The effect of Natural Halogens on Tropospheric Ozone Chemistry in the Pre-Industrial *vs* Present-Day

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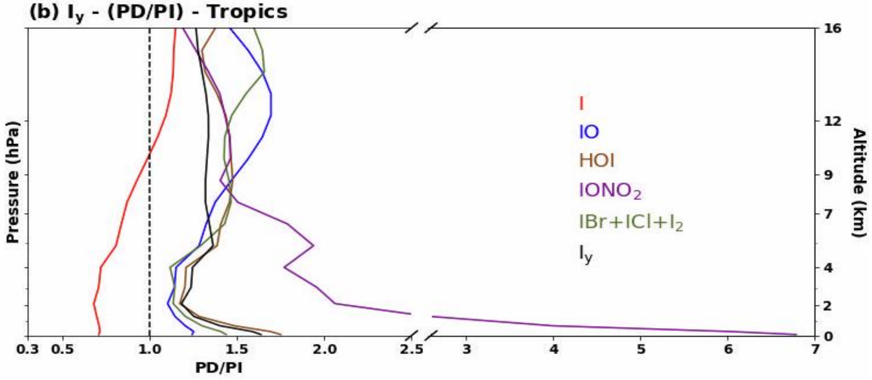
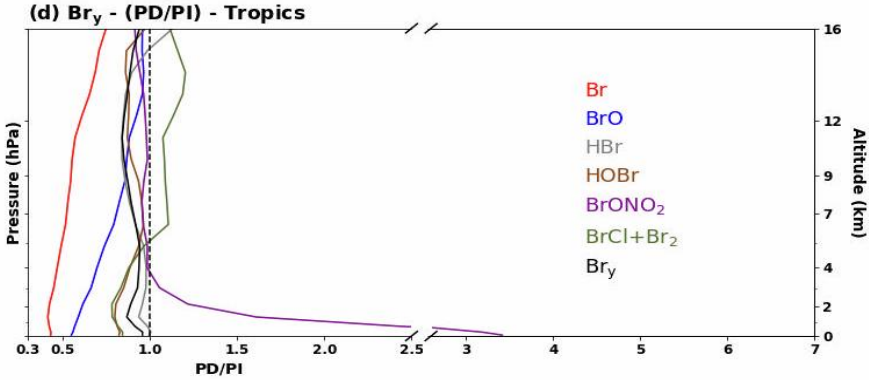
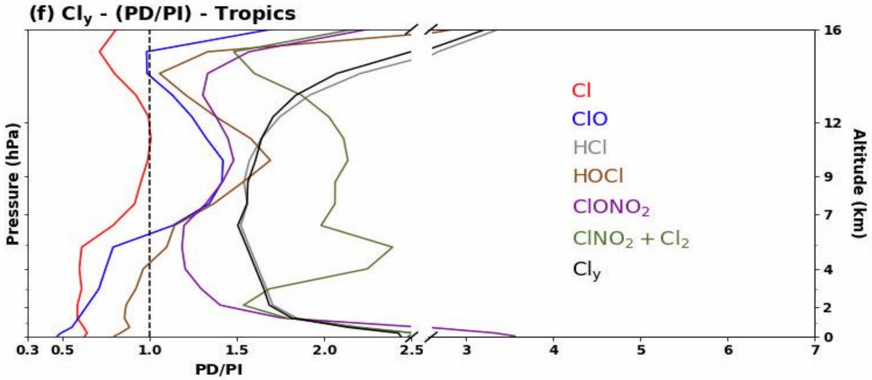
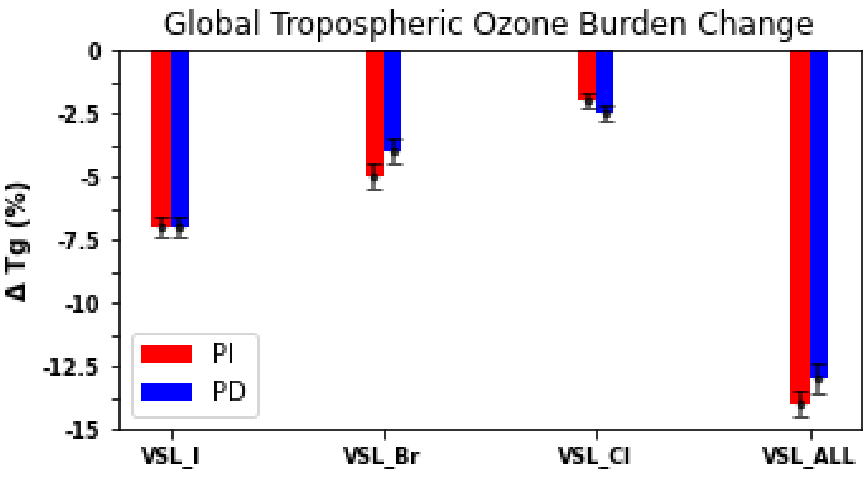


