Very Short Lived (VSL) Halogens in CAM-Chem

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Publications in 2014 / 2015

VSL Bromine (TTL):

- Fernandez, R. P., R. J. Salawitch, D. E. Kinnison, J-F. Lamarque, and A. Saiz-Lopez, Bromine partitioning in the tropical tropopause layer, implications for stratospheric injection, *Atmos. Chem. Phys.* , 14,13391-13410, doi:10.5194/acp-14-13391-2014, 2014.

VSL Iodine (Troposphere):

- Saiz-Lopez, A., R. P. Fernandez, C. Ordonez, D. E. Kinnison, J. C. Gomez, Martin, J-F. Lamarque, and S. Tilmes, Iodine chemistry in the troposphere and its effect on ozone, *Atmos. Chem. Phys.* , 14, 13119-13143, doi:10.5194/acp-14-13119-2014, 2014.

Marine Boundary Layer:

- Prados-Roman, C., C. A. Cuevas, T. Hay, R. P. Fernandez, A. S. Mahajan, S-J. royer, M. Gali, R. Simon, J. Dashs, K. GroBmann, D. E. Kinnison, J-F Lamarque, and A. Saiz-Lopez, Iodine oxide in the global marine boundary layer, *Atmos. Chem. Phys.*, 15, 583-593, doi:10.5194/acp-15-583-2015.

- Prados-Roman, C., C. A. Cuevas, R. P. Fernandez, D. E. Kinnison , J-F Lamarque, and A. Saiz-Lopez, A negative feedback between anthropogenic ozone pollution and enhanced ocean emissions of iodine, in press, *Atmos. Chem. Phys., 2015*.

Outline Continued

Other Studies in the Works…

CONTRAST / TORERO (TOGA Instrument – Eric Apel / Rebecca Hornbrook)

- Results will be presented at EGU2015.

CONTRAST / TORERO BrOy budget

- Collaboration with Ross Salawitch (U. of Maryland).
- Collaboration with Elliot Atlas and Maria Navarro (U. of Miami).

CONTRAST OH Budget

- Collaboration with Julie Nicely and Ross (U. of Maryland)

TORERO IOy budget in the TTL.

- Collaboration with Rainer Volkamer's group (U. of Colorado).

CAM-Chem with VSL Chemistry

NCAR CESM CAM-CHEM

- Global Chemistry-Climate Model
- ~1.0° horizontal resolution
- Specified Dynamics Version (GEOS5)
- 56 vertical levels (surface to ~ 2 hPa)

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

Tropospheric Halogen Chemistry

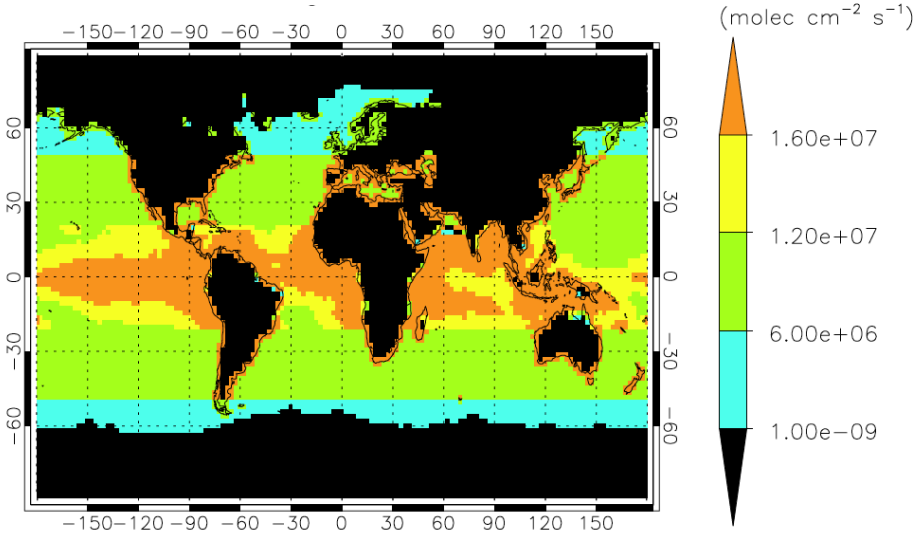
Halogenated sources from the ocean.

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

Organic Bromine in the TTL

Fernandez et al., ACP, 2014.

