Description of Short-Lived Halogen (SLH) chemistry in CESM2: Interconnection between Natural and Anthropogenic Sources

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Outline

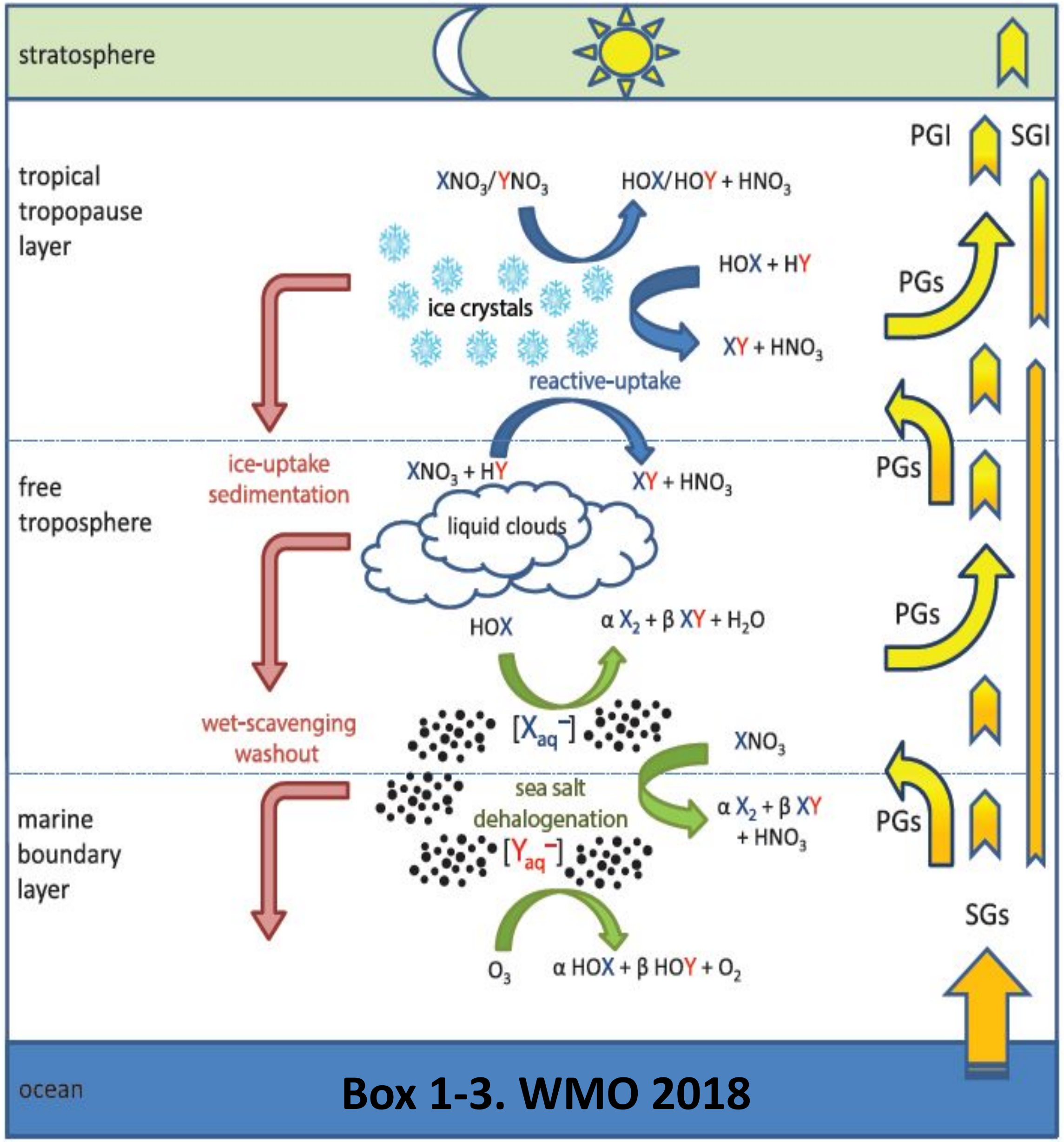
1. **Description of the dominant reactive transport pathways of SLH in CAM-Chem**
   - ***Similarities and differences between Chlorine, Bromine and Iodine burdens***
   - ***Dominant halogen atom (Cl, Br and I) sources in the troposphere and stratosphere***
   - ***Chemical partitioning of reactive and reservoir halogen species***
   - ***Inter-comparison between inorganic halogen distributions between CESM1 and CESM2***

2. **CAM-Chem sensitivity to dynamical configurations in CESM2**
   - ***Evaluation of nudging (NDG), Specified Dynamics (SD) and Free Running (FR) setups***
   - ***Dependence on spatial (f19 vs f09) and vertical (L32 vs L56) resolution***

3. **Influence of SLH over the oxidative capacity of the troposphere**
   - ***Importance of including SLH in climate evolution studies (next talk by A. Saiz-Lopez)***

Low-Resolution CAM-Chem: f19 (2°x2.5°) and 32L (40 km top)

Reactive transport of SLH-VSL: Sources and Sinks



Long-Lived ODS (stratosphere):

$CFC\text{-}12 + h\nu / O^1D \rightarrow 2\,Cl$

$CF_3Br + h\nu / O^1D \rightarrow 2\,Br$

$CH_3Cl + OH \rightarrow Cl + CH_3O_2$ — τ = 0.9 yr

$CH_3Br + OH \rightarrow Br + H_2O + HO_2$ — τ = 0.8 yr

VSL Halogens (Natural + Anthro):

$CH_2Cl_2 + h\nu \rightarrow 2\,Cl$

$CH_2Cl_2 + OH \rightarrow CHCl_2O_2 \rightarrow COCl_2 \rightarrow 2\,Cl$

$CH_2Br_2 + OH/Cl \rightarrow 2\,Br + H_2O/HCl$

$CHBr_3 + OH/Cl \rightarrow 3\,Br + H_2O/HCl$

τ < 0.5 yr

Inorganic Halogens Washout (NEU + FRA):

gas_wetdep_list: HCl,HBr,HOBr, $BrONO_2$, ~~HOI~~, $IONO_2$

Gas_wetdep_ice-uptake_list: HCl, ~~$BrONO_2$~~,~~$IONO_2$~~

$BrONO_2 \rightarrow$

$HOI / IONO_2 \rightarrow$

non-stoich. sink

SSA-dehalogenation (on-line computation)