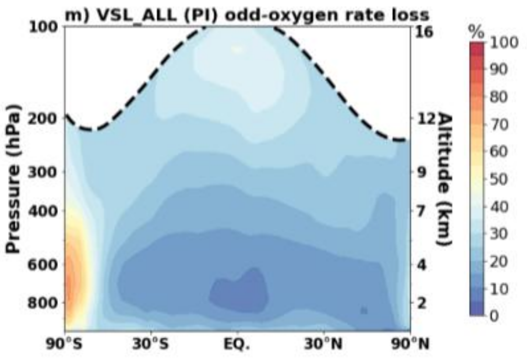


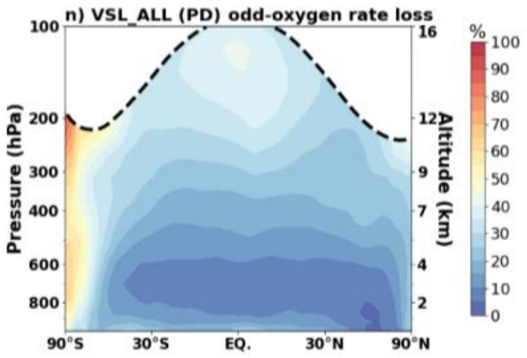


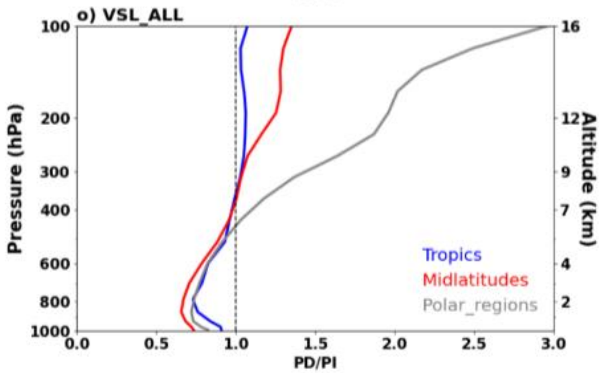
Scenarios	LL halocarbons	VSL halocarbons	I_2/HOI emission	SSA-recycling	acid-displacement
REF	YES	NO	NO	NO	NO
VSL_I	YES	YES	YES	NO	NO
VSL_Br	YES	YES	NO	YES	NO
VSL_Cl	YES	YES	NO	YES	YES
VSL_ALL	YES	YES	YES	YES	YES



- ↑ in anthropogenic ozone precursor emissions form PI to PD drives (i) ↑ natural halogen emissions (I_y) and (ii) alter the chemical partitioning
- Halogen-driven tropospheric ozone reduction is slightly higher in PI (-14 ± 0.5 %) vs. PD (-13 ± 0.5 %)
- Combined, the natural halogens maximize ozone depletion in the tropical UT and Antarctic FT
- In the lower troposphere, ozone reduction is PI > PD, while in the upper troposphere it is PD > PI.







The effect of Natural Halogens on Tropospheric Ozone Chemistry in the Pre-Industrial *vs* Present-Day

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1. Study objectives

- assessing the change in the partitioning of tropospheric inorganic halogens (I_y, Br_y and Cl_y) between reactive and reservoir species in PI and PD.
- Quantify the impact of individual iodine, bromine and chlorine chemistry, as well as a complete natural halogens scheme, on the tropospheric O_3 budget.
- Examine in detail the contribution of natural halogens to odd-oxygen chemical loss, discriminating the contribution of each of the odd-oxygen depleting chemical families (e.g. O_x, HO_x, NO_x, and Halogens)

2. CAM-Chem simulation design

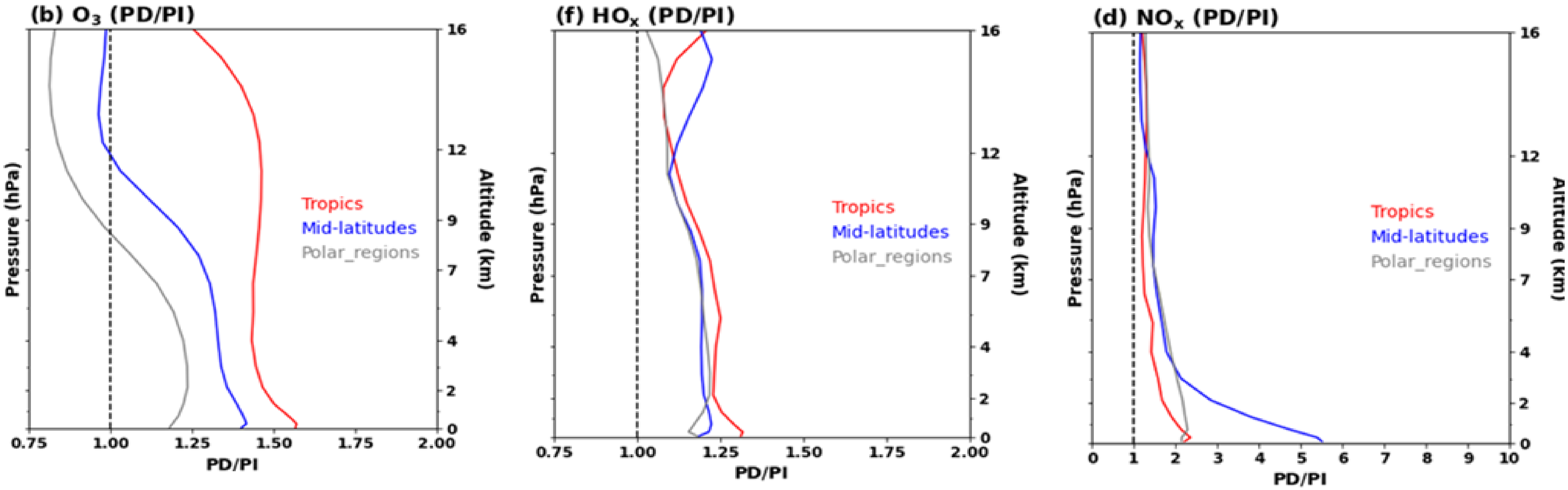
Table 1. Model scenarios for Pre-industrial (PI) and Present-day (PD) simulations.

