CESM Atmosphere / Whole Atmosphere / Chemistry Climate
WINTER WORKING GROUP MEETING

Comparing the effect of Natural Halogens on Tropospheric Ozone Chemistry between Pre-Industrial and Present-Day

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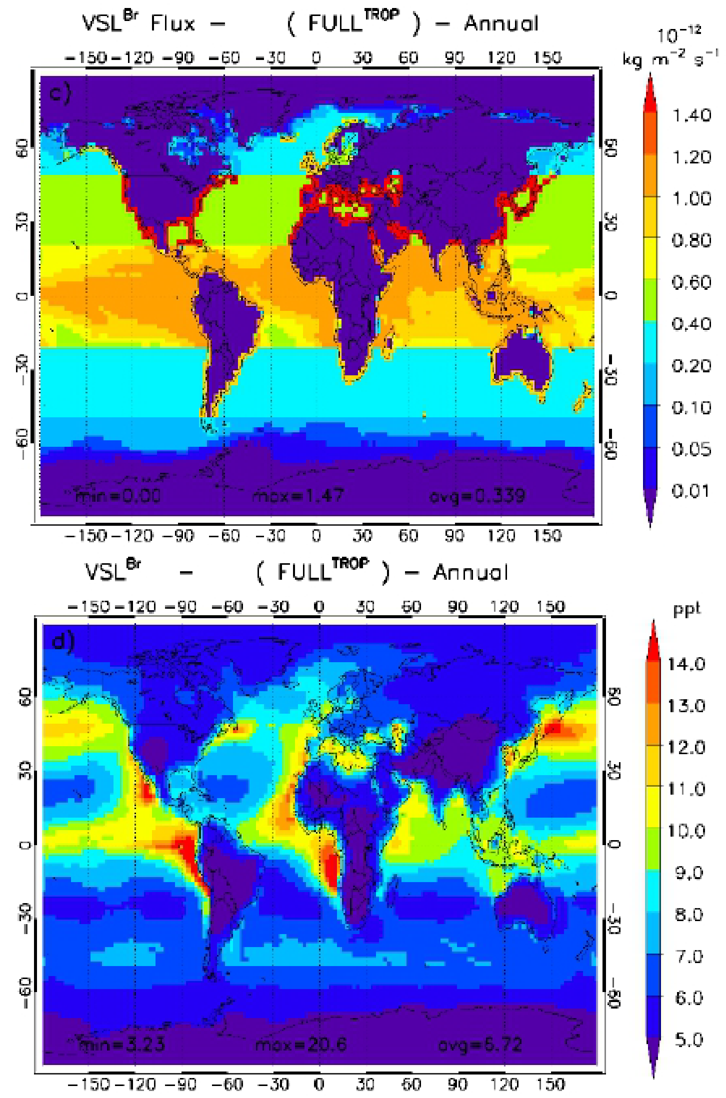
1. What are the natural sources of halogens?



- Very short-lived halocarbons (VSLs) have a photochemical lifetimes < 6 months and are naturally released from the ocean via the metabolism of marine organisms such as phytoplankton and algae.
- The current CAM-Chem set-up considers the Ordonez et al., (2012) emissions inventory by nine VSLs ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$, $CHBrCl_2$, CH_2IBr, CH_3I, CH_2I_2 and CH_2ICl), based on chlorophyll-a maps (SeaWIFS).
- Estimated global ocean emissions for the most abundant VSLs:

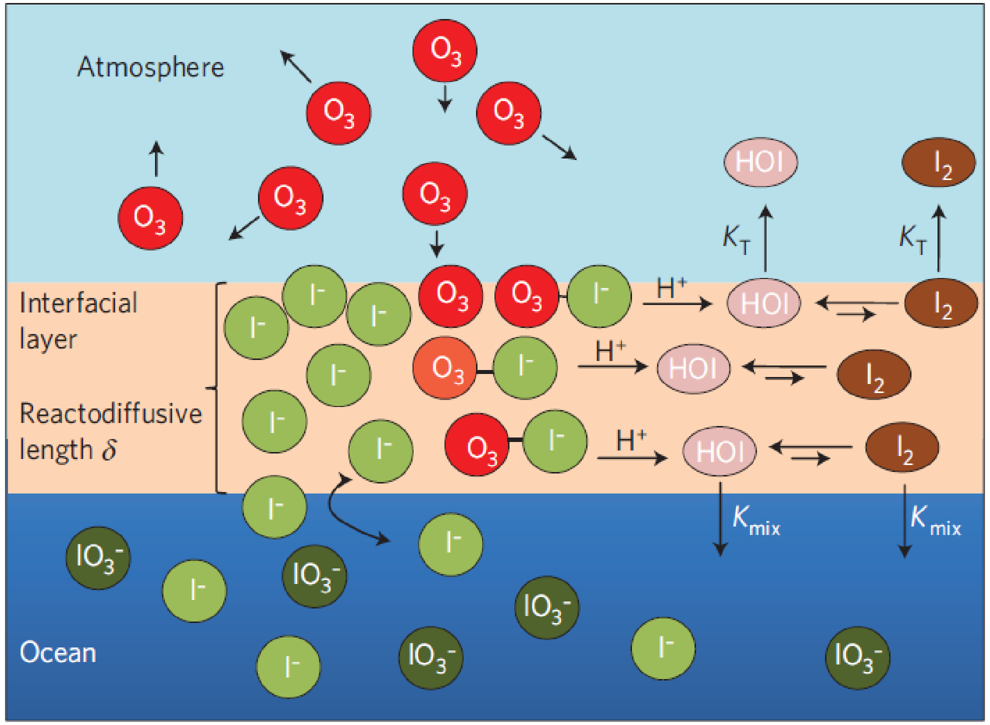
  $CHBr_3$ = 533 Gg yr^{-1}

  CH_2Br_2 =67.3 Gg yr^{-1}

Ordoñez et al., ACP, 2012

(top) annual oceanic bromine flux from the six VSL^{Br} included in the Ordóñez et al., (2012) emissions inventory
(bottom) annual VSL^{Br} mixing ratio at the model surface

