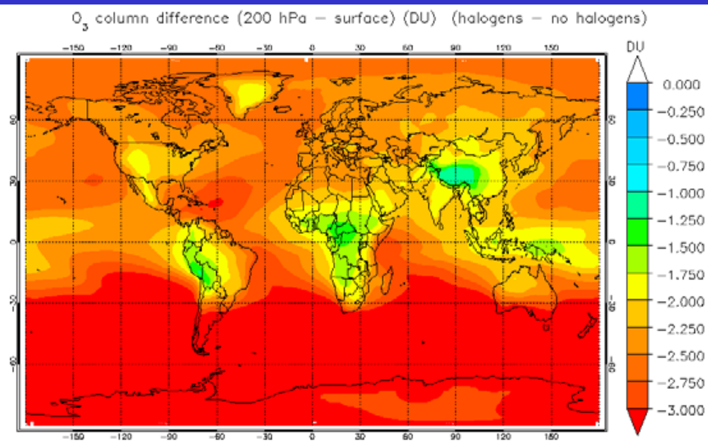
$I + O_3 \Rightarrow IO + O_2$
$IO + HO_2 \Rightarrow HOI + O_2$
$HOI + hv \Rightarrow I + OH$
$OH + O_3 \Rightarrow HO2 + O_2$

$2O_3 \Rightarrow 3O_2$

Halogen-driven ozone loss: BL and FT

Note:

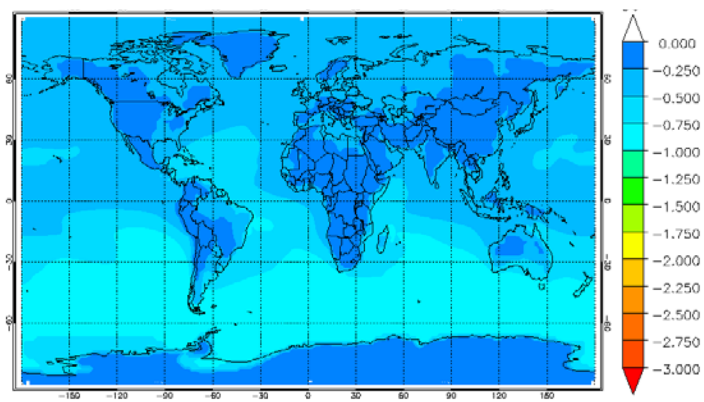
no ice emissions included.



Troposphere (200 hPa – surface);

max	mean	min
-4.8	-2.8	-0.9

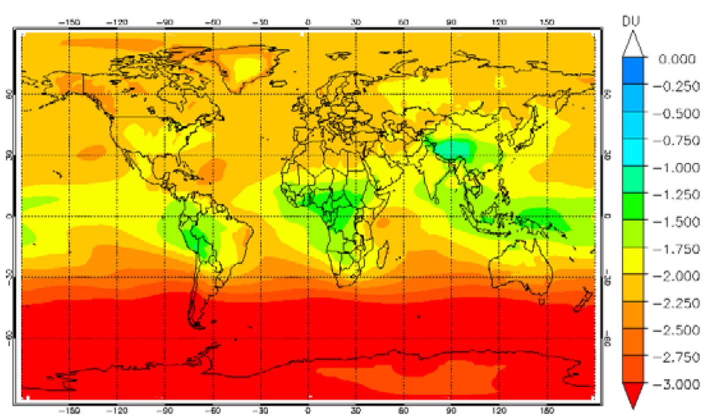
~ 11% of trop. column



BL (850 hPa – surface):