Scenarios	Long-lived halocarbons LBC	VSL halocarbons emissions	I_2/HOI emissions	SSA-recycling emissions	acid-displacement emissions
REF	YES	NO	NO	NO	NO
VSL_I	YES	YES	YES	NO	NO
VSL_Br	YES	YES	NO	YES	NO
VSL_Cl	YES	YES	NO	YES	YES
VSL_ALL	YES	YES	YES	YES	YES

1. Specified dynamic simulation
2. Imposed sea surface temperature (SST) and representative of each period
3. Emissions:

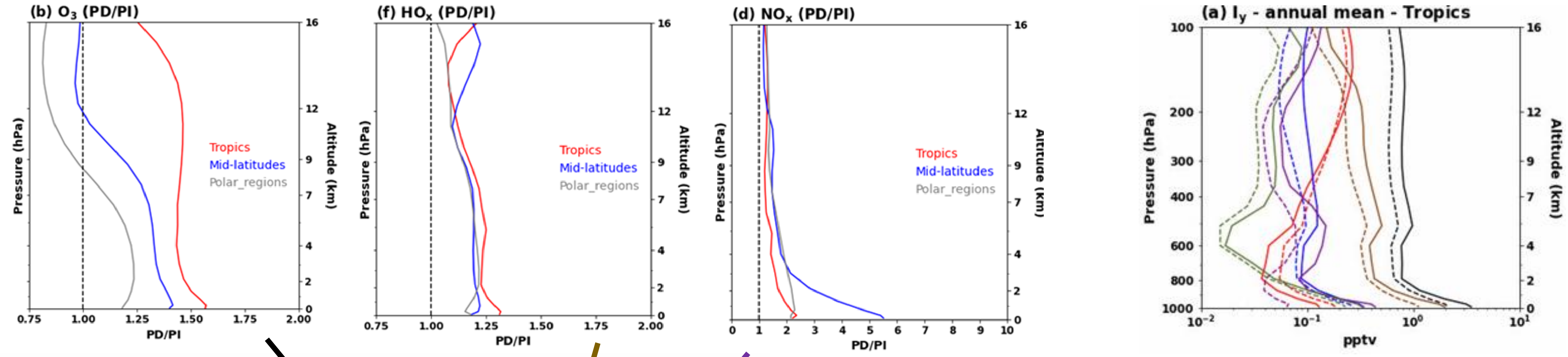
- Long-lived halocarbons are based on the A1 halogen scenario (WMO 2011) for PD and zeroed for PI
- Very short-lived (VSL) halocarbons is based on the Ordoñez et al., (2012) emissions inventory
- Oceanic emission of inorganic iodine (HOI/I_2) depends on near-surface O_3, wind speed and SST (Prados-Roman et al., 2015)
- The SSA-heterogeneous recycling of inorganic halogen is a tropospheric net source of Br and Cl (Fernandez et al., 2014)
- The acid-displacement heterogeneous reactions of odd-nitrogen is a tropospheric net source of Cl (Li et al., 2022)
- Greenhouse gas and non-halogenated species on based IPCC (2019) and Meinshausen et al. (2011)

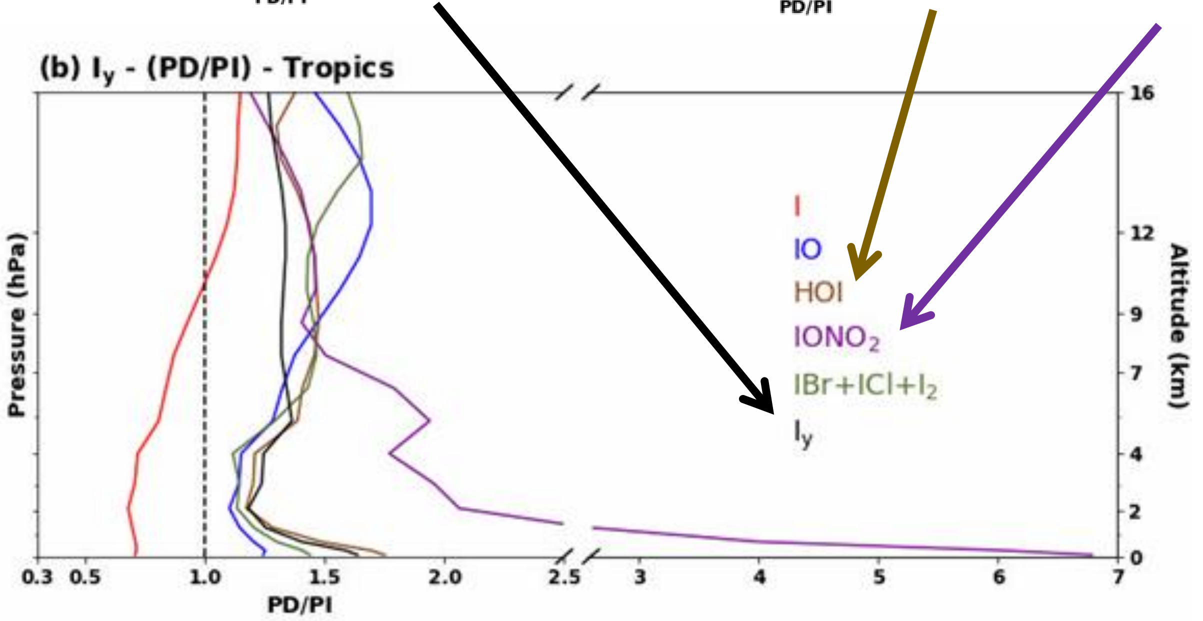
3. Result: background changes between PI and PD