Ocean source of inorganic iodine



HOI and I_2 emissions depends on:
Ozone
wind-speed
Iodide

$$F_{HOI} = [O_{3(g)}] \times \left(4.15 \times 10^5 \times \left(\frac{\sqrt{[I^-_{(aq)}]}}{ws}\right) - \left(\frac{20.6}{ws}\right) - 23\,600 \times \sqrt{[I^-_{(aq)}]}\right) \quad (2)$$

$$F_{I_2} = [O_{3(g)}] \times [I^-_{(aq)}]^{1.3} \times \left(1.74 \times 10^9 - \left(6.54 \times 10^8 \times \ln ws\right)\right), \quad (3)$$

$$[I^-_{(aq)}] = 1.46 \times 10^6 \times \exp\left(\frac{-9134}{SST}\right)$$

Seawater iodide depends on SST

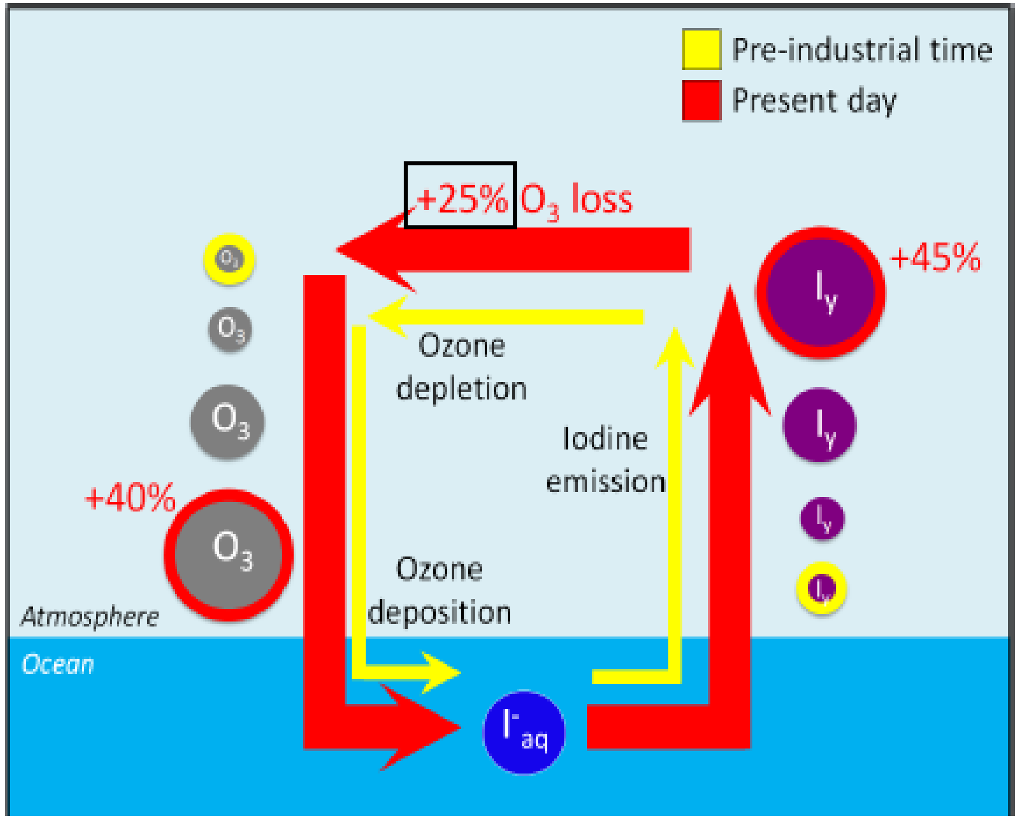
Prados-Roman et al., ACP, 2015

- This route accounts for up to 75% of iodine atmospheric budget
- The iodine flux strongly depends on the model surface O_3 levels

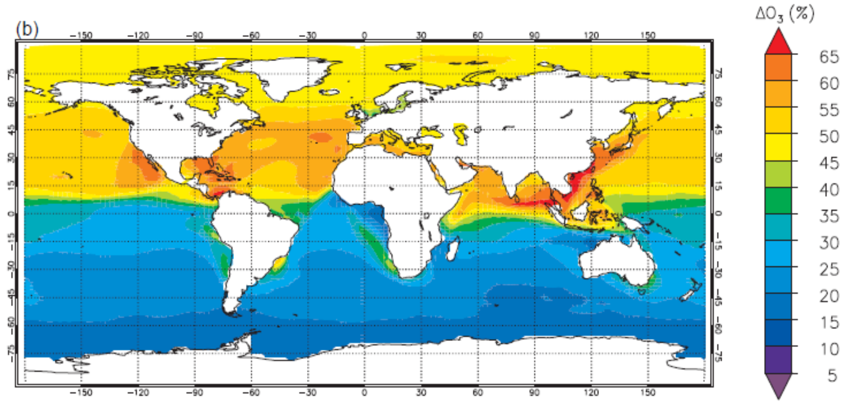
Carpenter et al., Nat. Coms, 2013
MacDonald et al., ACP, 2014