max	mean	min
-0.9	-0.4	-0.1

15%

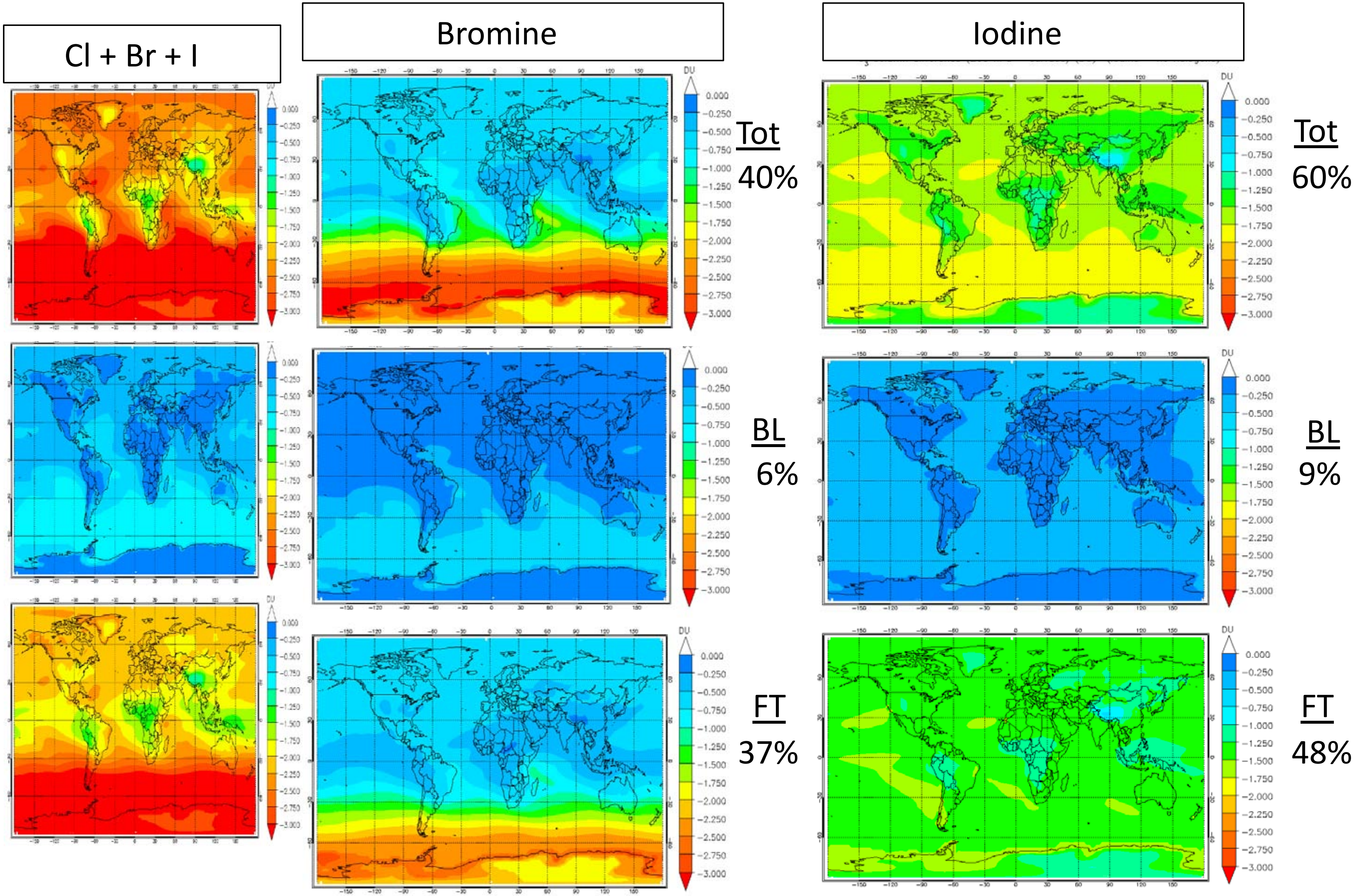


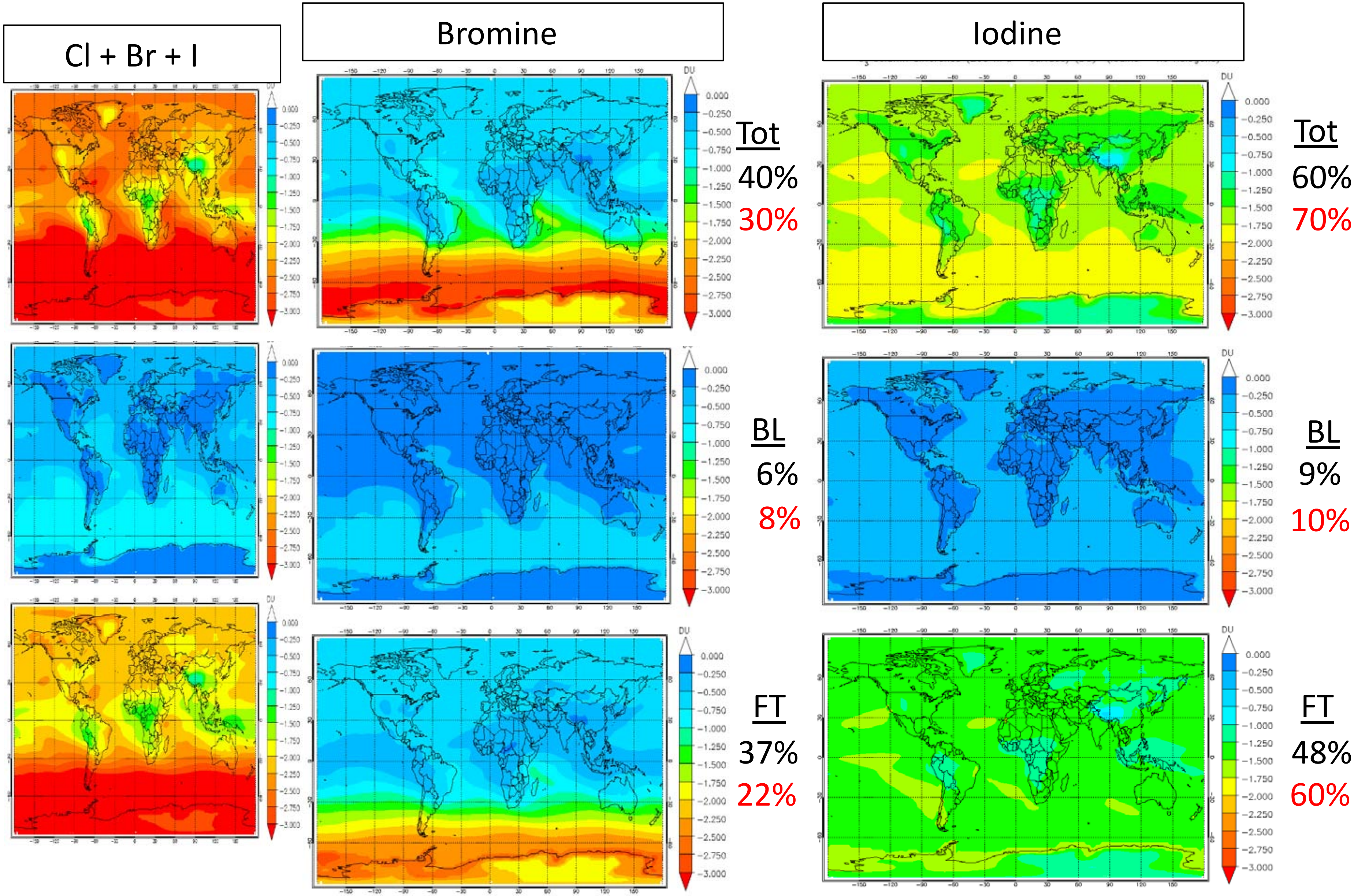
FT (850 hPa – 200 hPa):