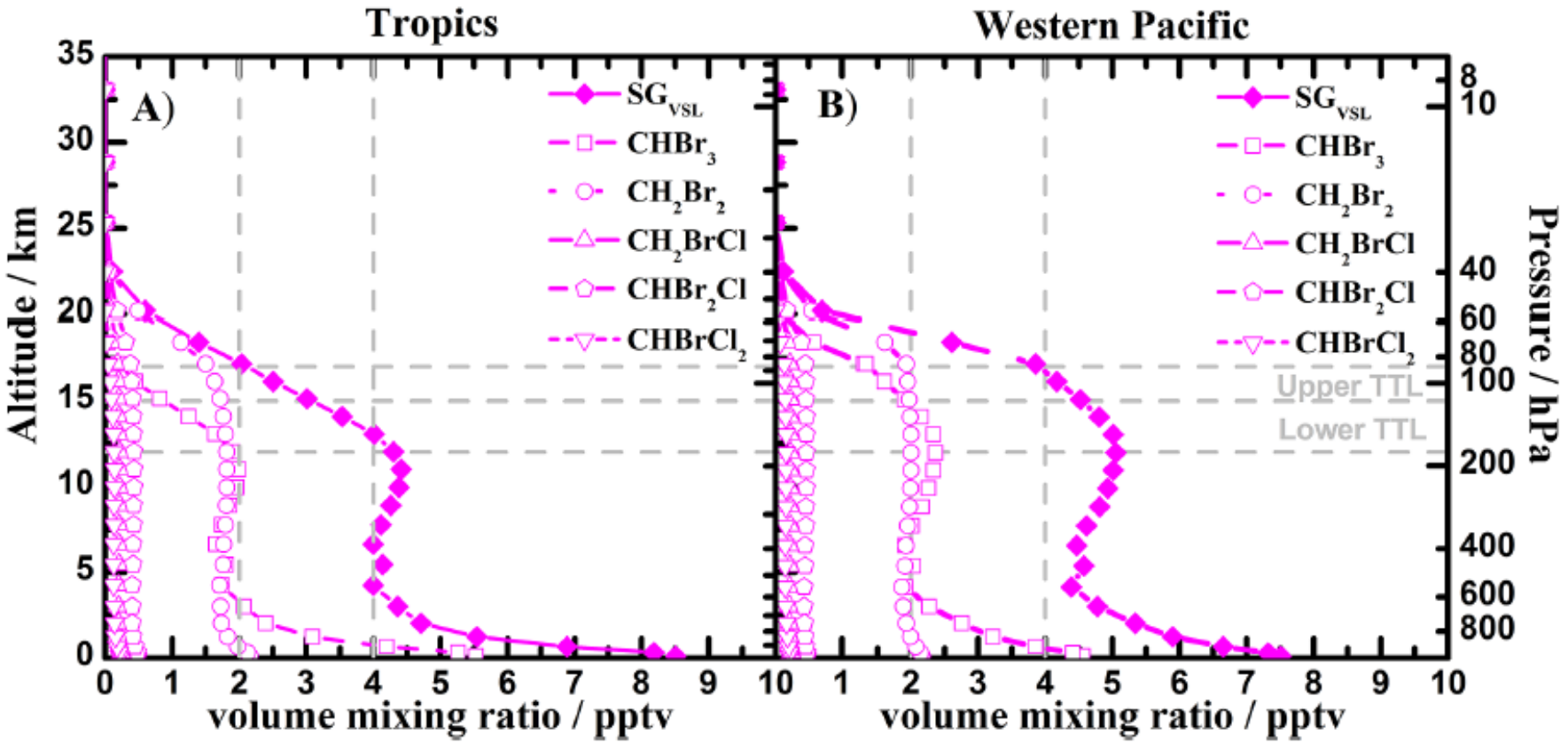


Figure 2. Vertical profile abundances of the five VSL bromocarbons considered in CAM-Chem for the tropical annual average (**a**) and the Western Pacific region (**b**). All halocarbon abundances are multiplied by their respective atomicity in order to represent their contribution to Br_y after photolysis or reaction with OH. The total organic SG_{VSL} contribution is also shown by the filled diamonds.

Inorganic (and Org.) Bromine in the TTL

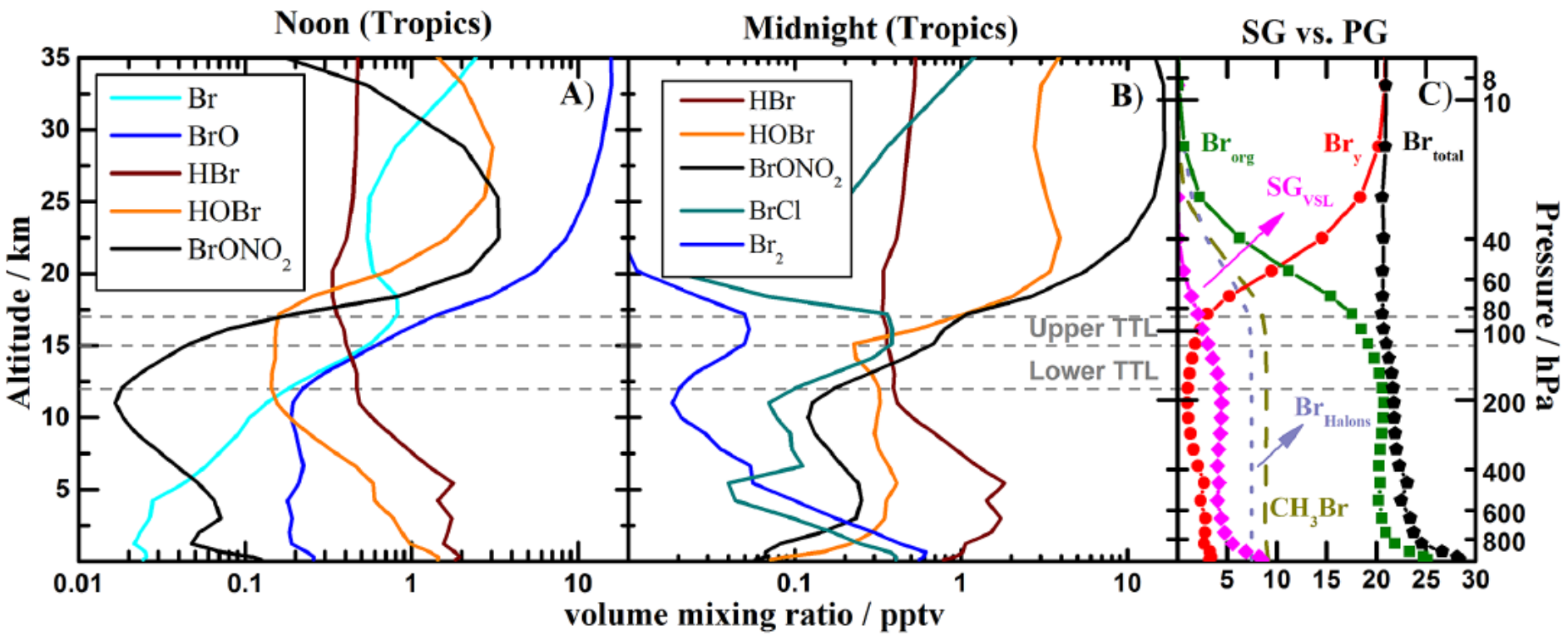
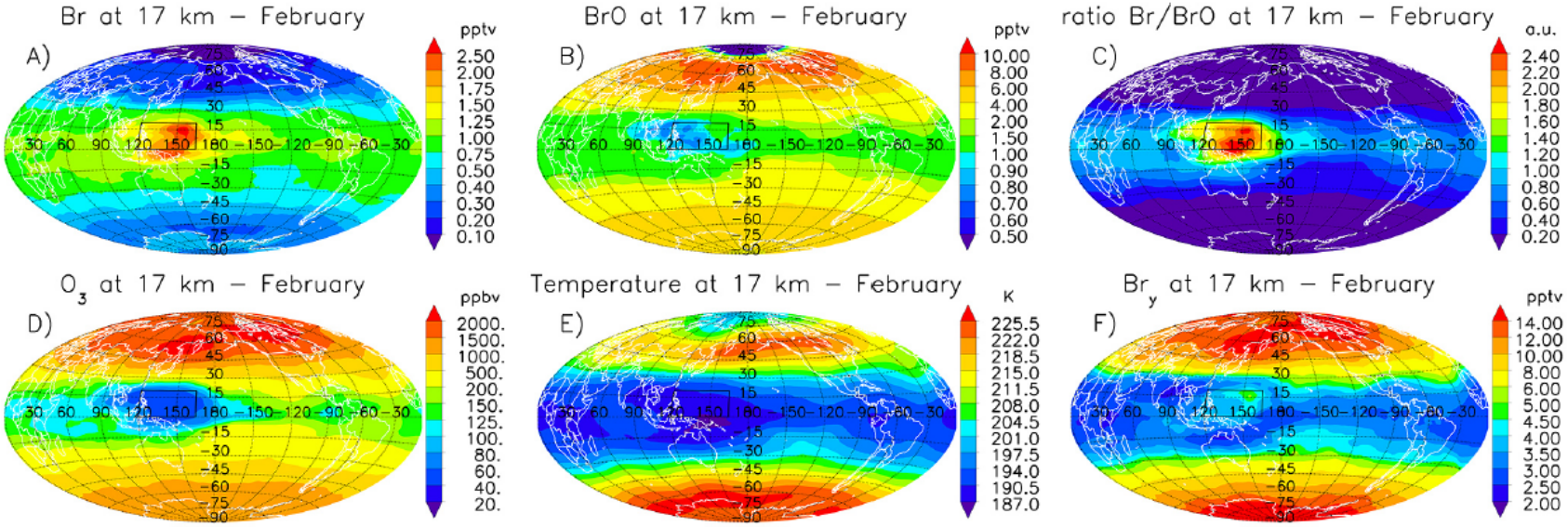