$BrONO_2 + SSA \rightarrow Br_2 + BrCl \rightarrow Cl + 2\,Br$

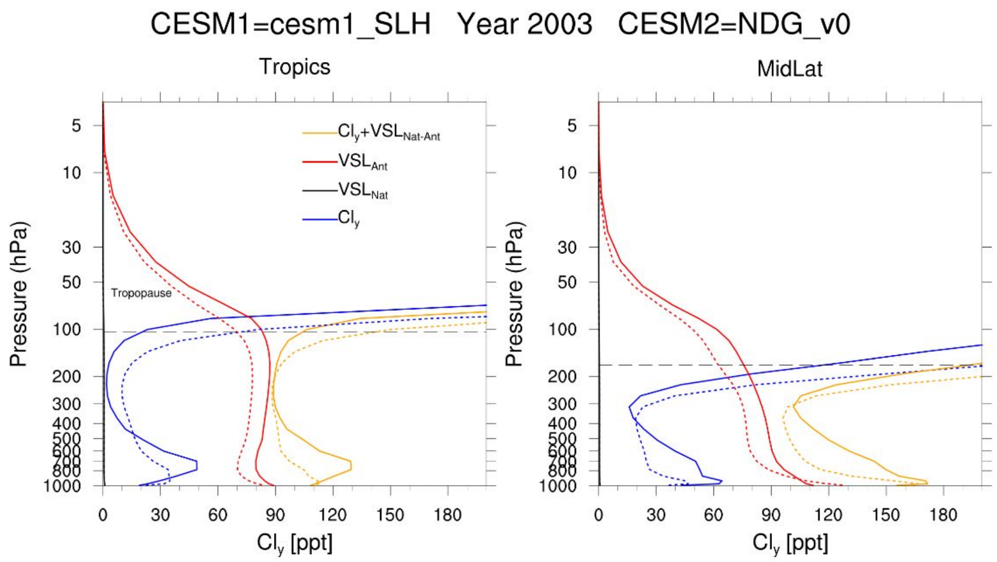
$HOCl + SSA \rightarrow Cl_2 \rightarrow 2\,Cl$

$HNO_3 + SSA \rightarrow HCl \rightarrow Cl$

$N_2O_5 + SSA \rightarrow ClNO_2 + HNO_3 \rightarrow Cl$

non-stoich. sources

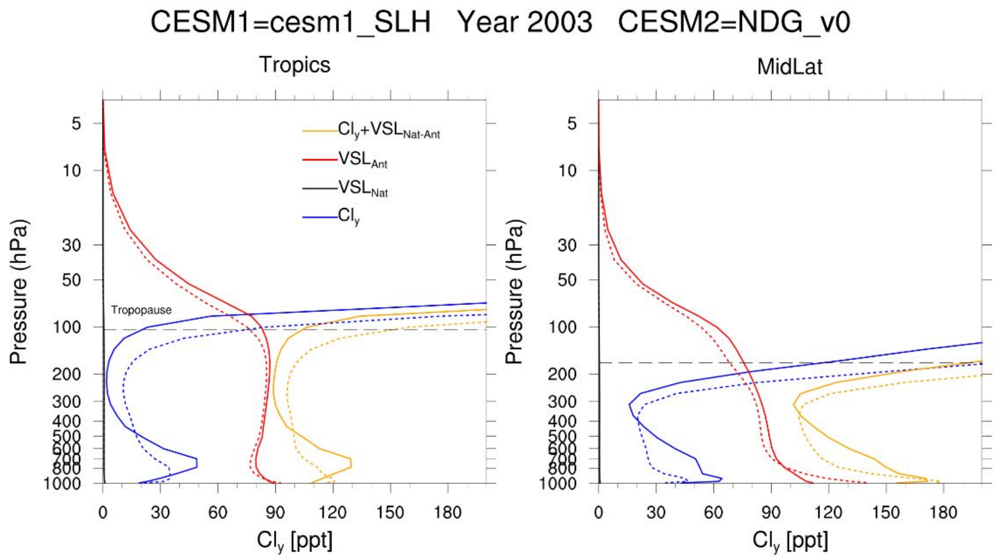
CESM1 vs CESM2: Chlorine



- **Halogen distributions in the MBL and FT are equivalent**
  - **Natural VSL^{Cl} are negligible compared to Antrho VSL^{Cl}**
  - **Emissions/LBCs for VSL^{Cl} must be increased by 15% in CESM2**
  - **Anthro VSL^{Cl} and Cl_y present a pronounced hemispheric asymmetry**

VSL^{Cl} x 1.15

Comparison with ATom Observations
(Behrooz Roozitalab)
CESM1



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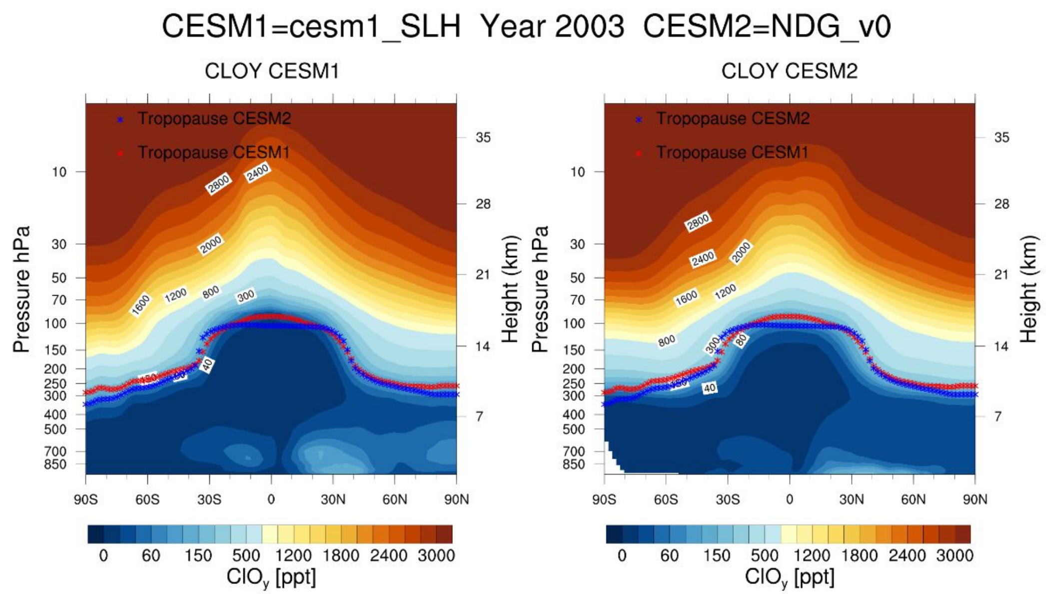
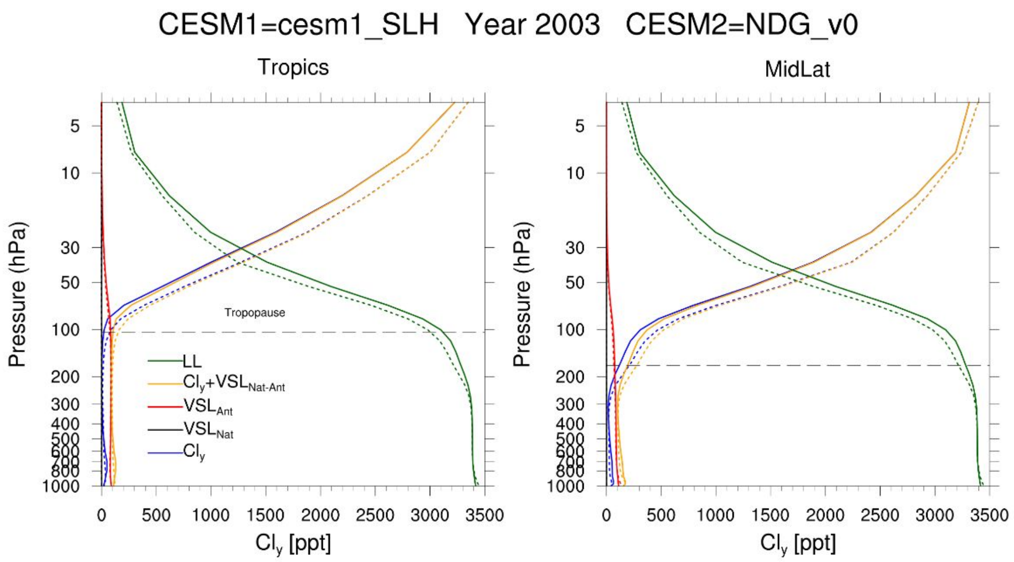
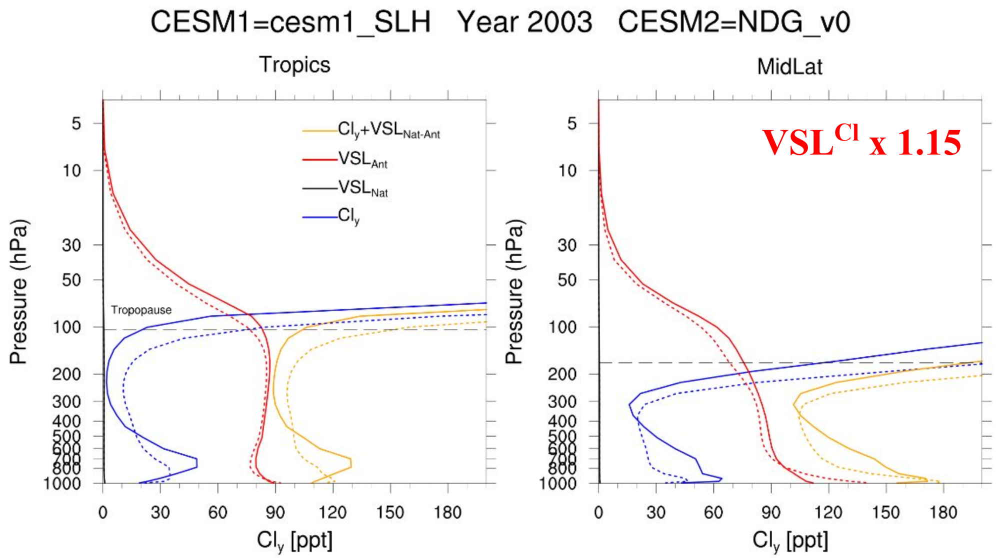