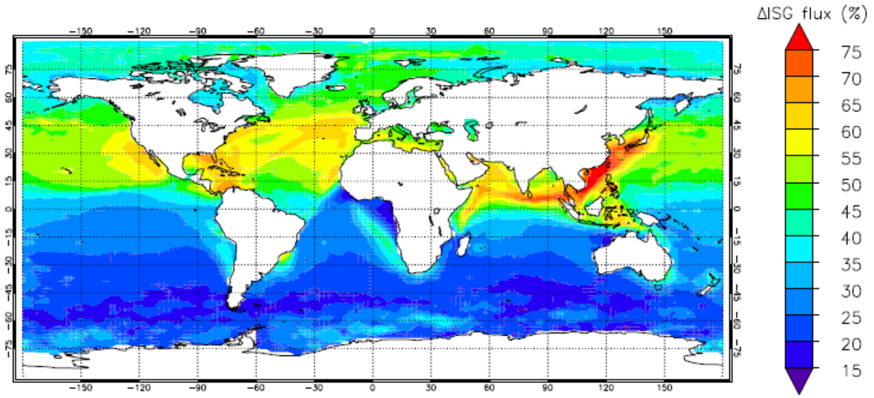
Geochemical feedback mechanism

↑ near-surface ozone →→ ↑ iodine flux →→ ↑ ozone loss driven Iodine



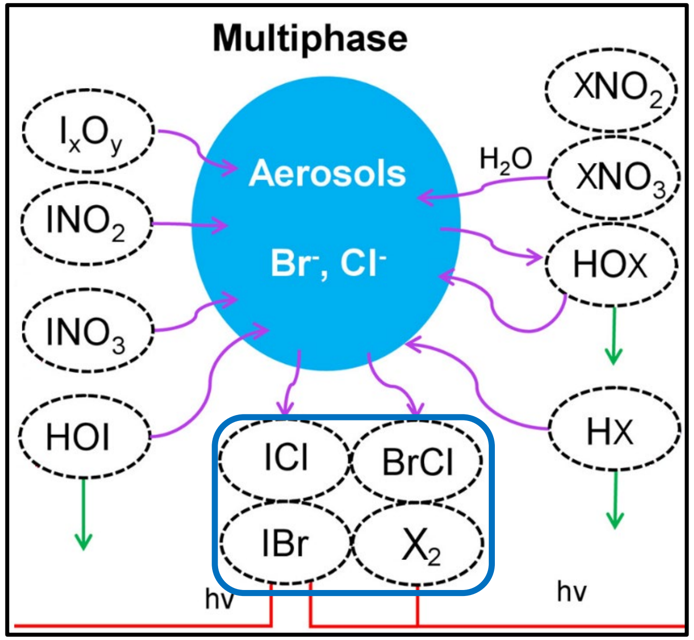
Ozone-Iodine negative feedback mechanism





Prados-Roman et al., ACP, 2015

SSA-dehalogenation (Br and Cl source)



3a. SSA-dehalogenation (Halogen Reservoirs):

$BrONO_2 + SSA \rightarrow 0.65\ Br_2 + 0.35\ BrCl$
$BrNO_2 + SSA \rightarrow 0.65\ Br_2 + 0.35\ BrCl$
$HOBr + SSA \rightarrow 0.65\ Br_2 + 0.35\ BrCl$
…
$ClONO_2 + SSA \rightarrow 1.00\ Cl_2$
$ClNO_2 + SSA \rightarrow 1.00\ Cl_2$
$HOCl + SSA \rightarrow 1.00\ Cl_2$

(Fernandez et al., 2014; 2021)

Updates for chlorine chemistry

→

3b. SSA-dehalogenation (Acidification):

$HNO_3 + SSA \rightarrow HCl$

$N_2O_5 + SSA \rightarrow ClNO_2 + HNO_3$

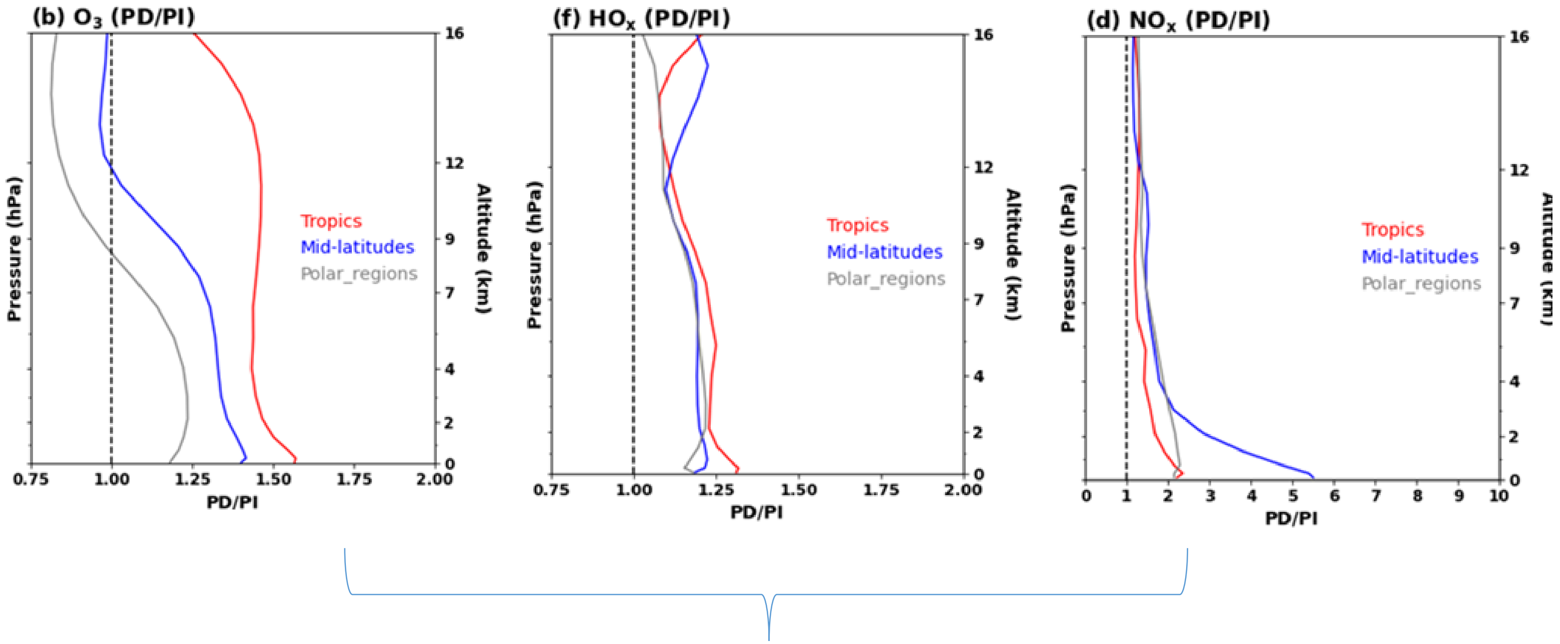
Enhanced Chlorine-production due to anthropogenic pollution
(Li et al., 2022; based on Hossaini et al., 2016)