Figure 1. Annual vertical profile abundances of organic and inorganic bromine species within the tropics (20° N–20° S): (**a**) main Br_y species at noon; (**b**) main Br_y species at midnight; and (**c**) 24 h average contribution of organic and inorganic species to total bromine. The horizontal dotted lines represent the approximate location of the TTL.

Noontime Geographical Distribution



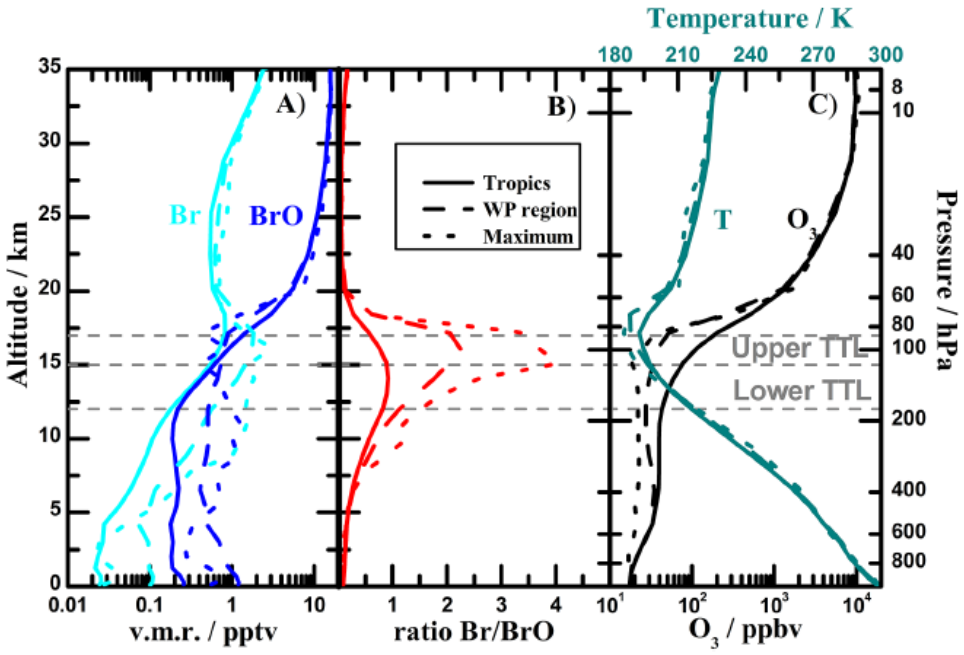
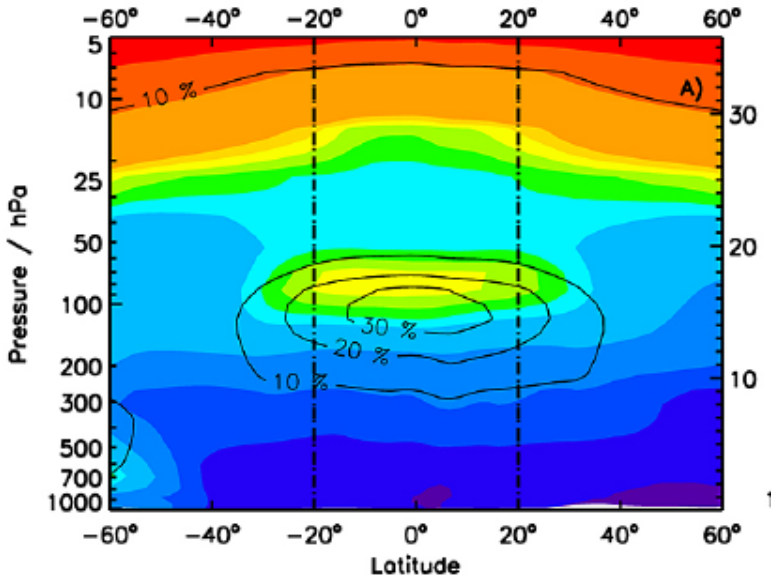