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 + $IONO_2$ …**

<u>Change PI to PD:</u>

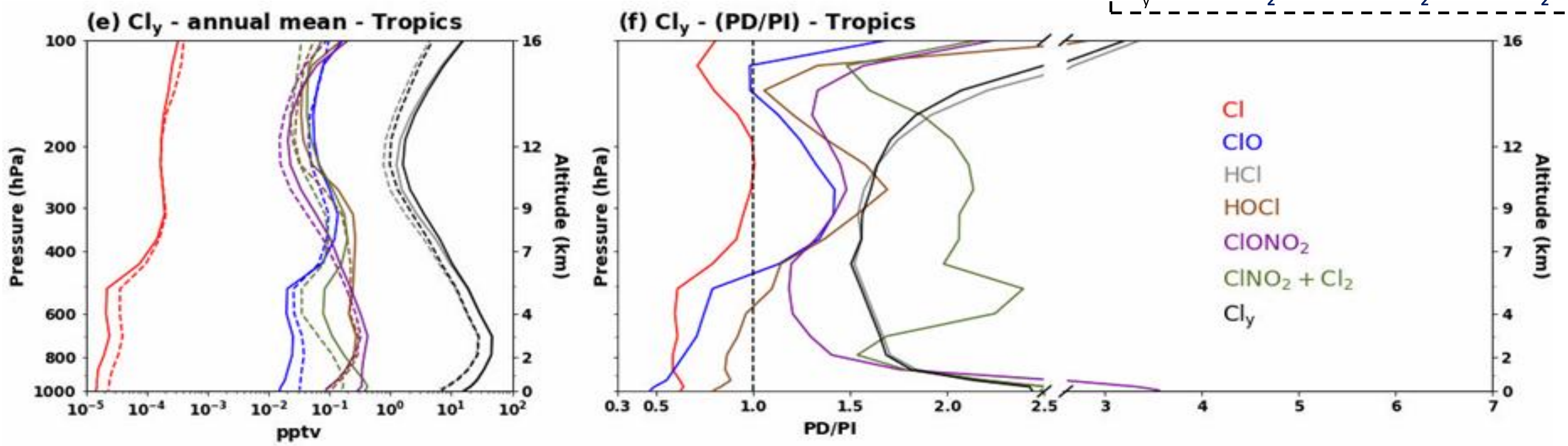
1. increase in I_y driven by O_3 and SST changes (ozone-iodine feedback mechanism)

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

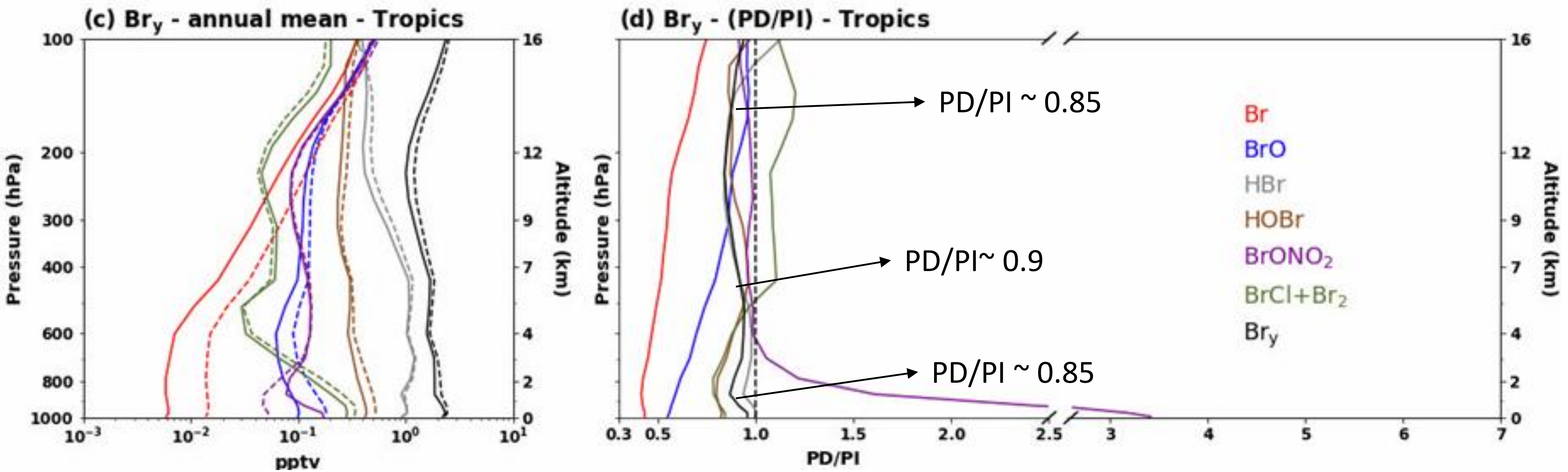
reactive reservoirs
Cl_y= $Cl+ClO+Cl_2+HOCl+ClONO_2+HCl+ClNO_2$ …