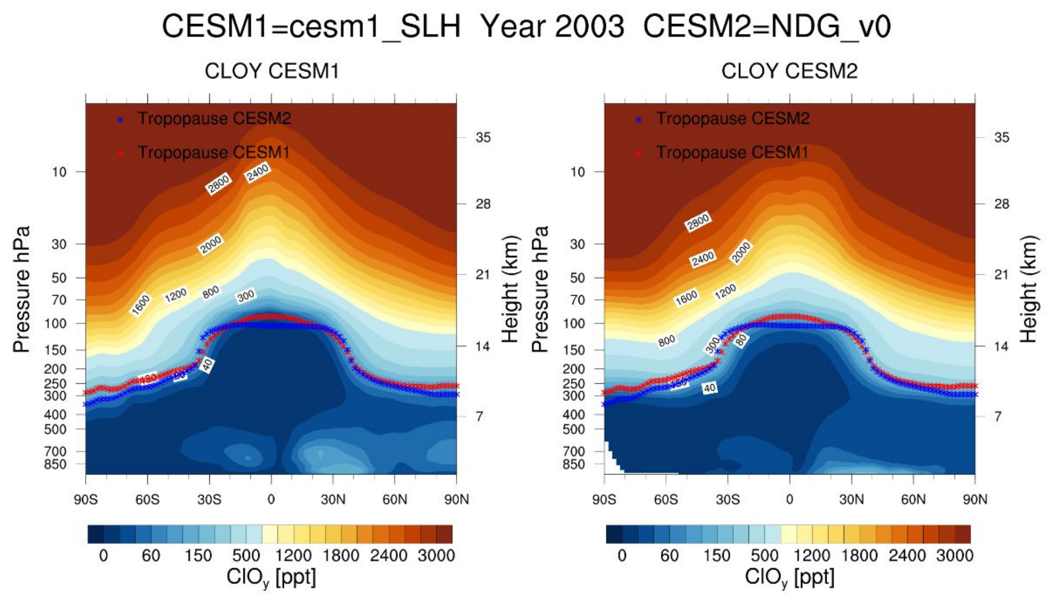


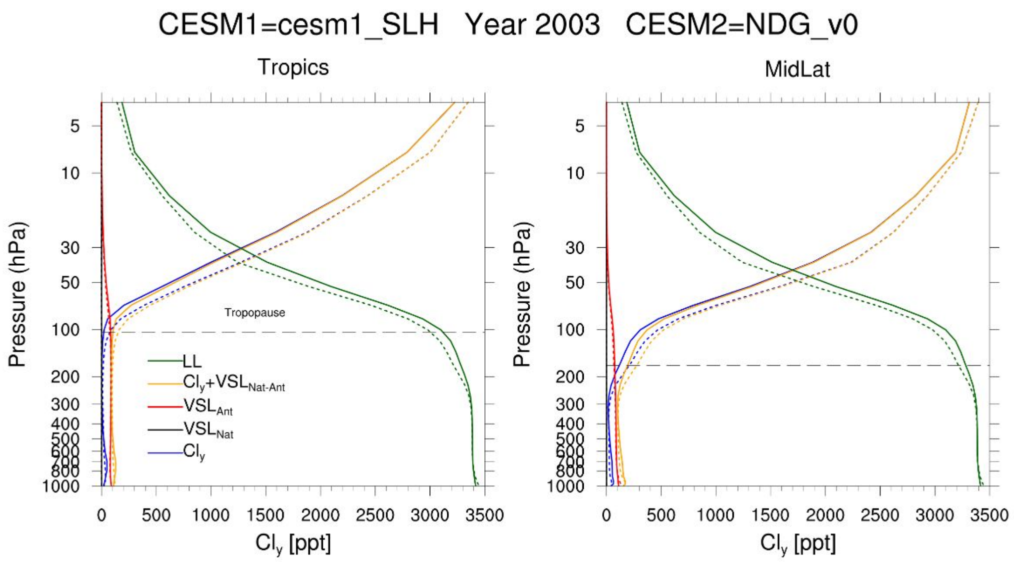
- **Stratospheric chlorine remains equivalent between model versions**
  - **Top of model Cl_y increases by 2.5-3.0 % due to higher PGI in CESM2**
- **CESM1 shows larger Cl_y in the LT, while CESM2 shows larger Cl_y in the UT**
  - **PGI is aprox. 2 times larger in CESM2**
  - **Minimum Cl_y values are observed in the TTL**