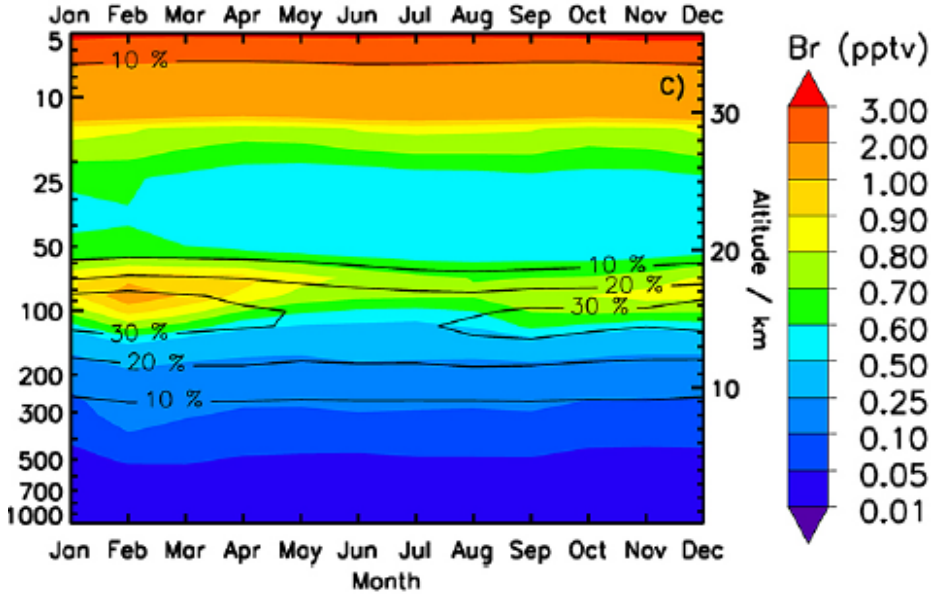
Figure 4. Vertical noontime profiles of Br and BrO vmr (**a**), the Br / BrO ratio (**b**), and T and O_3 (**c**) in the tropics. Vertical profiles have been averaged over different regions and time periods: (solid) annual tropical averages (20° N–20° S); (dashed) WP region during February; (dotted) at the midpoint of a strong convective cell within the WP during a 3-day period in February.

Tropical Ring of Atomic Bromine in the TTL

Annual Average



Zonally Averaged Seasonal Evolution



Summary Bromine in TTL

- Using a state-of-the-art photochemical mechanism within a global CCM (CAM-Chem), we calculate that ~5pptv VSL bromine inters the lower stratosphere.
  - 3 pptv as Product Gases (Inorganic)
  - 2 pptv as Source Gases (Organic)

- Our calculations indicate that atomic Br should be the dominant inorganic species in the TTL region during daylight.
  - Nighttime reservoirs are HOBr and BrCl

- We propose the existence of a “tropical ring” of atomic Br.
  - Located between ~15-19km and 30°N-30°S.

- Daytime ratios of Br/BrO approach a factor of ~4.

- Experimental programs should include a strategies to measure atomic Br during daytime hours (along with HOBr and BrCl during nighttime).

Tropospheric Iodine Chemistry

Reaction	k cm^{-3} molecule^{-1} s^{-1}	Notes
$I + O_3 \rightarrow IO + O_2$	$2.1 \times 10^{-11}\, e^{(-830/T)}$	1
$IO + O_3 \rightarrow OIO + O_2$	3.6×10^{-16}	2
$I + HO_2 \rightarrow HI + O_2$	$1.5 \times 10^{-11}\, e^{(-1090/T)}$	3
$IO + NO \rightarrow I + NO_2$	$7.15 \times 10^{-12}\, e^{(300/T)}$	1
$IO + HO_2 \rightarrow HOI + O_2$	$1.4 \times 10^{-11}\, e^{(540/T)}$	1
$IO + IO \rightarrow OIO + I$	$2.13 \times 10^{-11}\, e^{(180/T)} \times [1 + e^{(-p/191.42)}]$	1, 4
$IO + IO \rightarrow I_2O_2$	$3.27 \times 10^{-11}\, e^{(180/T)} \times [1 - 0.65\, e^{(-p/191.42)}]$	1, 4
$IO + OIO \rightarrow I_2O_3$	$w_1 \cdot \exp(w_2 \cdot T)^a$	4, 5, 6[g]
$OIO + OIO \rightarrow I_2O_4$	$w_1 \cdot \exp(w_2 \cdot T)^b$	4, 5, 6[g]
$I_2 + O \rightarrow IO + I$	1.25×10^{-10}	1
$IO + O \rightarrow I + O_2$	1.4×10^{-10}	1
$IO + OH \rightarrow HO_2 + I$	1.0×10^{-10}	7
$I_2O_2 \rightarrow OIO + I$	$w_1 \cdot \exp(w_2 / T)^c$	5, 6, 8[g]
$I_2O_2 \rightarrow IO + IO$	$w_1 \cdot \exp(w_2 / T)^d$	5, 6, 8[g]
$I_2O_4 \rightarrow 2\,OIO$	$w_1 \cdot \exp(w_2 / T)^e$	5, 8[g]
$I_2 + OH \rightarrow HOI + I$	1.8×10^{-10}	3
$I_2 + NO_3 \rightarrow I + IONO_2$	1.5×10^{-12}	9
$I + NO_3 \rightarrow IO + NO_2$	1.0×10^{-10}	1
$OH + HI \rightarrow I + H_2O$	$1.6 \times 10^{-11}\, e^{(440/T)}$	1
$I + IONO_2 \rightarrow I_2 + NO_3$	$9.1 \times 10^{-11}\, e^{(-146/T)}$	5
$HOI + OH \rightarrow IO + H_2O$	2.0×10^{-13}	10
$IO + DMS \rightarrow DMSO + I$	$3.2 \times 10^{-13}\, e^{(-925/T)}$	11
$INO_2 \rightarrow I + NO_2$	$1008 \times 10^{15}\, e^{(-13670/T)}$	12, 13, 14
$IONO_2 \rightarrow IO + NO_2$	$w_1 \cdot \exp(w_2 / T)^f$	5, 15
$INO + INO \rightarrow I_2 + 2NO$	$8.4 \times 10^{-11}\, e^{(-2620/T)}$	3
$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	$4.7 \times 10^{-13}\, e^{(-1670/T)}$	1
$OIO + NO \rightarrow IO + NO_2$	$1.1 \times 10^{-12} e^{(542/T)}$	14
$HI + NO_3 \rightarrow I + HNO_3$	$1.3 \times 10^{-12} e^{(-1830/T)}$	16
$IO + BrO \rightarrow Br + I + O_2$	$0.30 \times 10^{-11} e^{(510/T)}$	1
$IO + BrO \rightarrow Br + OIO$	$1.20 \times 10^{-11} e^{(510/T)}$	1
$I + BrO \rightarrow IO + Br$	1.44×10^{-11}	17, 18, 19
$IO + ClO \rightarrow I + OClO$	$2.585 \times 10^{-12}\, e^{(280/T)}$	1
$IO + ClO \rightarrow I + Cl + O_2$	$1.175 \times 10^{-12}\, e^{(280/T)}$	1
$IO + ClO \rightarrow ICl + O_2$	$0.940 \times 10^{-12}\, e^{(280/T)}$	1
$IO + Br \rightarrow I + BrO$	2.49×10^{-11}	18, 19
$IO + NO_3 \rightarrow OIO + NO_2$	9.0×10^{-12}	20
$IO + CH_3O_2 \rightarrow CH_2O + I + HO_2$	2.0×10^{-12}	2[h]