2. CAM-Chem simulation design

1. Specified dynamic simulation
2. All simulations have identical meteorology under pre-industrial (PI) and present-day (PD) conditions
3. Emissions:
    - Long-lived halocarbon: are zeroed for PI & from the WMO (2011) recommendation for PD
    - NO_x, CO and NMVOCs: from IPCC (2019) in both periods
    - greenhouse gas (i.e., CH_4, CO_2, and N_2O): from Meinshausen et al. (2011) in both periods

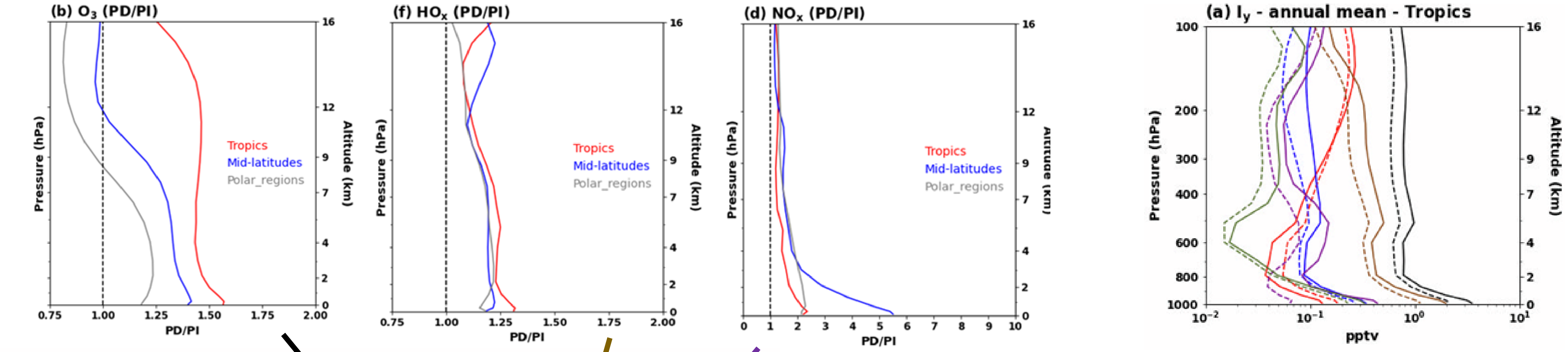
Scenario Name	LL halocarbons LBC	VSL halocarbons Emissions	I_2/HOI Emissions	SSA-recycling Emissions
REF	YES	NO	NO	NO
VSL_I	YES	YES	YES	NO
VSL_Br	YES	YES	NO	YES
VSL_Cl	YES	YES	NO	YES
VSL_ALL	YES	YES	YES	YES

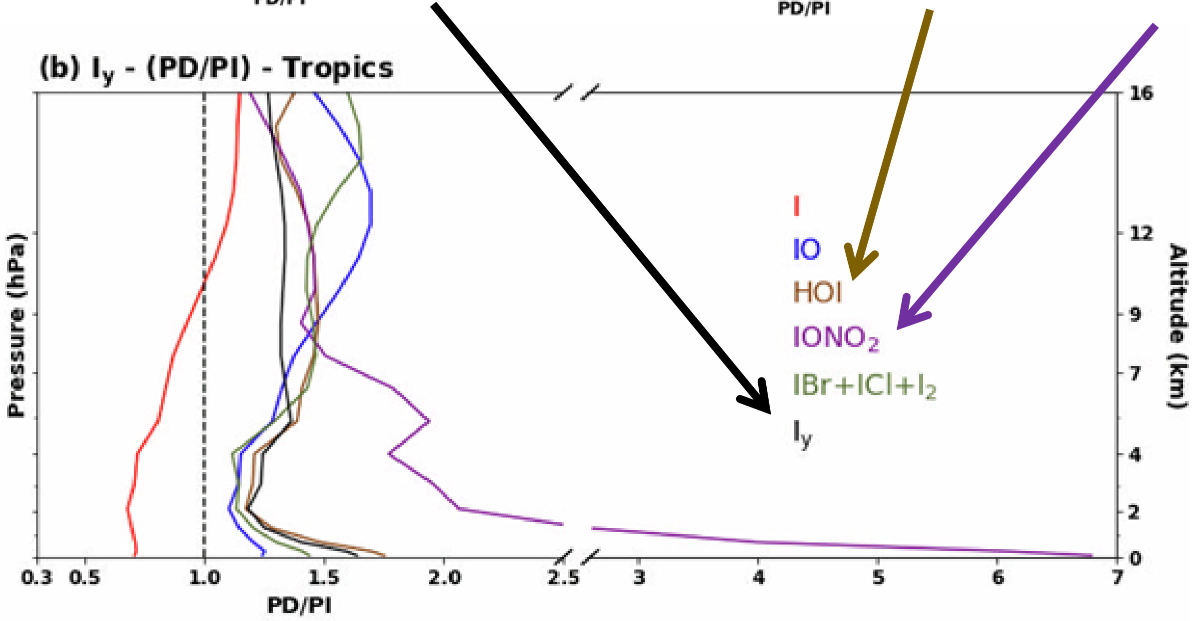
3. Result: background changes between PI and PD



The increase in tropospheric O_3, HO_x and NO_x burden from PI to PD is closely linked to the increase in surface emissions of the main anthropogenic O_3 precursors (e.g. NO_x, CO, CH_4 and NMVOC)

3. Changes in inorganic halogen partitioning





reactive **reservoirs**

I_y = **I + IO** + I_2 + IBr + ICl **+ HI + HOI + INO + INO_2 + $IONO_2$ …**

Change PI to PD:

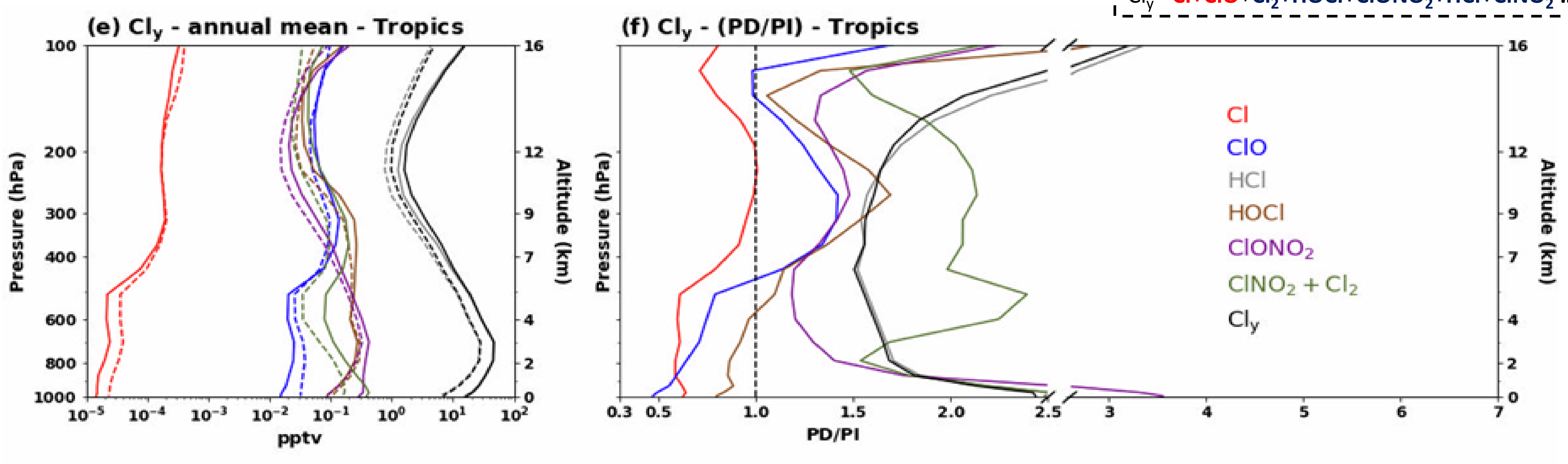
1. increase in I_y driven by O_3 change (ozone-iodine feedback mechanism)

2. change in I_y partitioning (shift from reactive to reservoirs) driven by changes in HO_x and NO_x

- Increase of reservoirs (HOI and $IONO_2$) drives an indirect accumulation of IBr and ICl via SSA-dehalogenation

3. Changes in inorganic halogen partitioning

reactive reservoirs
Cl_y= $Cl+ClO+Cl_2+HOCl+ClONO_2+HCl+ClNO_2$ …

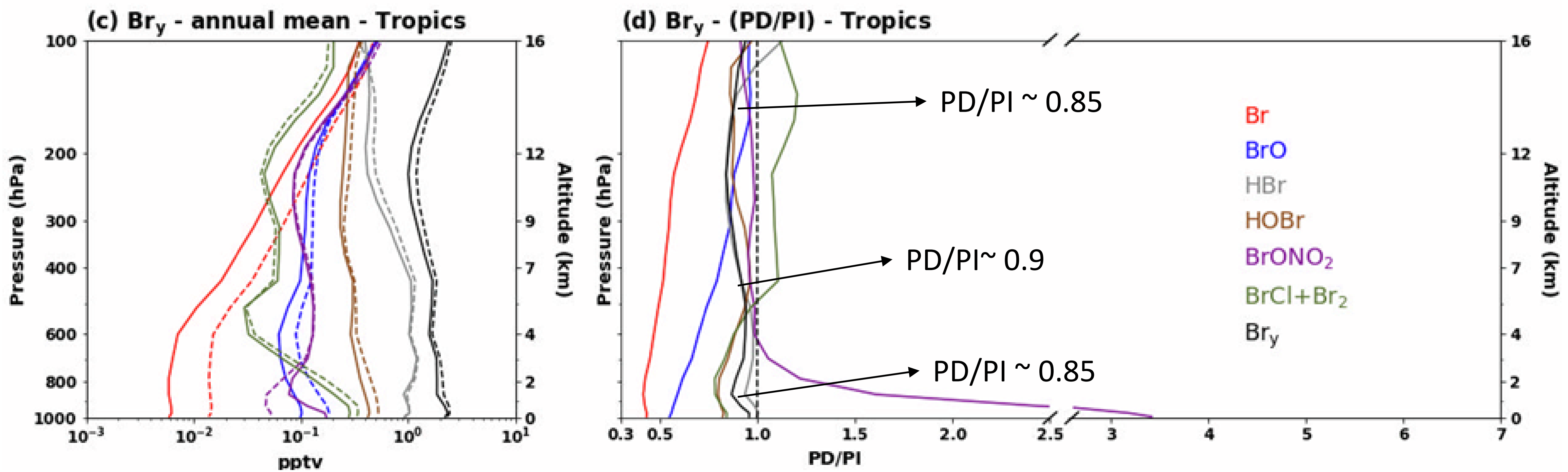


- Similar to iodine, there is a strong partitioning into reservoirs mainly in the lower troposphere
- The PI to PD increase in Cl_y is due to:
  - stratospheric-to-tropospheric transport of Cl_y rich air masses
  - enhanced SSA-dehalogenation driven by more halogens
  - chlorine production from odd-nitrogen uptake in SSA driven by an increase in near-surface NO_x abundance