max	mean	min
-4.3	-2.4	-0.8

85%

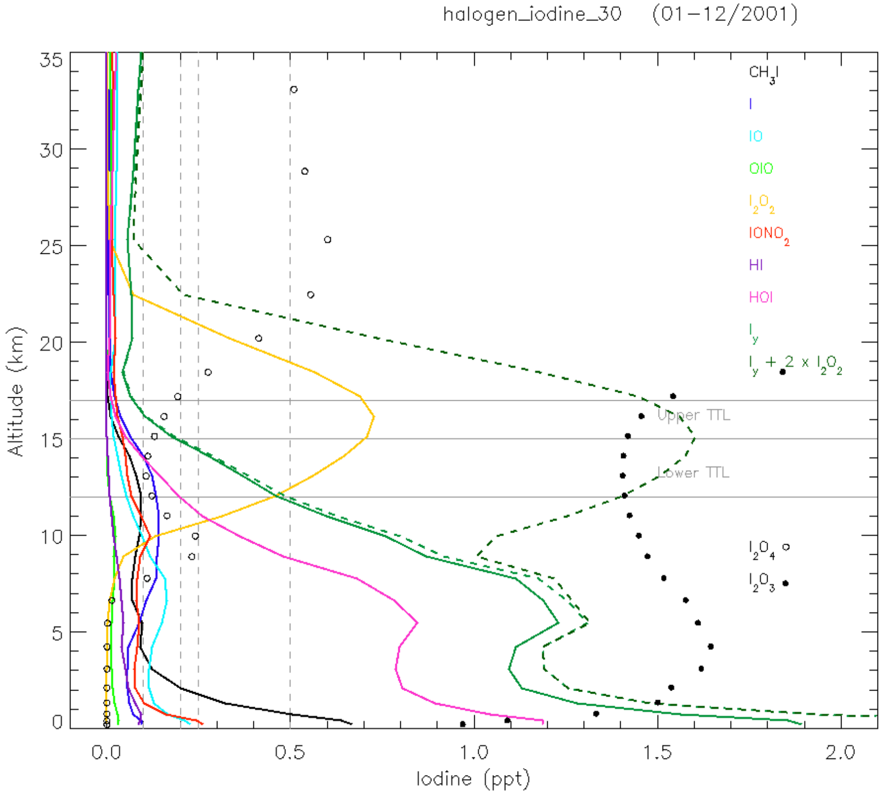
Ozone loss: Br/I contribution to trop. column - Global