Reaction	k cm^{-3} molecule^{-1} s^{-1}	Notes
$CH_3I + OH \rightarrow I + H_2O + HO_2$	$2.90 \times 10^{-12}\, e^{(-1100/T)}$	3
$I + NO_2\,(+M) \rightarrow INO_2\,(+M)$	$k_0 = 3 \times 10^{-31} \times (T/300)^{-1}$ $k_\infty = 6.6 \times 10^{-11}$	3[i]
$IO + NO_2\,(+M) \rightarrow IONO_2\,(+M)$	$k_0 = 6.5 \times 10^{-31} \times (T/300)^{-3.5}$ $k_\infty = 7.6 \times 10^{-12} \times (T/300)^{-1.5}$	3[i]
$I + NO\,(+M) \rightarrow INO\,(+M)$	$k_0 = 1.8 \times 10^{-32} \times (T/300)^{-1}$ $k_\infty = 1.7 \times 10^{-11}$	3[i]
$OIO + OH\,(+M) \rightarrow HOIO_2\,(+M)$	$k_0 = 1.5 \times 10^{-27} \times (T/300)^{-3.93}$ $k_\infty = 7.76 \times 10^{-10} \times (T/300)^{-0.8}$	14[j]

Reaction
$CH_3I + h\nu \rightarrow CH_3O_2 + I$
$CH_2I_2 + h\nu \rightarrow 2I^a$
$CH_2IBr + h\nu \rightarrow Br + I^a$
$CH_2ICl + h\nu \rightarrow Cl + I^a$
$I_2 + h\nu \rightarrow 2I$
$IO + h\nu \rightarrow I + O$
$OIO + h\nu \rightarrow I + O_2$
$INO + h\nu \rightarrow I + NO$
$INO_2 + h\nu \rightarrow I + NO_2^b$
$IONO_2 + h\nu \rightarrow I + NO_3$
$HOI + h\nu \rightarrow I + OH$
$IBr + h\nu \rightarrow I + Br$
$ICl + h\nu \rightarrow I + Cl$
$I_2O_2 + h\nu \rightarrow I + OIO^c$
$I_2O_3 + h\nu \rightarrow IO + OIO^c$
$I_2O_4 + h\nu \rightarrow OIO + OIO^c$

~15 species; ~60 reactions

Saiz-Lopez et al., ACP, 2014.

Photolysis Rate of: I_2O_2, I_2O_3, I_2O_4

Reaction
$CH_3I + h\nu \rightarrow CH_3O_2 + I$
$CH_2I_2 + h\nu \rightarrow 2I$[a]
$CH_2IBr + h\nu \rightarrow Br + I$[a]
$CH_2ICl + h\nu \rightarrow Cl + I$[a]
$I_2 + h\nu \rightarrow 2I$
$IO + h\nu \rightarrow I + O$
$OIO + h\nu \rightarrow I + O_2$
$INO + h\nu \rightarrow I + NO$
$INO_2 + h\nu \rightarrow I + NO_2$[b]
$IONO_2 + h\nu \rightarrow I + NO_3$
$HOI + h\nu \rightarrow I + OH$
$IBr + h\nu \rightarrow I + Br$
$ICl + h\nu \rightarrow I + Cl$
$I_2O_2 + h\nu \rightarrow I + OIO$[c]
$I_2O_3 + h\nu \rightarrow IO + OIO$[c]
$I_2O_4 + h\nu \rightarrow OIO + OIO$[c]