3. Changes in inorganic halogen partitioning

reactive reservoirs

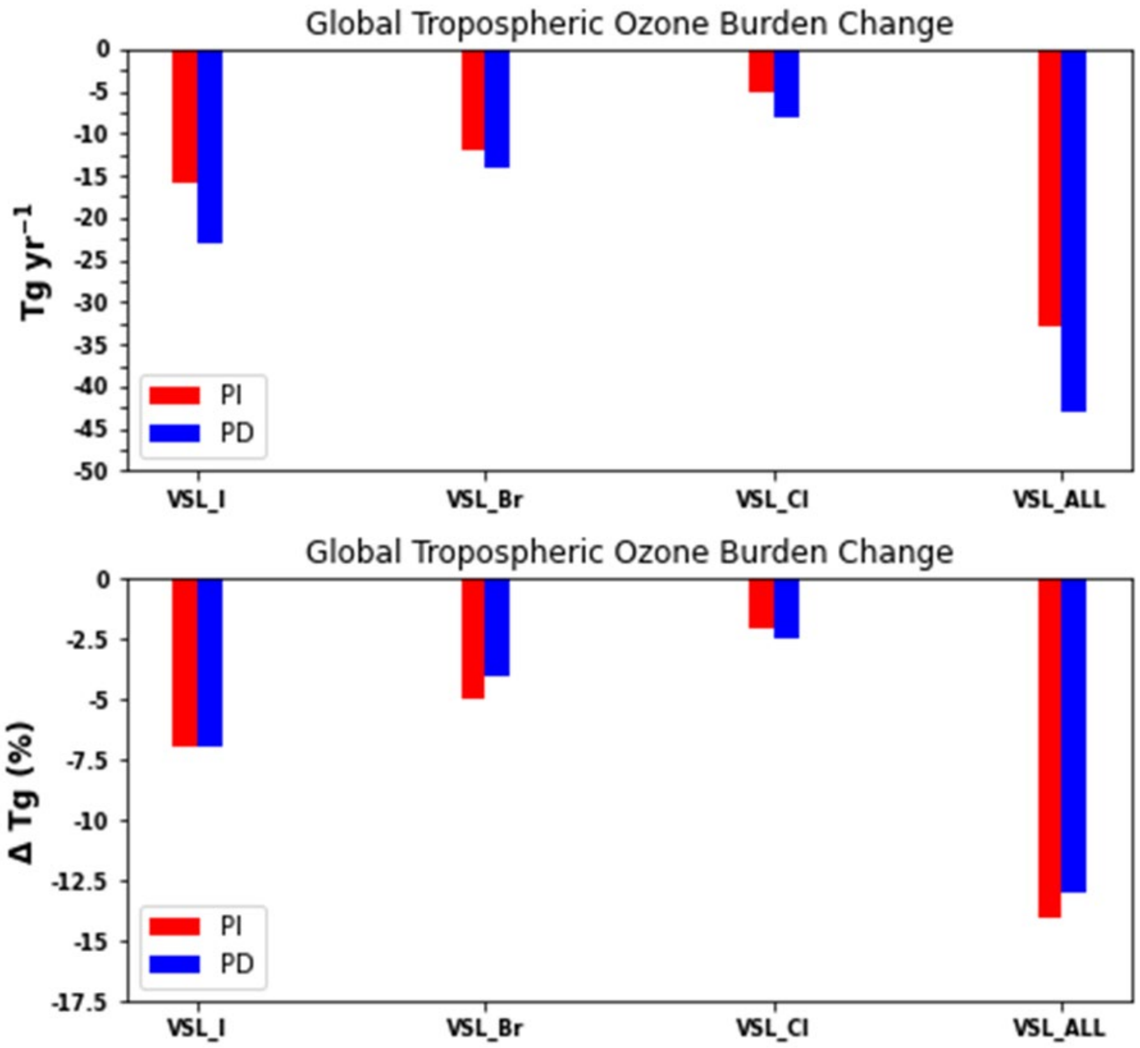
$Br_y = Br + BrO + BrCl + IBr + HOBr + Br_2 + BrONO_2 + HBr\ldots$



Tropospheric Br_y is slightly reduced in the transition PI to PD:

- VSL bromocarbons emissions are assumed equal in both periods
- increased conversion of reactive to reservoirs improves the bromine wet-removal via washout and scavenging

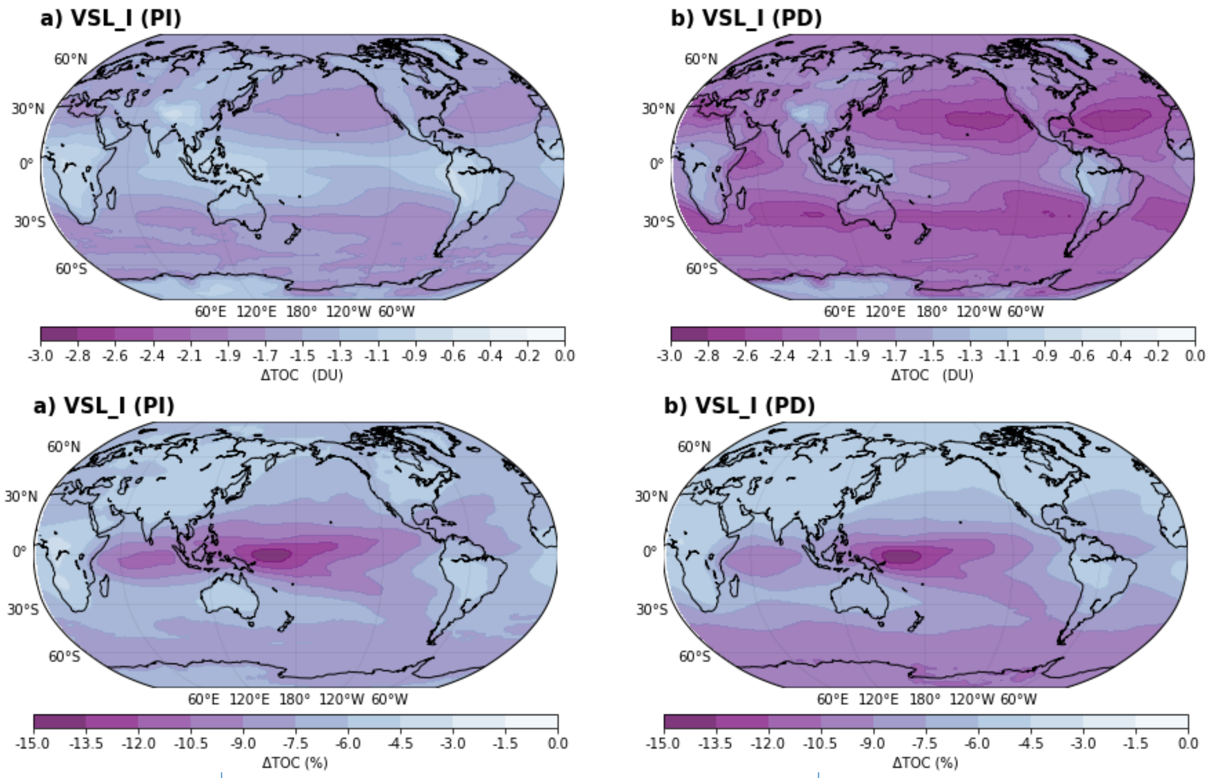
3. Changes in global tropospheric ozone



- In percentage terms, halogens induce a larger ozone depletion in PI (−14 %) than PD (−13 %)
- This effect is mainly governed by iodine and then bromine
- Individually:
- iodine has a role equal in both periods (−7 %)
- bromine has a larger role in PI (−5 %) vs. PD (−4%)
- Chlorine has a larger role in PD (−2.5%) vs. (PI: −2 %)