Cl + Br + I
Bromine
Iodine
Tot
40%
30%
Tot
60%
70%
BL
6%
8%
BL
9%
10%
FT
37%
22%
FT
48%
60%

Sensitivity runs: photolysis of I_2O_y

High levels of I_2O_2, I_2O_3, I_2O_4



I_2O_2 Chemistry in the model...

IO + IO => I_2O_2

I_2O_2 => OIO + I

I_2O_2 => IO + IO

I_2O_3 Chemistry in the model...

IO + OIO -> I_2O_3

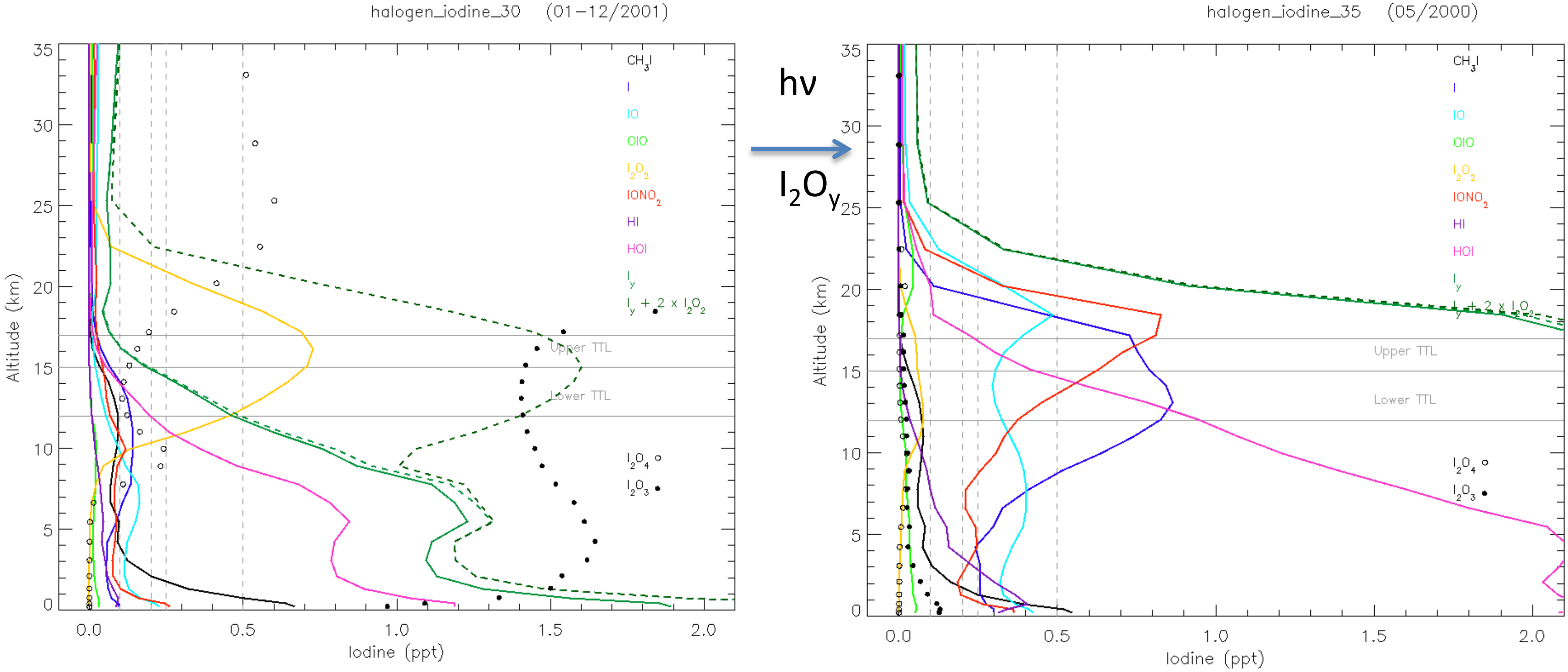
I_2O_4 Chemistry in the model...