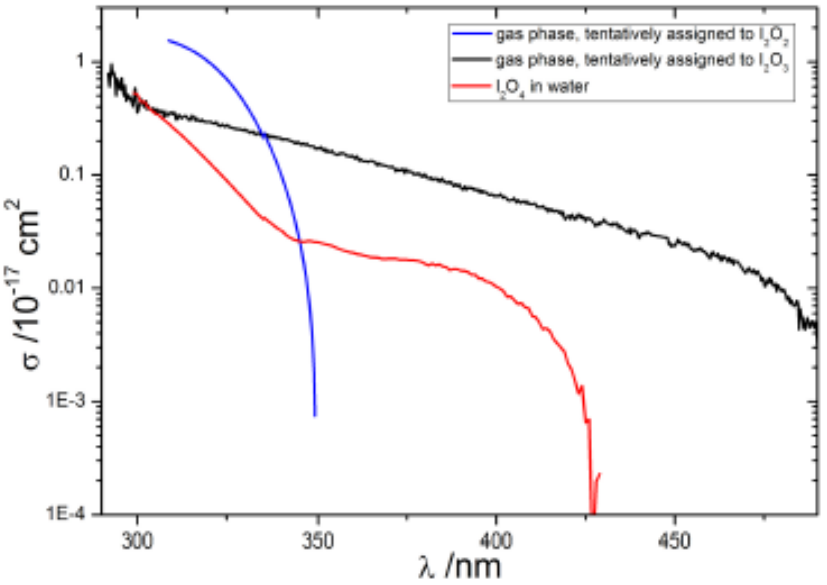


Figure 1. Absorption cross-sections of the higher iodine oxides I_xO_y ($x = 2$, $y \geq 2$). Gas phase experimental spectra tentatively assigned to I_2O_2 and I_2O_3 (Gómez Martín et al., 2005, 2007; Spietz et al., 2005) are plotted in blue and black respectively. The I_2O_2 spectrum has been smoothed by fitting a polynomial through it. The red line corresponds to the absorption spectrum of I_2O_4 in water (Russell Saunders, personal communication).

Photolysis of IxOy increase reactive IOx!

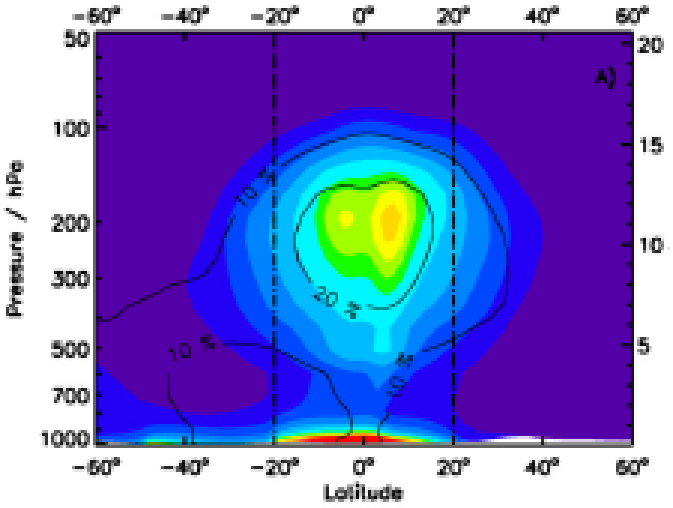
Saiz-Lopez et al., ACP, 2014.