- 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

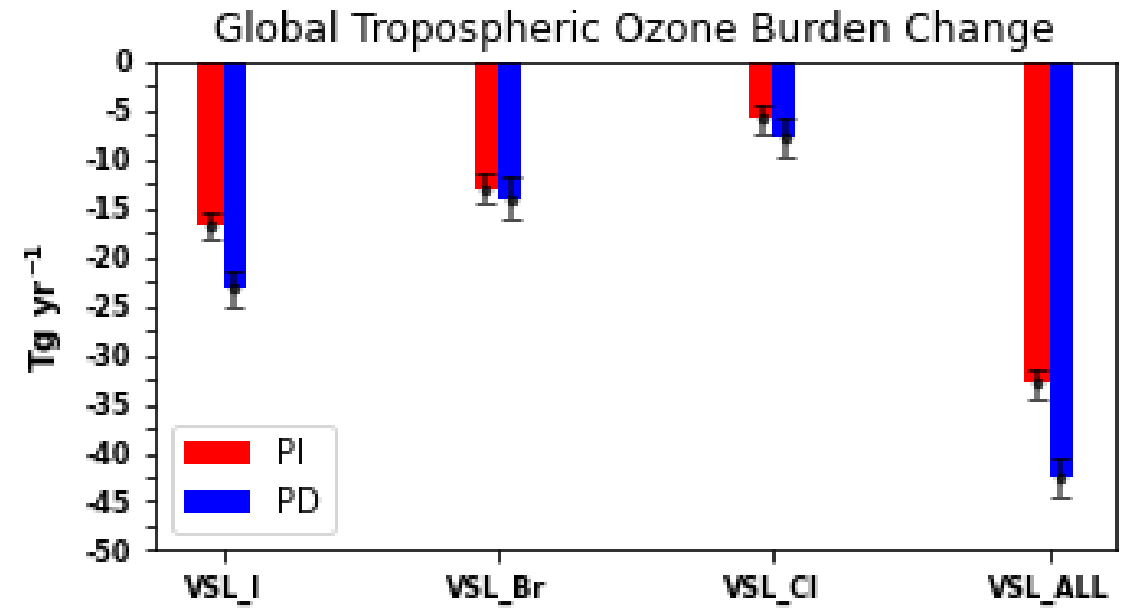
reactive reservoirs
Br_y=**Br+BrO**+BrCl+IBr+**HOBr+Br_2+$BrONO_2$+HBr…**

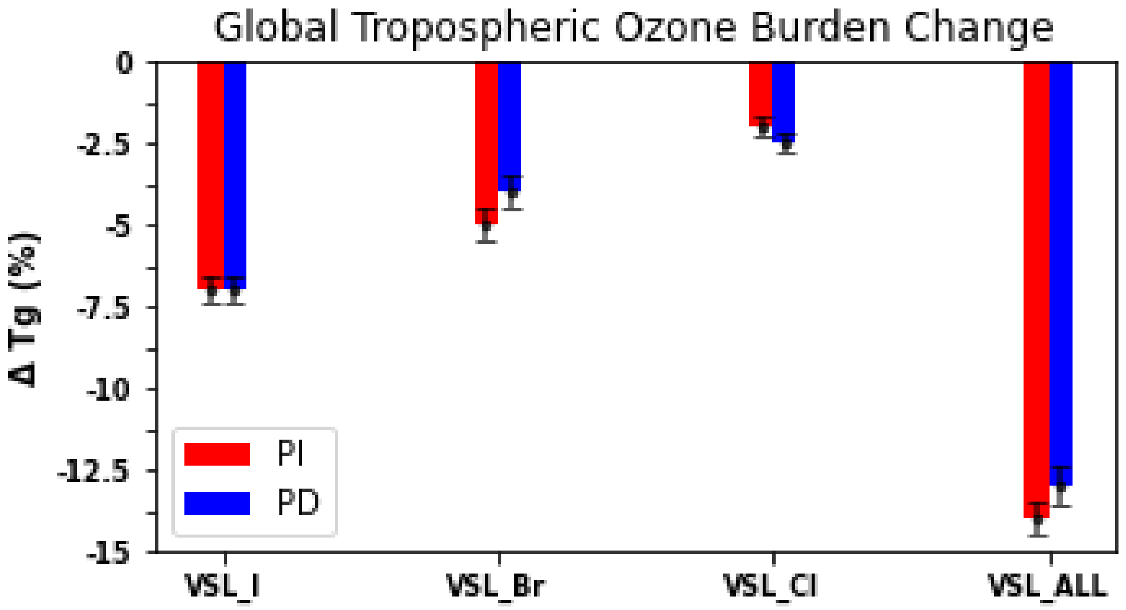


Tropospheric Br_y is slightly reduced in the transition PI to PD:

- 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

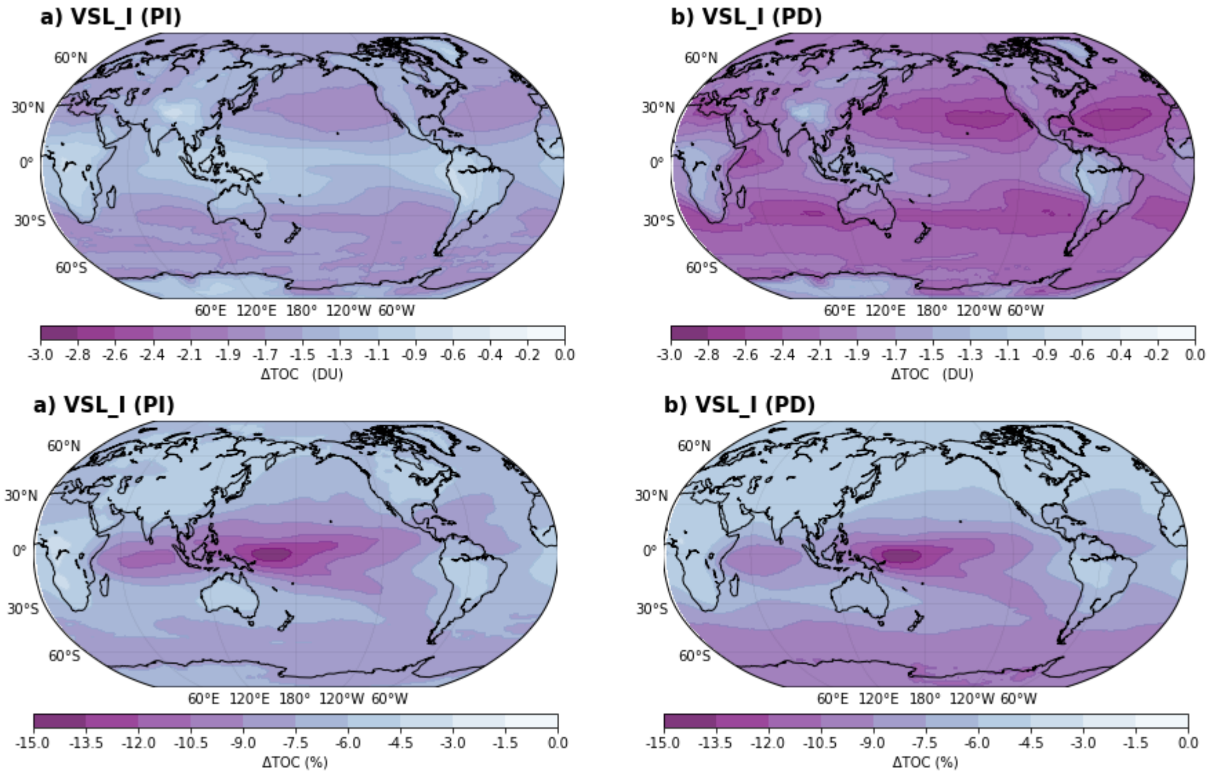




- In percentage terms, halogens induce a larger ozone depletion in PI (−14 ± 0.5 %) than PD (−13 ± 0.5 %)
- This effect is mainly governed by iodine and then bromine
- Individually:
- iodine has a role equal in both periods (−7 %)
- bromine has a larger role in PI (−5 ± 0.4 %) vs. PD (−4 ± 0.4 %)
- Chlorine has a larger role in PD (−2.5 ± 0.4 %) vs. (PI: −2 ± 0.4 %)

3. Changes in tropospheric ozone distribution

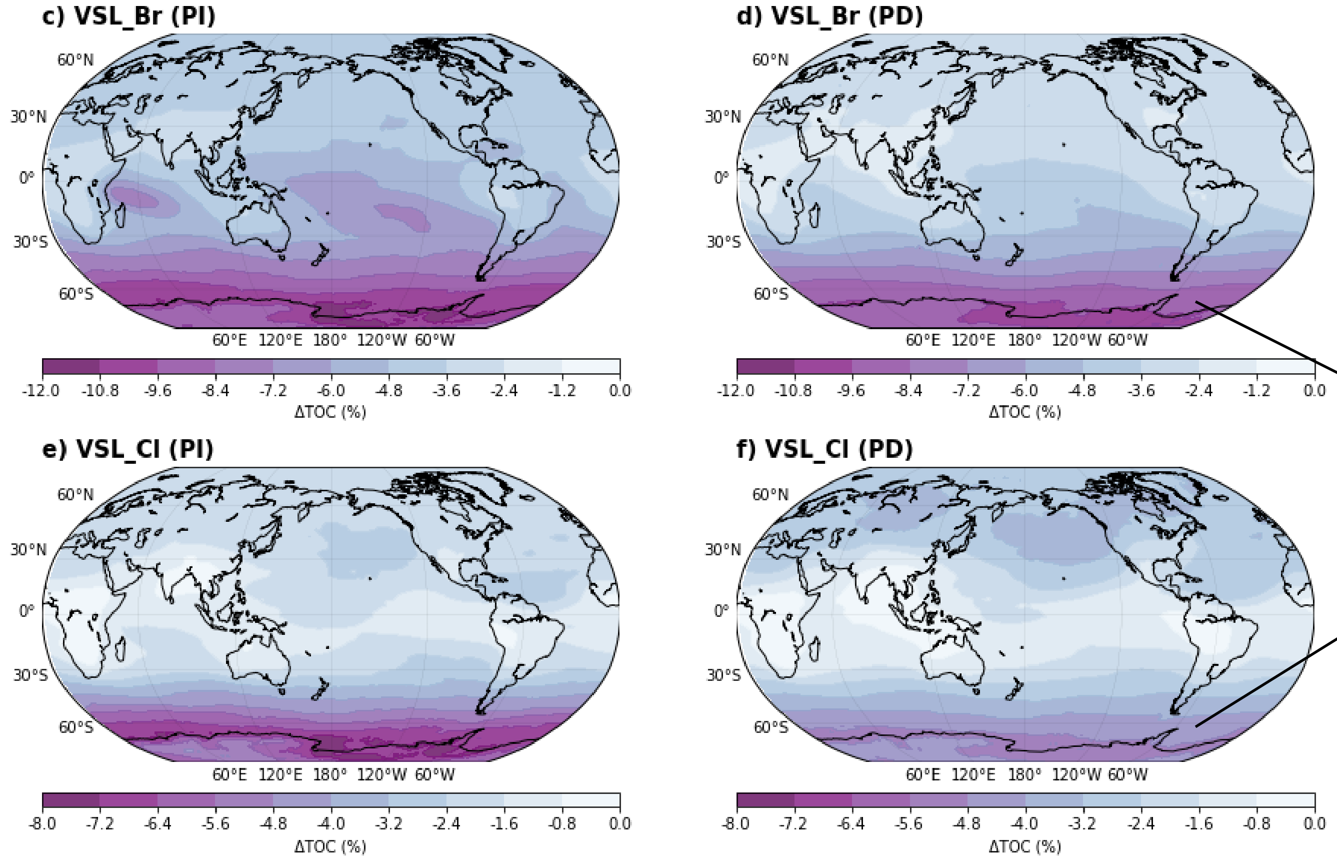
iodine induces TOC reduction mainly over marine environments