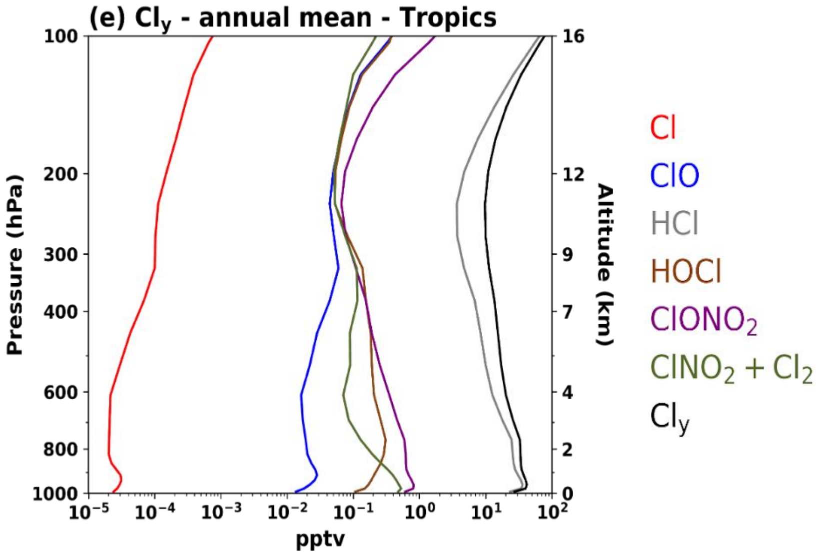
VSLS Best Estimate (ppt)	SGI[1]	PGI[2]	Total (SGI + PGI)[3]
Chlorine	105 (85–125)	25 (13–50)	130 (100–160)
Bromine	2.1 (0.5–4.4)	2.8 (1.8–4.2)	5 (3–7)
Iodine	0–0.1	0.3–0.8	0.3–0.9

Table 1-6. WMO 2022

CESM1 vs CESM2: Chlorine







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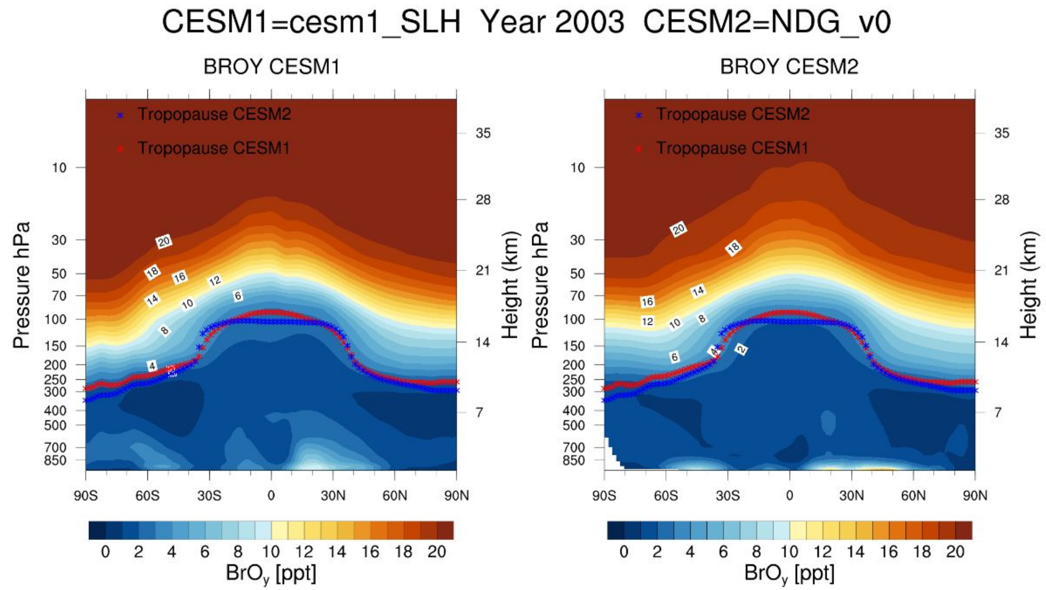
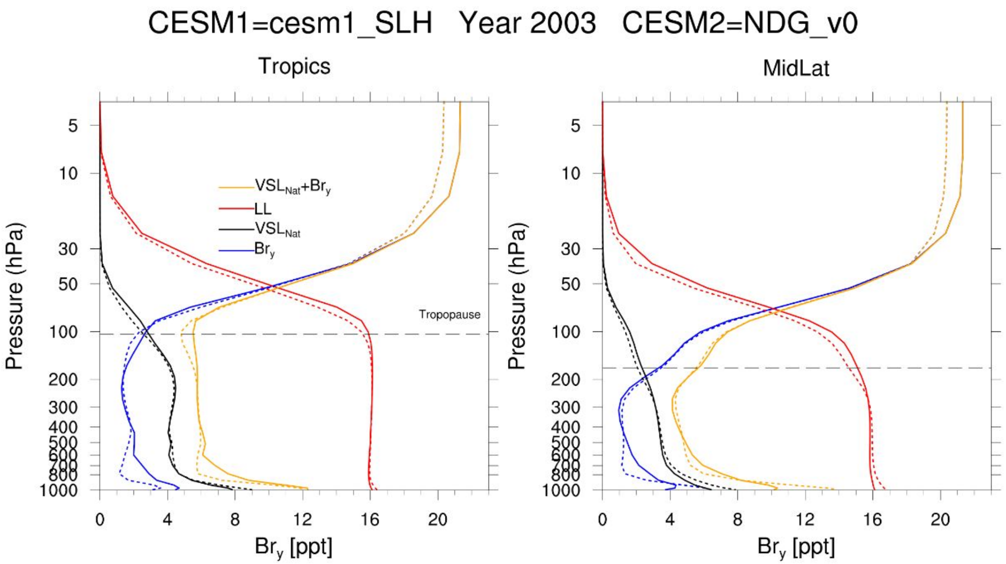
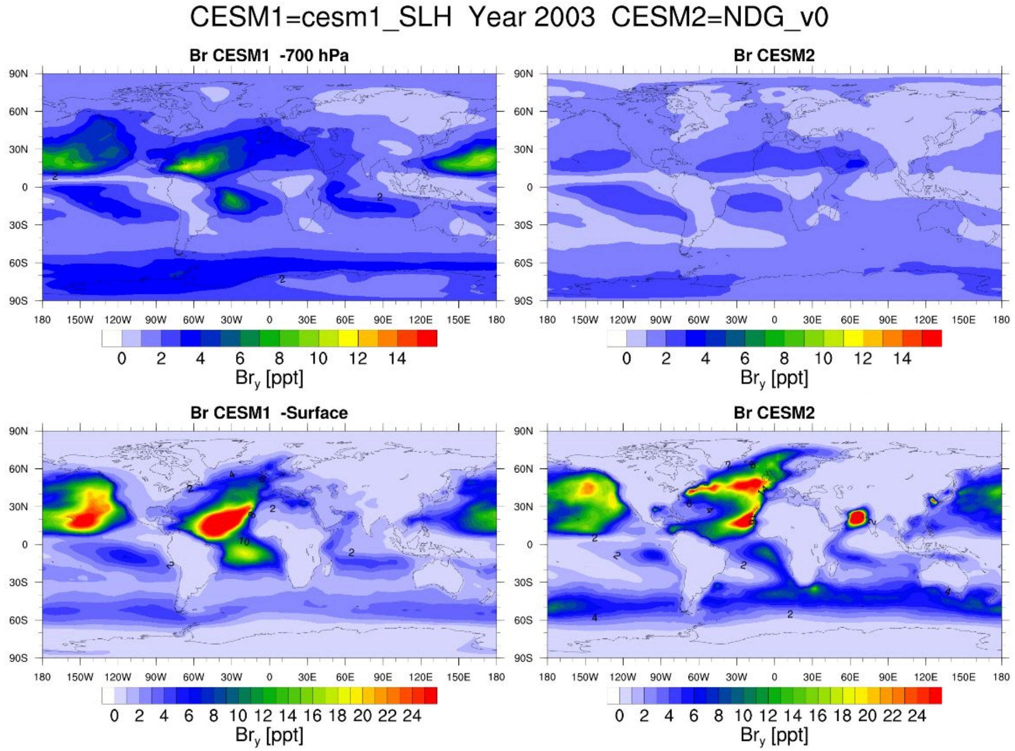
  - **PGI is aprox. 2 times larger in CESM2**
  - **Minimum Cl_y values are observed in the TTL**
- **HCl dominates Cl_y partitioning in the UT and controls washout and PGI.**
  - **Reactive chlorine (Cl, ClO) are minor species**
  - **smaller impacts w.r.t. Br/I**