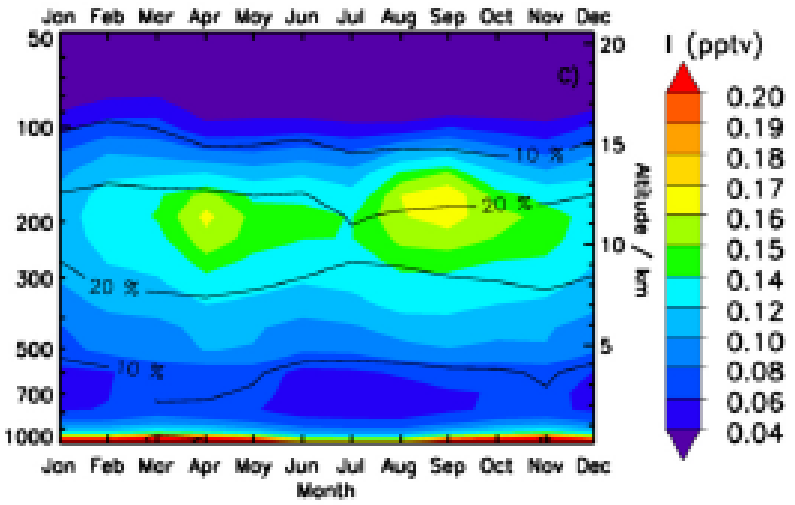
Tropospheric Iodine Ring

Annual Average

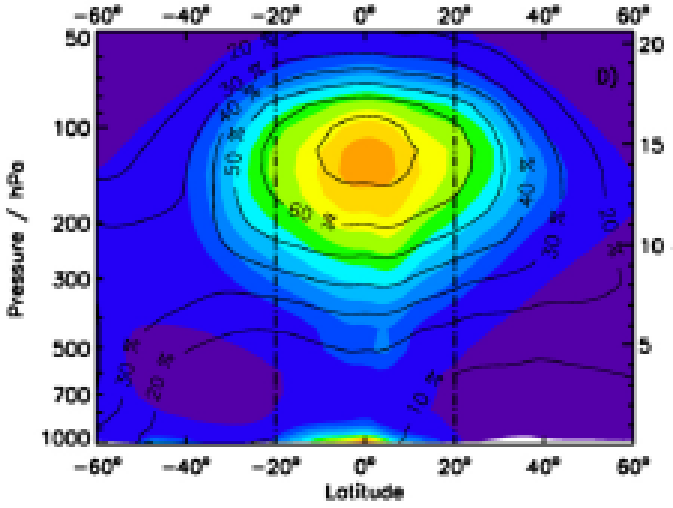
Zonally Averaged Seasonal Evolution

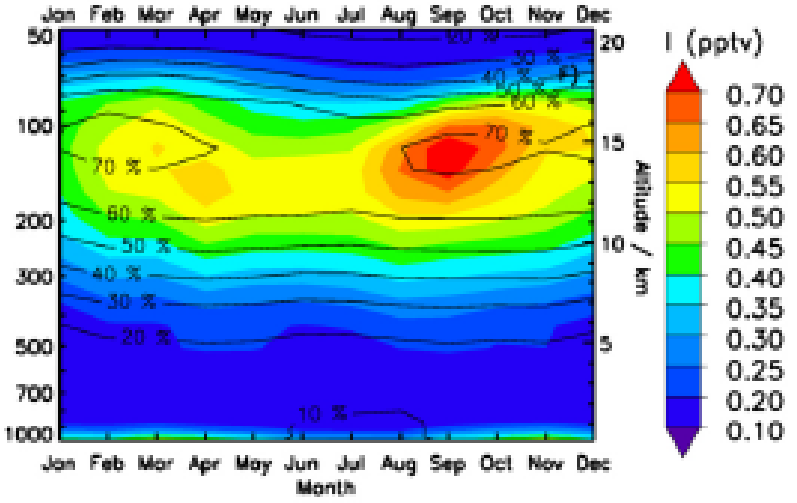
wo JxOy





with JxOy





Tropospheric Iodine Ring

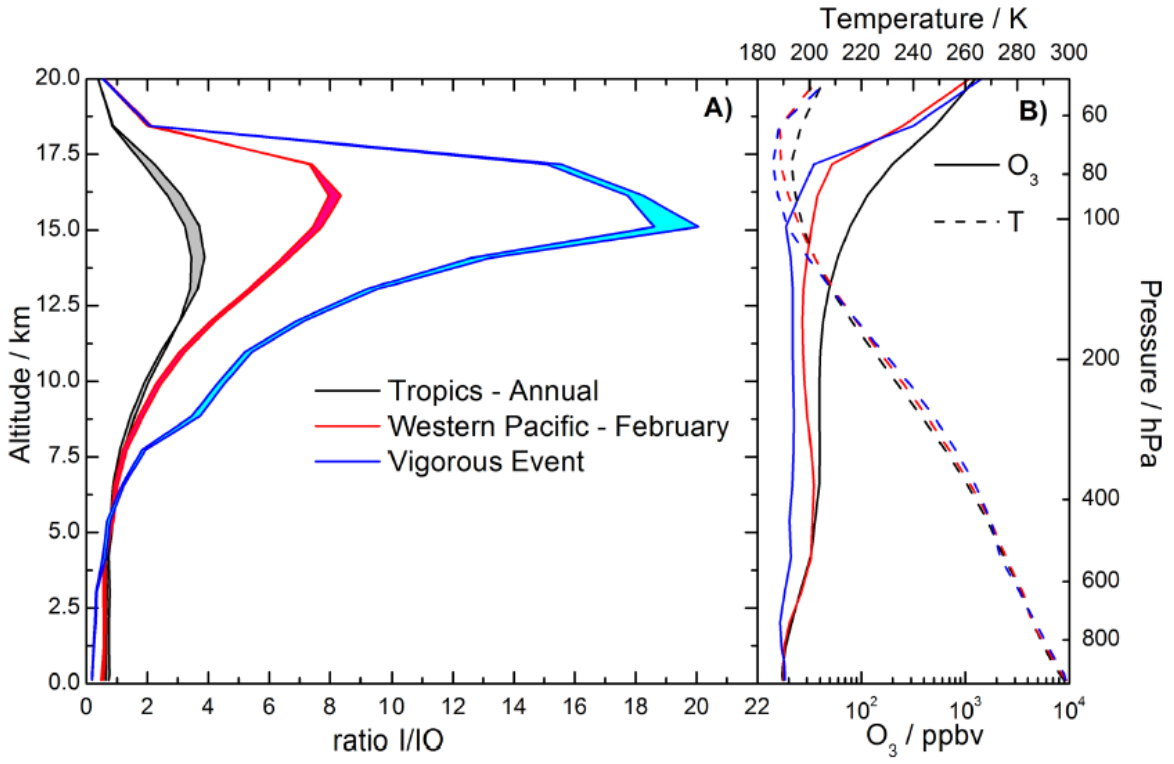


Figure 6. (a) Vertical profiles for the I / IO ratio averaged over different regions and periods of time: (black) annual tropical (20° N–20° S) averages; (red) Western Pacific (WP) warm pool during February; (blue) at the midpoint of a strong convective cell within the WP region during a 3-day period in February. The upper and lower limits correspond to simulations with the *Base* and $J_{I_xO_y}$ schemes, respectively. **(b)** The vertical variation of O_3 abundances and temperature for each region and period of time.