OIO + OIO -> I_2O_4

I_2O_4 -> 2*OIO

Sensitivity runs: photolysis of I_2O_y

High levels of I_2O_2, I_2O_3, I_2O_4



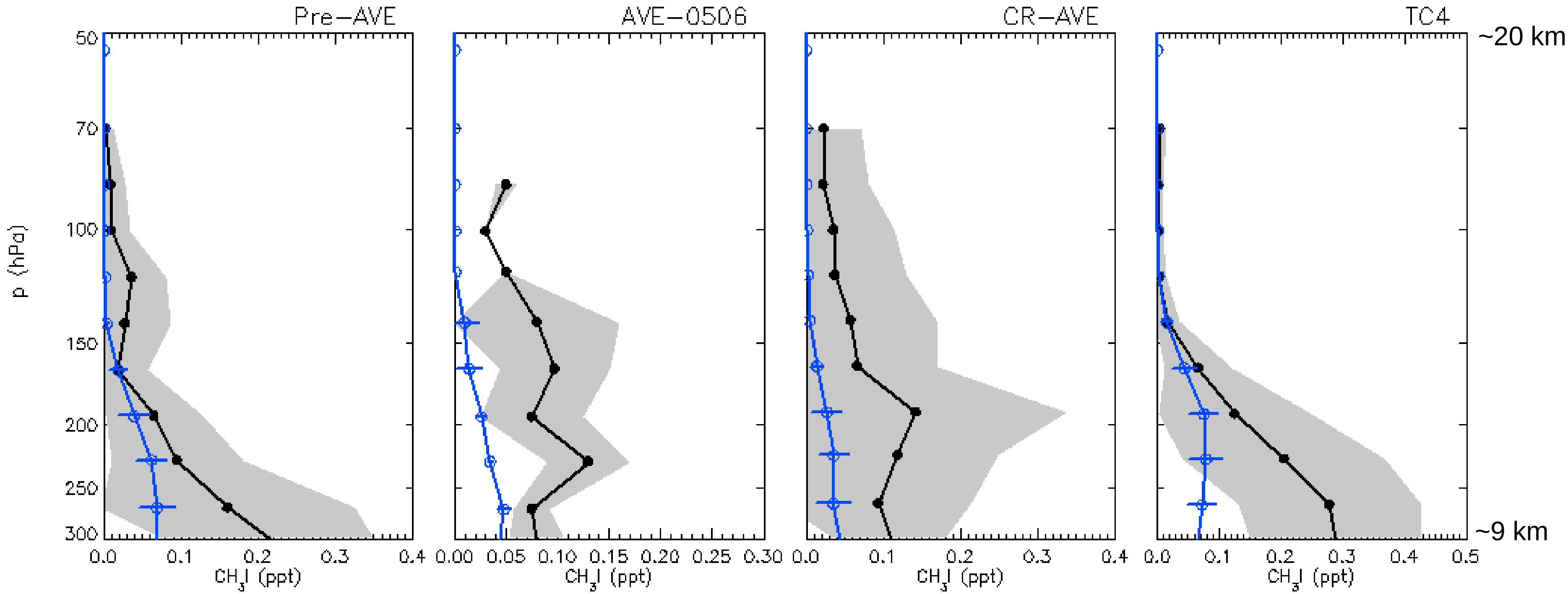
Ozone impact:

Ozone depletion efficiency by iodine is enhanced 2-3 times if I_2O_y photolysis is included !

Summary

- Oceanic sources and chemistry of **iodine** implemented **in a CCM**.
- Iodine partitioning shows high I/IO ratio in tropical UTLS
- Iodine-mediated ozone depletion, compared to bromine, **is predominant** throughout most of the troposphere and significant in the tropical LMS
- Experimental work on I_2O_y is key to further determine the role of iodine in UTLS O3 destruction

Methyl iodide (CH_3I)



aircraft (mean ± stdev)

model (mean ± stdev)

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

Sensitivity runs: photolysis of I_2O_y

Estimation of XS of I_2O_y

High levels of I_2O_2, I_2O_3, I_2O_4