CESM1 vs CESM2: Bromine



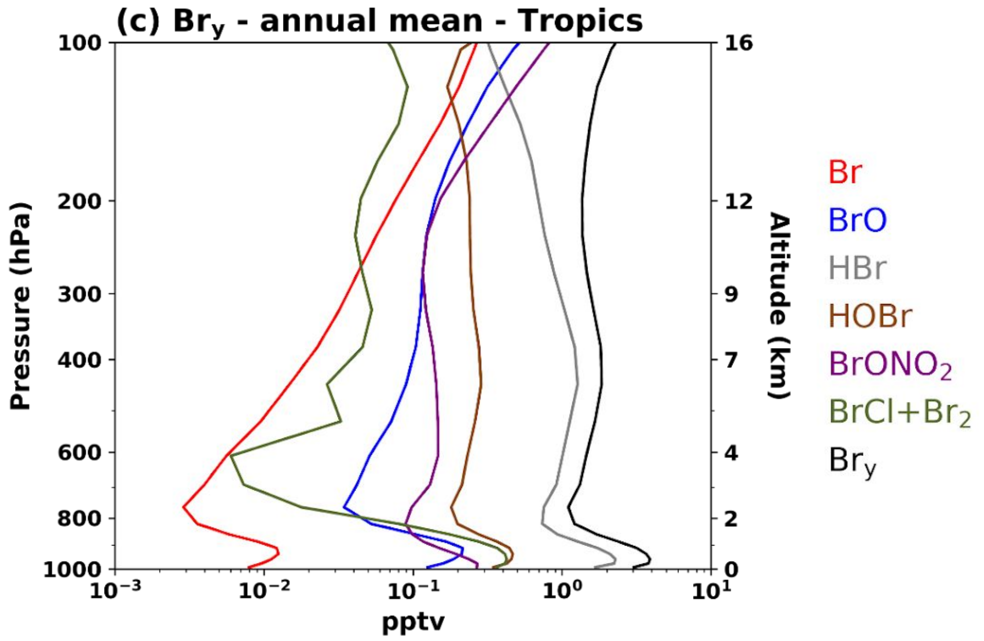


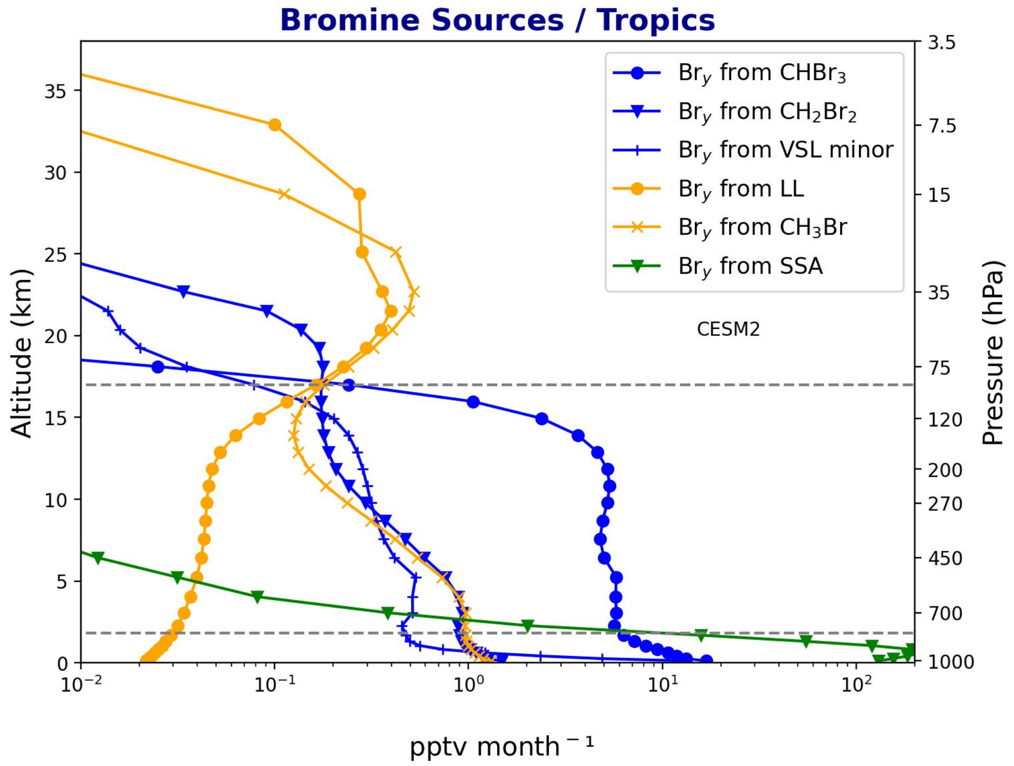
VSL^{Cl} x 1.15



- **Zonal distribution of VSL and Br$_y$ depend on SSA distributions**
  - **Bromine-VSL emissions must be increased by 15% to reproduce VP**
- **CESM2 results in a less efficient transport from the MBL to the FT**
  - **Br$_y$ hotspots are observed in the NH surface (SSA-dehalogenation)**
  - **At 700 hPa CESM2 does not show hemispheric asymmetry**
  - **LT Br$_y$ is lower in CESM2 on the global mean**
- **Total Br$_y$ at the top of the model is aprox. 1 pptv smaller in CESM2**