3. Changes in tropospheric ozone distribution

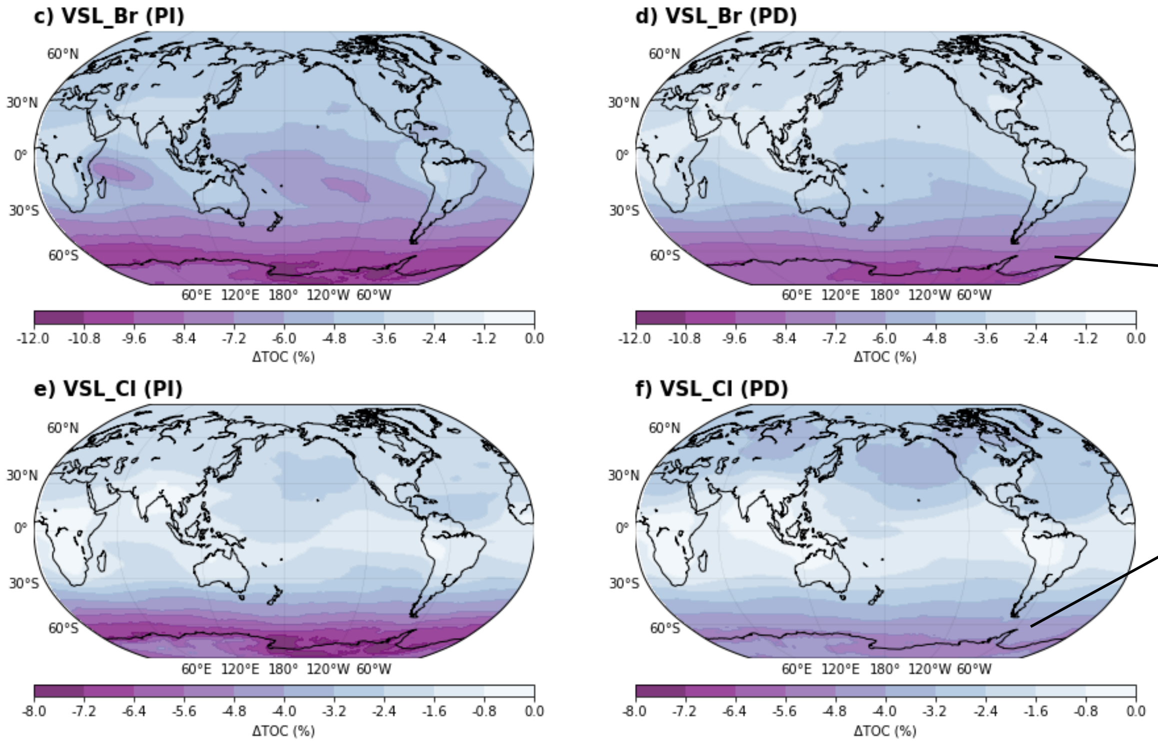
iodine induces TOC reduction mainly over marine environments



Larger TOC reduction in PD than PI due to “ozone-iodine feedback mechanism”

In percentage terms, the iodine peaks the TOC reduction in the western pacific warm pool and Antarctica

3. Changes in tropospheric ozone distribution

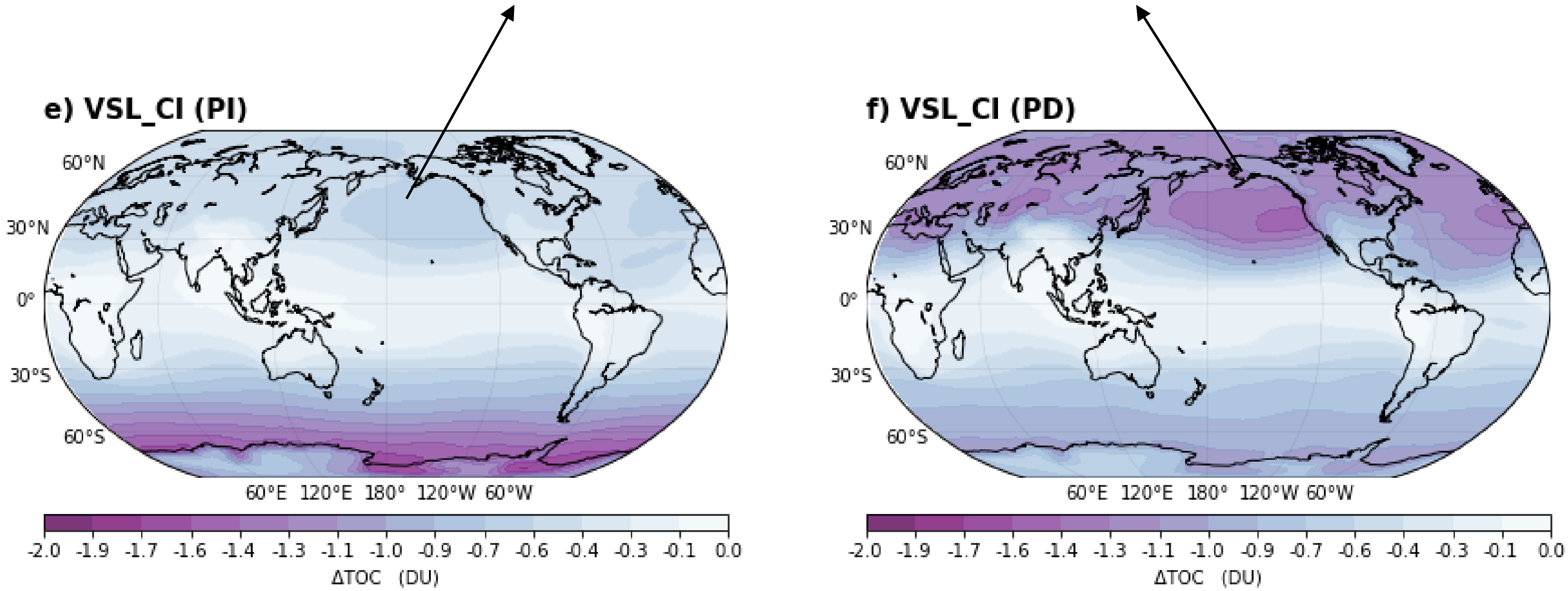


natural halogens induces a TOC reduction around Antarctica driven by SSA-dehalogenation