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

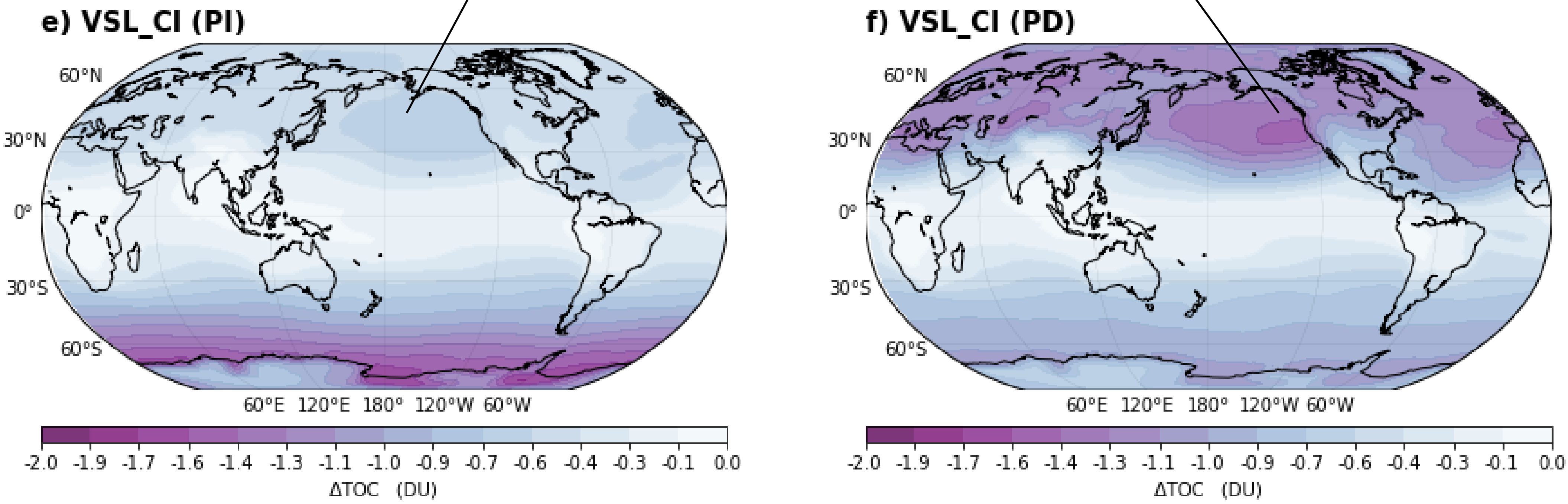


natural halogens induces a TOC reduction around Antarctica driven by SSA-dehalogenation

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

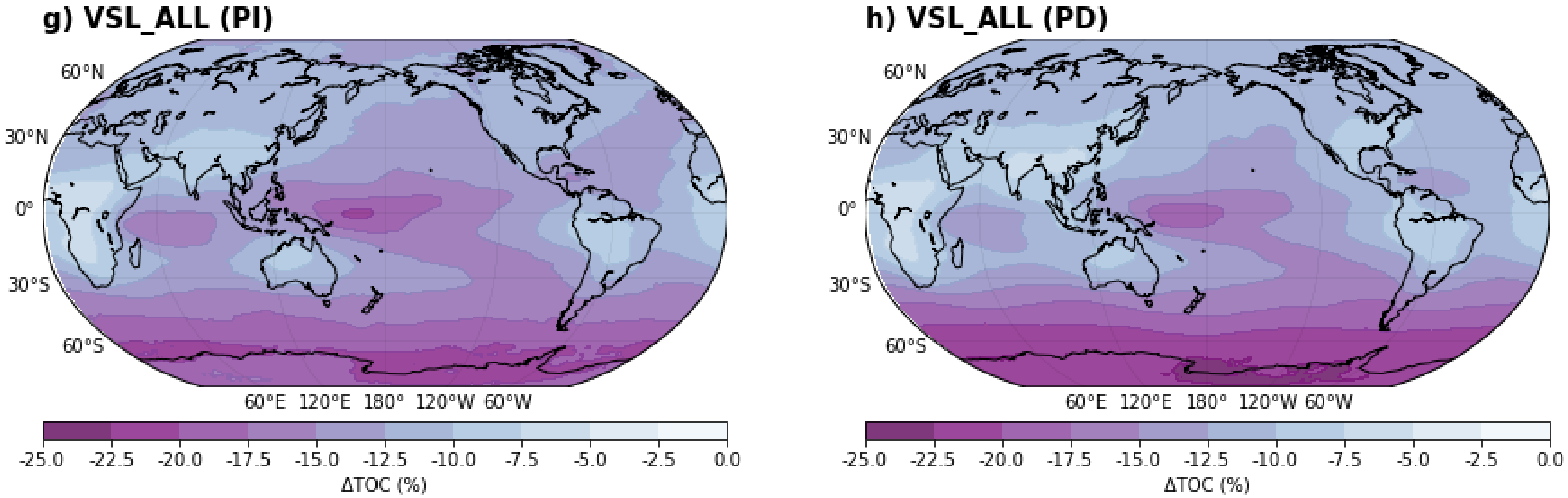
Chlorine induces a TOC reduction in the Northern Hemisphere due to "acid-displacement" on SSA of odd-nitrogen species (N_2O_5 and HNO_3)