Bromine in CESM2: Sources and Partitioning



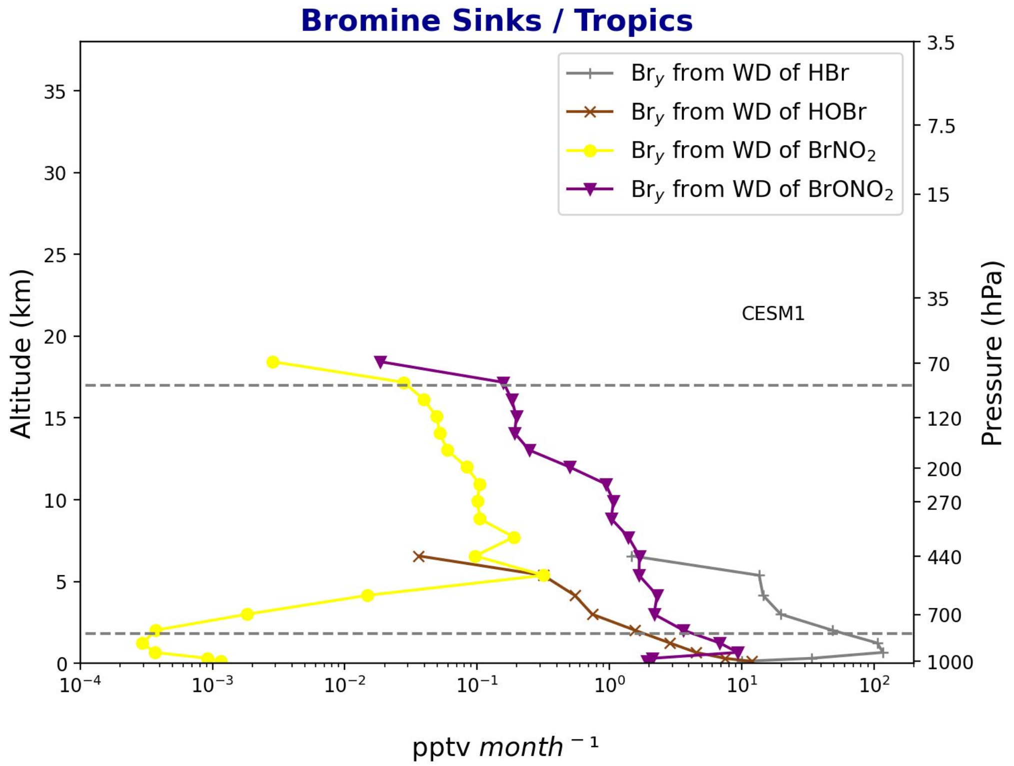


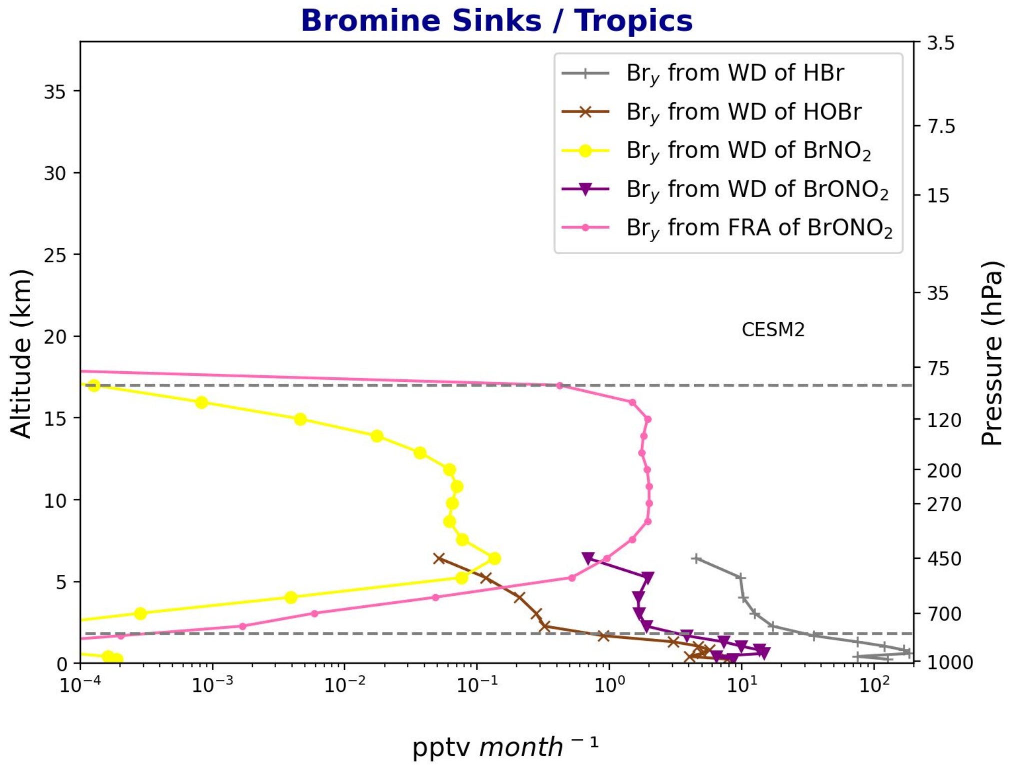
- HBr and HOBr are the dominant Br_y species.
  - Reactive bromine (Br, BrO) is important in the UT
  - □ larger ozone impact in the LMS compared to Cl
- SSA-dehalogenation is the dominant source in the MBL (84%)
- Oceanic VSL^{Br} represent ~90% of the Br atoms source in the FT
  - No anthropogenic VSL^{Br} sources are considered.
- CH_3Br (LL) contribute more to FT Br_y and PGI than CH_2Br_2 and minor VSL

GLOBAL (90°N-90°S)	Bromine Sources (Gg/yr)							
	Natural VSL			Long Lived (LL)		SSA	Total Br	Perc
	$CHBr_3$	CH_2Br_2	Minor VSL	CH_3Br	Halons	Br_y		
Photolysis	379	0.34	43.3	0.14	4.02	0	426.8	**8.7**
OH + O¹D	199	68.6	21.1	73.5	0	0	362.2	**7.3**
Cl	0.17	0.19	0	0.83	0	0	1.19	**0**
SSA	0	0	0	0	0	4139	4139	**84**
Total Br	578.17	69.13	64.4	74.47	4.02	4139	4929.19	**100**
Percentage	**11.7**	**1.4**	**1.3**	**1.5**	**0.1**	**84**		
Percentage	**73.2**	**8.7**	**8.2**	**9.4**	**0.5**	**--**		

90%

Bromine in CESM2: Sinks





- **Bromine washout based on NEU scheme is less efficient in CESM2 and results in a significantly larger PGI**
  - **We applied the FRA for $BrONO_2$ following original implementation for $IONO_2$ in CESM1**