Unlike iodine, the impact of bromine and chlorine is reduced over these latitudes in the PI to PD transition

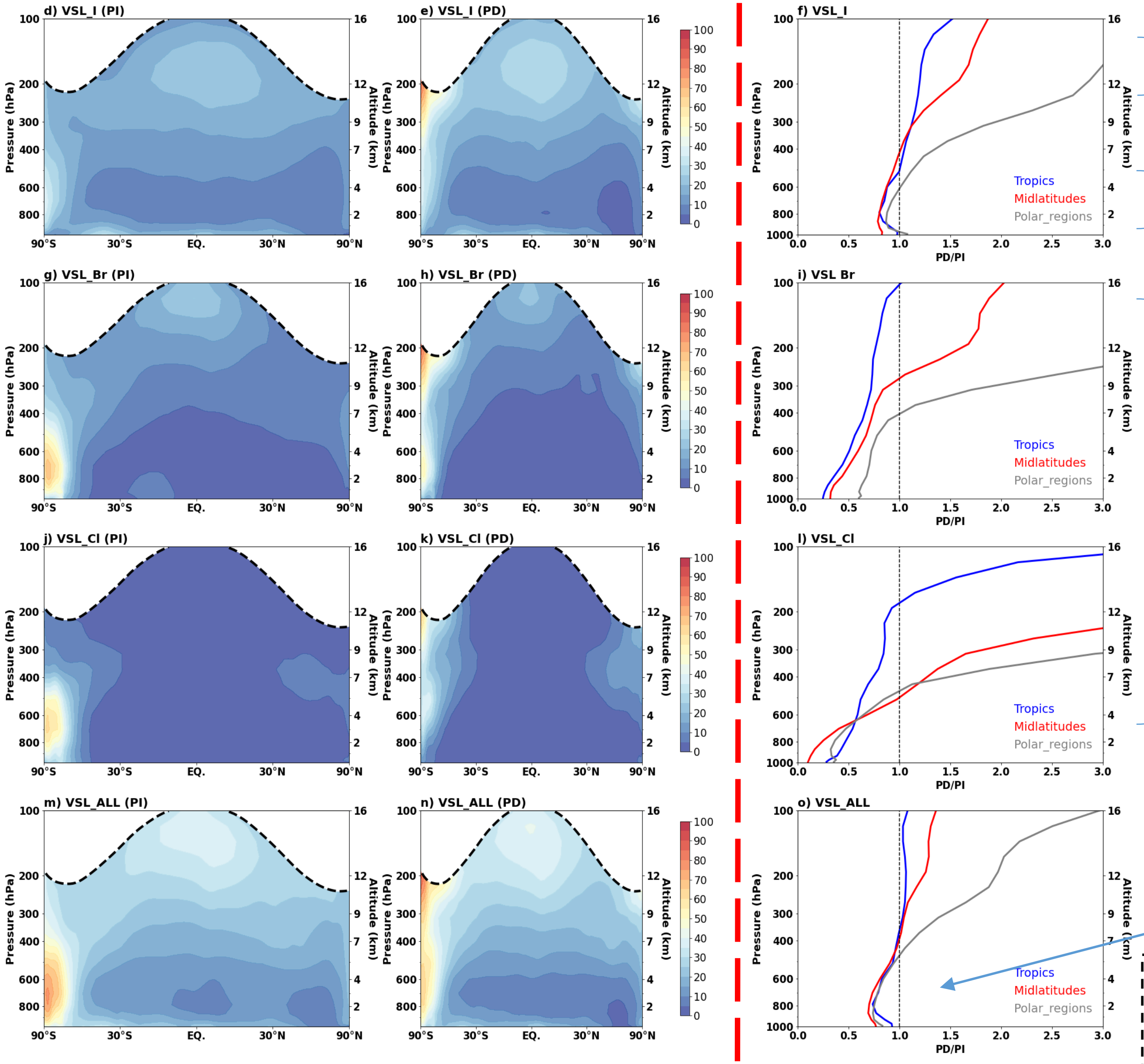
3. Changes in tropospheric ozone distribution

Chlorine induces a TOC reduction in the Northern Hemisphere due to “acid-displacement” on SSA of odd-nitrogen species (N_2O_5 and HNO_3)



Chlorine production intensifies in the transition from PI to PD

3. Changes in ozone vertical distribution

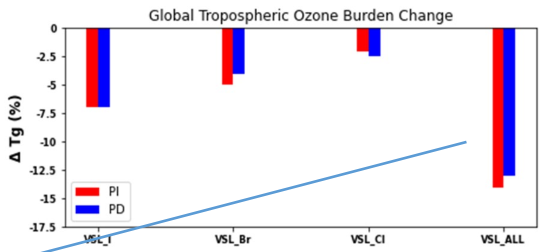


Halogen odd-oxygen loss (%) for PI (Left) and PD (center); and the PD/PI ratio (right)

mainly due the higher availability of reactive iodine in PD vs. PI

mainly due to an increased conversion of reactive iodine to HOI and $IONO_2$

bromine and chlorine play a smaller role in PD vs. PI, due to an increased conversion of reactive to reservoirs



The larger global tropospheric ozone depletion in PI vs. PD driven by natural halogens is mainly explained by their effects in the lower troposphere

Thanks you for your attention