Tropospheric Iodine Budgets

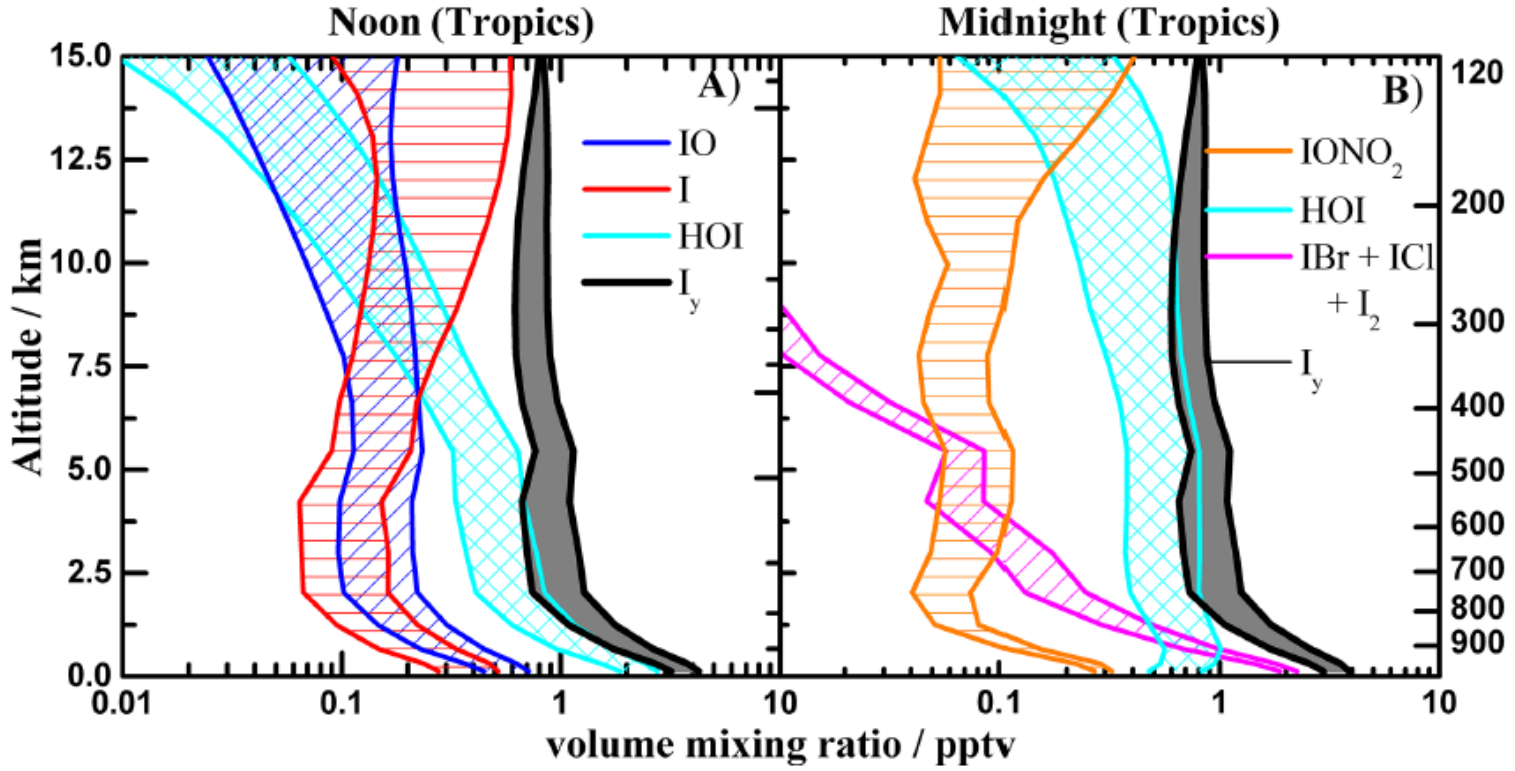


Figure 3. Lower and upper limits of I_y abundances within the tropical troposphere (20° N–20° S): **(a)** main inorganic species at noon (11:30–12:30 LT); **(b)** major I_y species at midnight (23:30–00:30 LT). The lower limit corresponds to the *Base* scheme, while the upper limit is for the $J_{I_xO_y}$ scheme.

Tropospheric Iodine Odd-Oxygen Loss

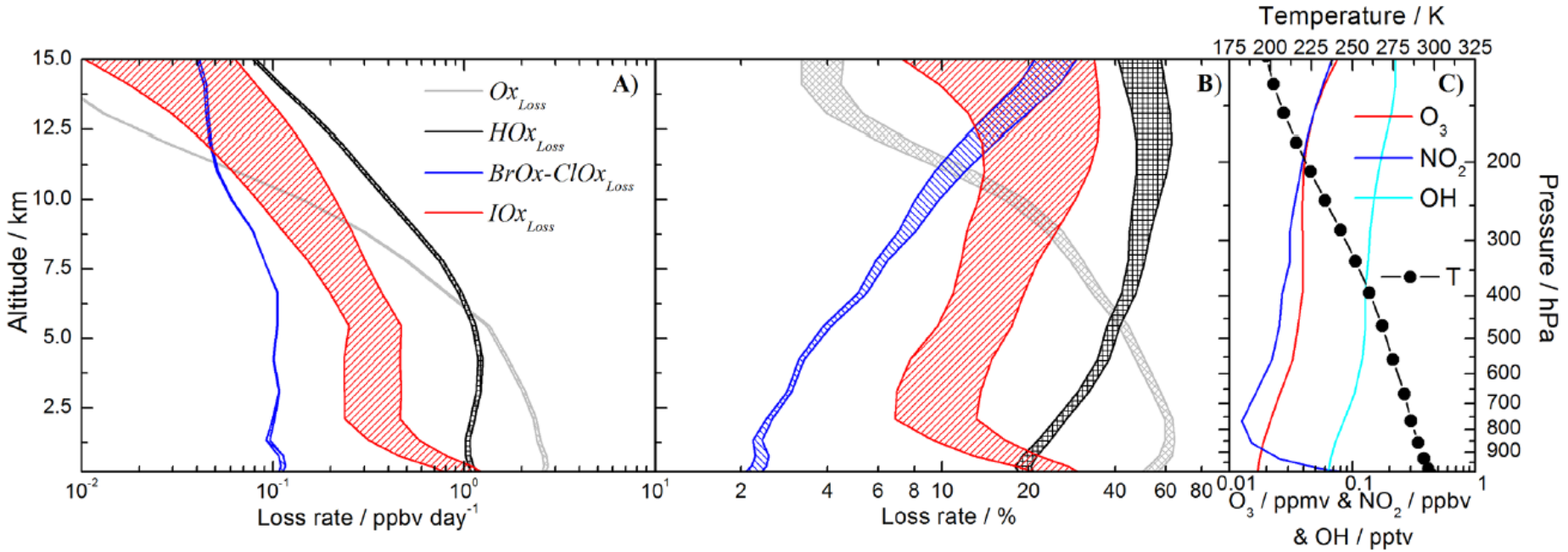


Figure 13. Modelled range of odd oxygen destruction for each of the ozone depleting families: **(a)** Annual total loss rates for the O_X, HO_X, BrO_X-ClO_X and IO_X families within the tropical troposphere (20° N–20° S); **(b)** Percentage contribution of each family to the total loss rate for each scheme; **(c)** Vertical profiles of O_3, NO_2, OH and temperature within the tropics. Lower and upper limits of the range are for the *Base* and $J_{I_xO_y}$ schemes, respectively.

Summary of Tropospheric Iodine

- Here we presented a comprehensive global modeling experiment aimed at estimating lower and upper limits of the inorganic iodine burden and its impact of tropospheric ozone.

- To define the range of inorganic iodine loading, partitioning and impact, two set of simulations were conducted with and without photolysis of I_xO_y oxides (I_2O_2, I_2O_3, and I_2O_4).

- Results show the most abundant daytime iodine species throughout the middle to upper troposphere is atomic iodine.
  - Annual tropical abundance of 0.15-0.55 pptv.

- Like atomic Br, we propose a “tropical ring” of atomic iodine.
  - Located between ~11-14km and 30°N-30°S.
  - I/IO ratios of up to a factor of 20 (convective regions).

- With I_xO_y photolysis included we derive for IOx odd-oxygen loss an upper limit of approximately 27% (MBL), 14% (Free Troposphere), and (27% UT) of the total loss.

- We suggest that iodine sources and its chemistry need to be included in global tropospheric chemistry models.

Thank you for your attention!