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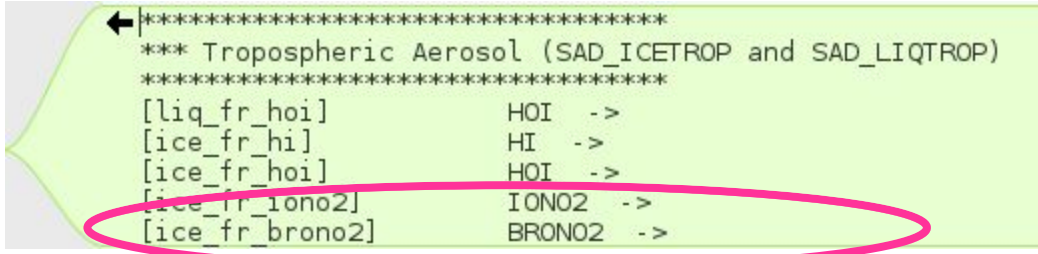
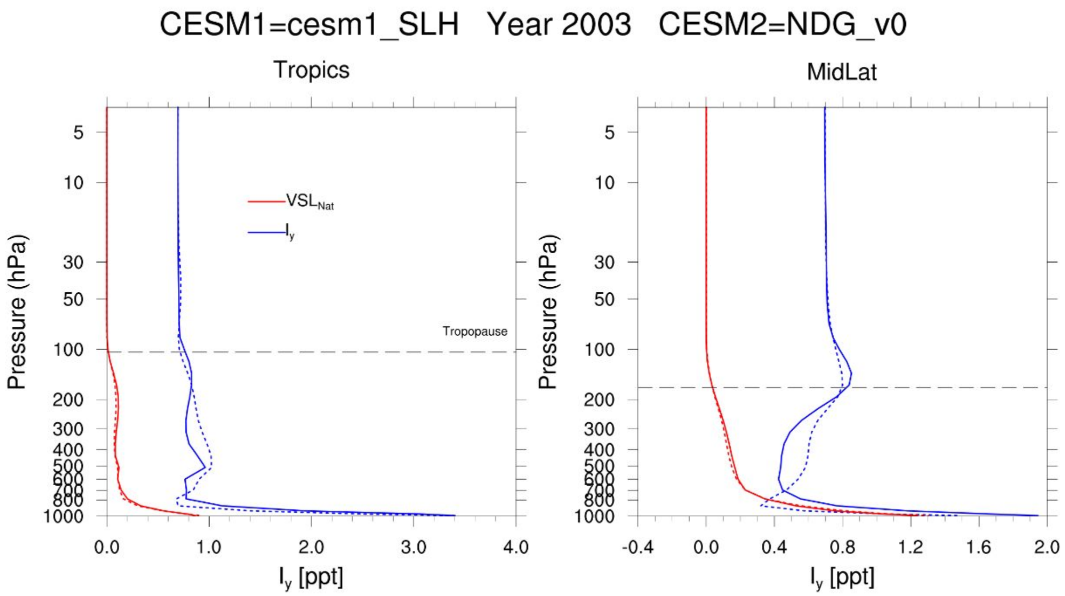
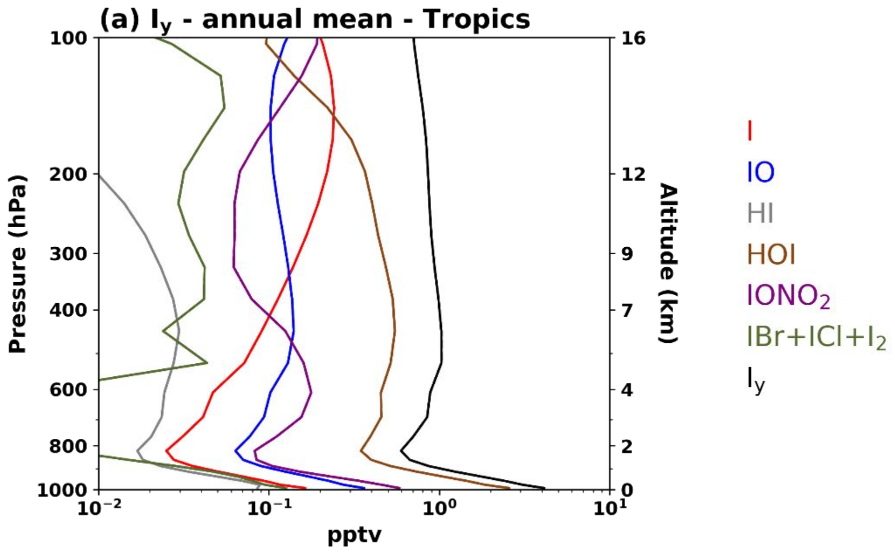
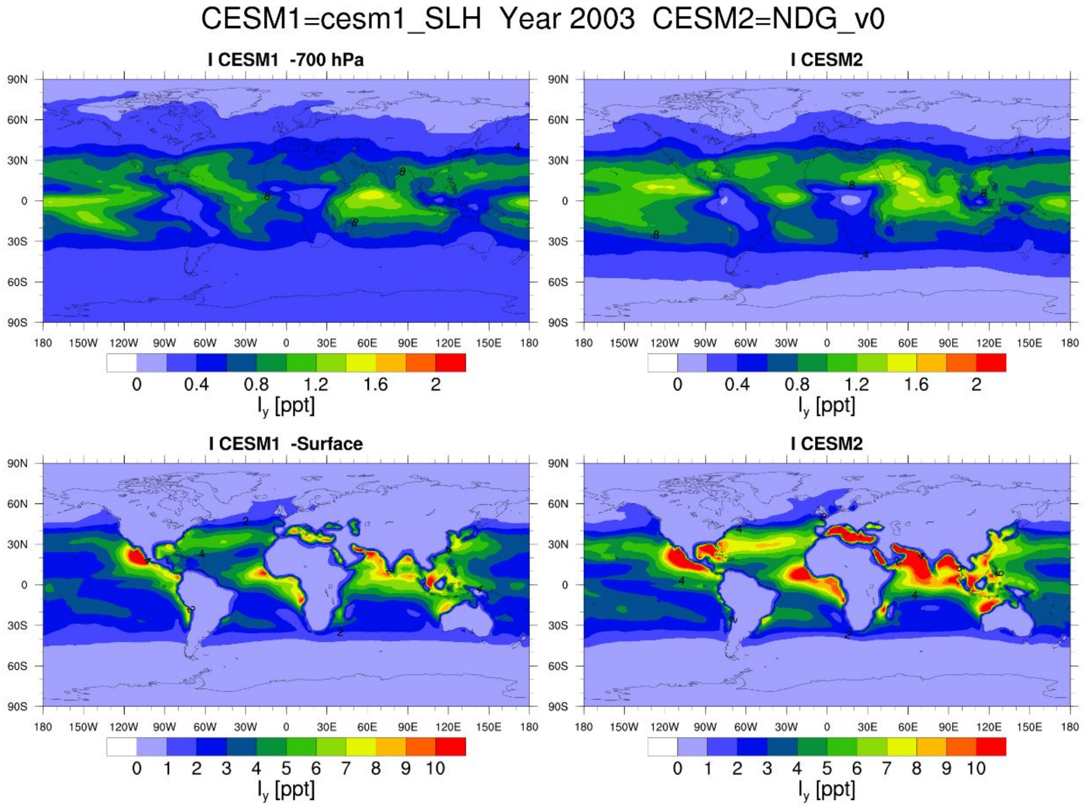
Table 1-6
WMO 2022