Chlorine production intensifies in the transition from PI to PD

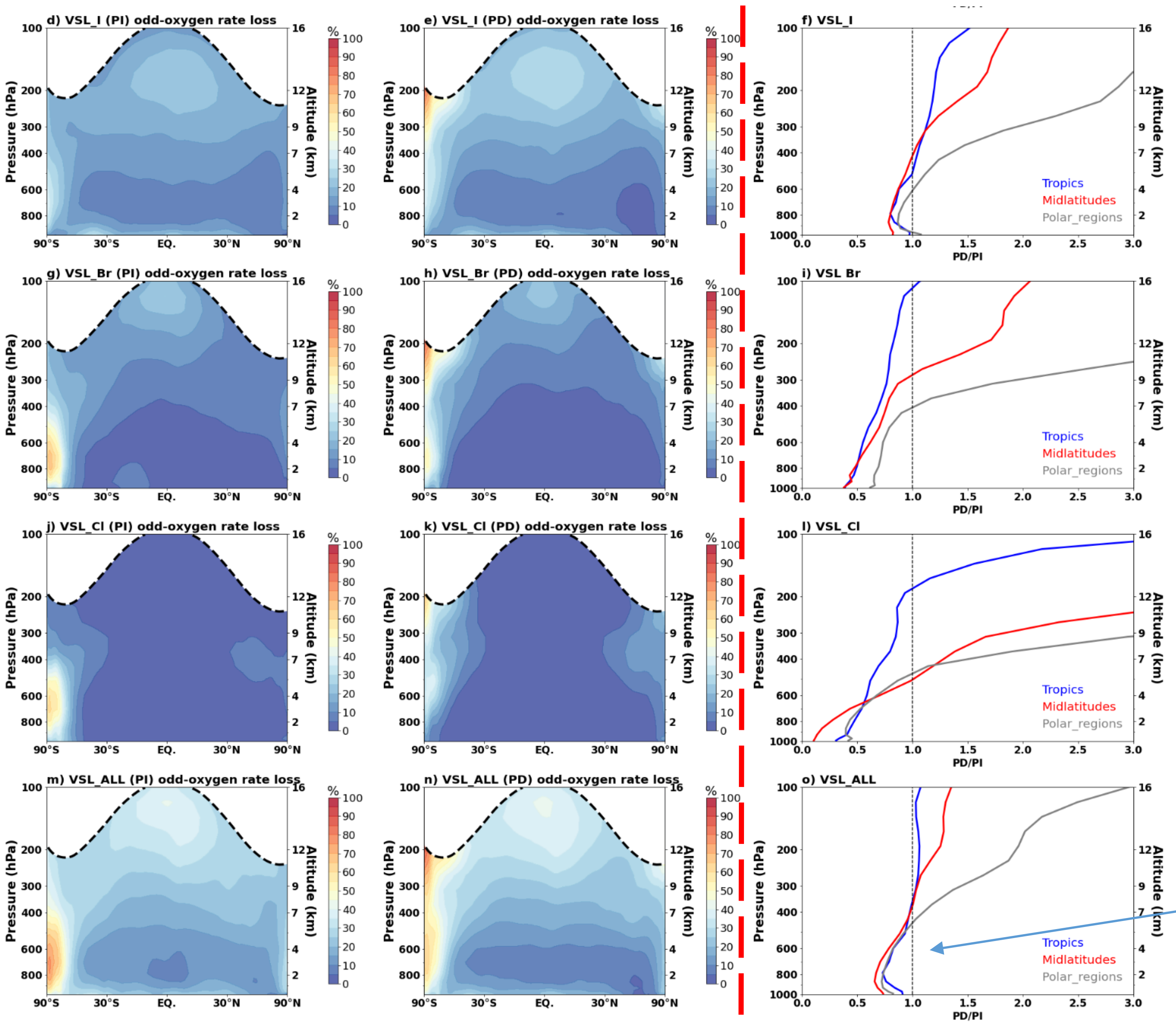
3. Changes in tropospheric ozone distribution

For the VSL_ALL scenario, the tropical TOC reduction over the oceans is governed by iodine, while chlorine and bromine play a major role in the mid-high latitudes



TOC reduction driven by natural halogen decreases from PI to PD, except over the Southern mid-high latitudes

3. Changes in ozone vertical distribution

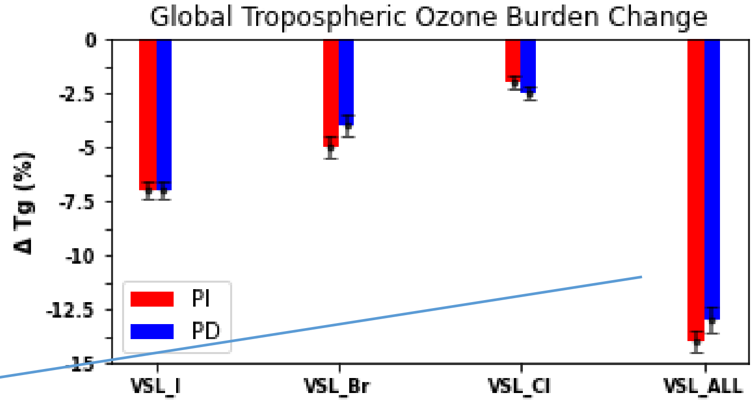


Odd-oxygen loss (%) by halogens for PI (Left) and PD (center); and the PD/PI ratio (right)

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

4. Conclusion

- Our analysis shows that increasing surface emissions of the main anthropogenic ozone precursors (e.g. NOx, CO, CH_4 and NMVOC) increase natural emissions of halogens and alter the chemical partitioning between reactive and reservoir species, which directly affects their behavior on tropospheric ozone depletion.
- The tropospheric ozone reduction is more sensitive to natural halogens in PI than PD, with percentage changes in TOB of -14 ± 0.5 % for PI and -13 ± 0.5 % for PD.
- The iodine role in TOB reduction is equivalent in both periods (−7%), with an impact on ozone in marine environment.
- Bromine plays a larger role in the PI (−5 ± 0.4 %) vs. PD (−4 ± 0.4 %), with a larger impact on Antarctic ozone.
- Chlorine plays a minor role, with a larger impact on ozone in polluted environments (PD: −2.5 ± 0.4 % vs. PI: −2 ± 0.4 %).
- Combined, the natural halogens maximize ozone depletion in the tropical UT and Antarctic FT.
- The halogen-driven ozone depletion from surface to FT decreases in the transition from PI to PD

Thanks for your attention