CESM1 vs CESM2: Iodine







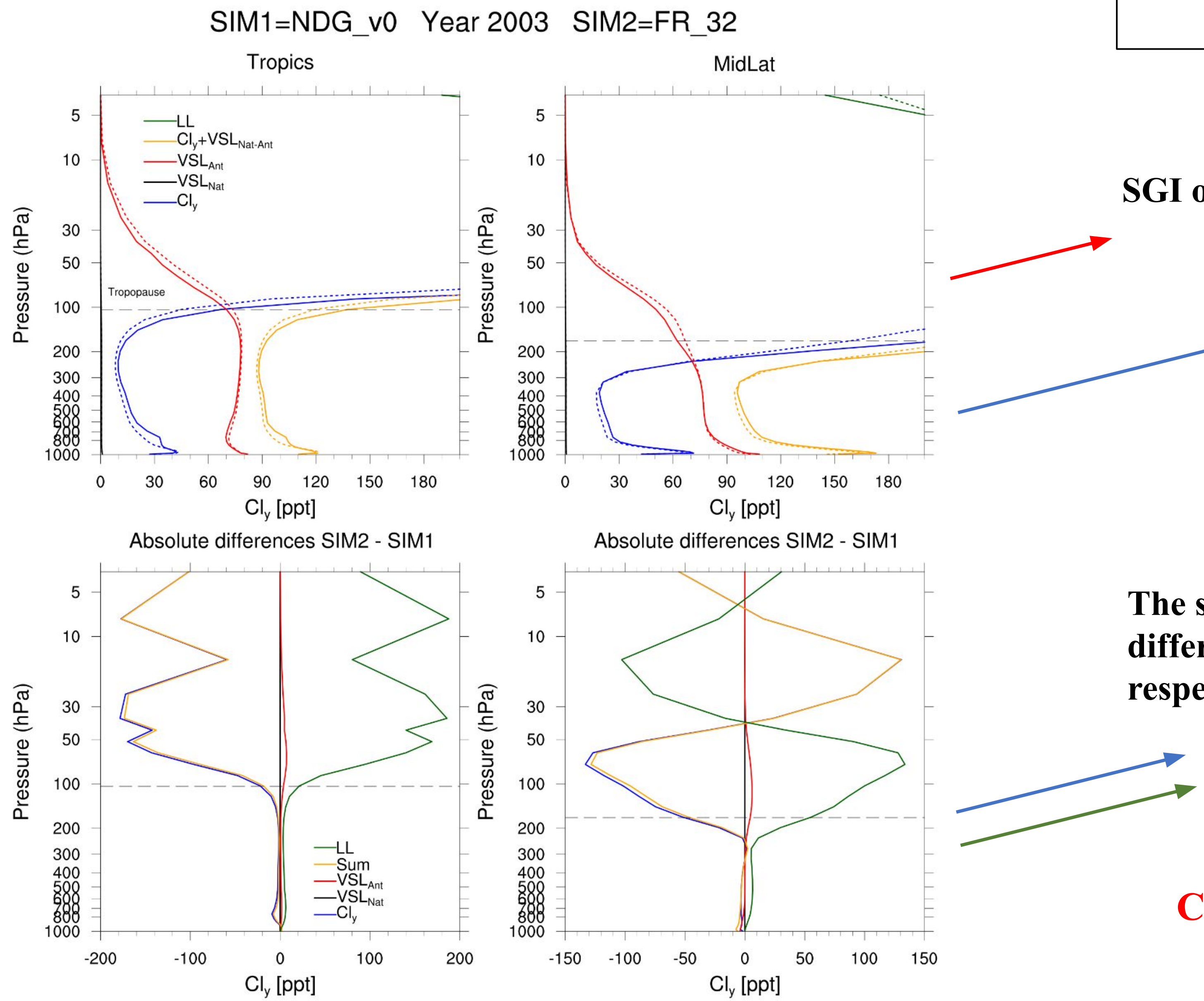
- **HI is a minor species. HOI dominates I_y partitioning.**
  - **Reactive iodine (I, IO) largest of all halogens**
  - **□ dominant O_3 impact**

- **Stratospheric I_y injection is 0.70 pptv (all gas-phase).**
  - **Particulate iodine formation is not included in CESM2**

- **Higher I_y values are observed at the surface**
  - **Oceanic HOI/I_2 (online) source reaches 2.1 Tg I yr^{-1}**

Evaluating CESM2 configurations

Evaluating CESM2-SLH setup: Nudging vs. Free Running



NDG_v0 vs. FR_32 for Chlorine

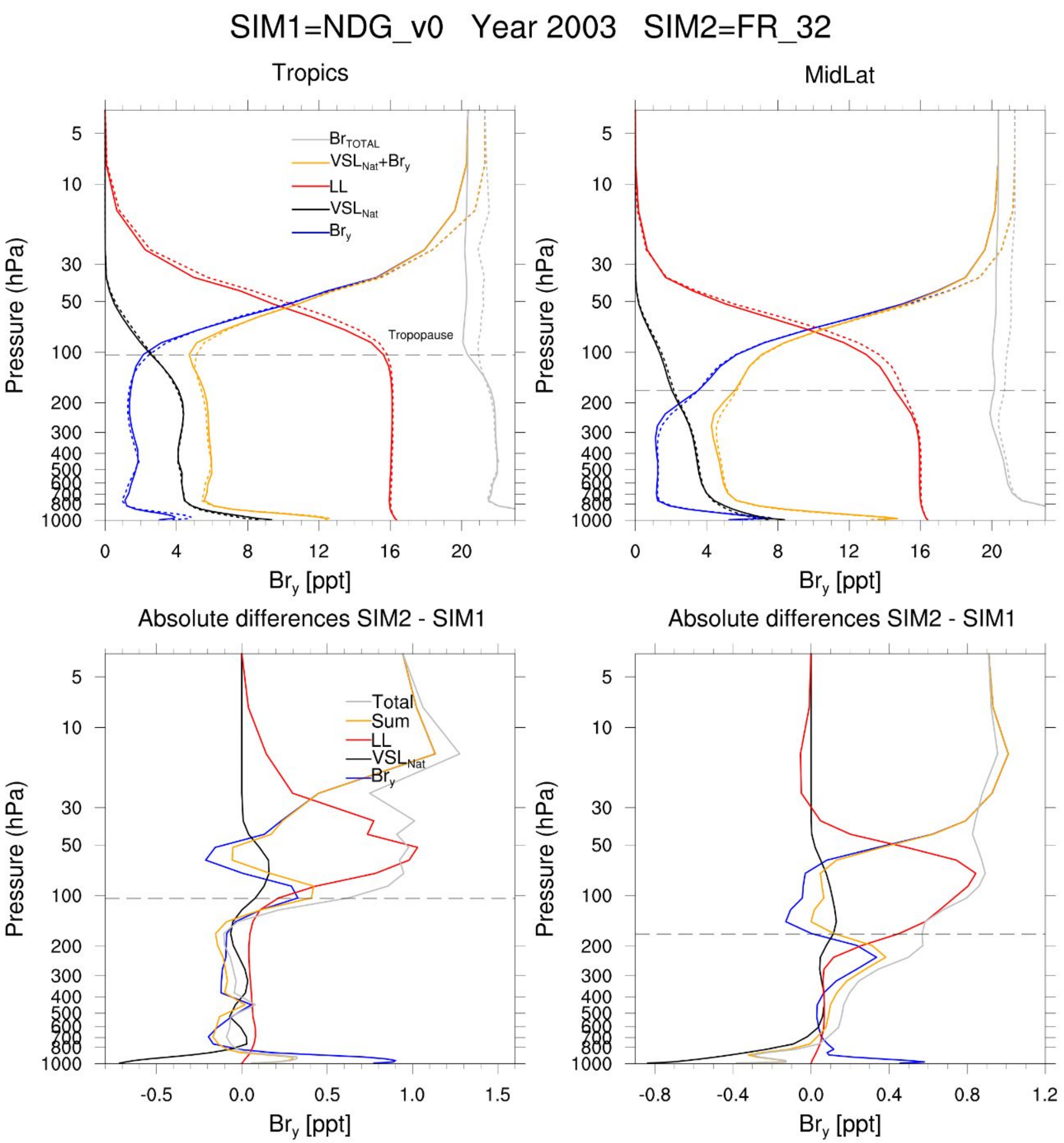
SGI of VSL^{Cl} is equivalent

PGI of Cl_y is 10-20 pptv larger for FR

The stratospheric distribution between NDG and FR differs by up to 200 pptv, with a mirrored profile with respect to the sum of LL species (CFCs and HCFCs)

Could this be due to BDC or QBO changes?

Evaluating CESM2-SLH setup: Nudging vs. Free Running



NDG_v0 vs. FR_32 for Bromine

SGI of VSL^{Br} is identical

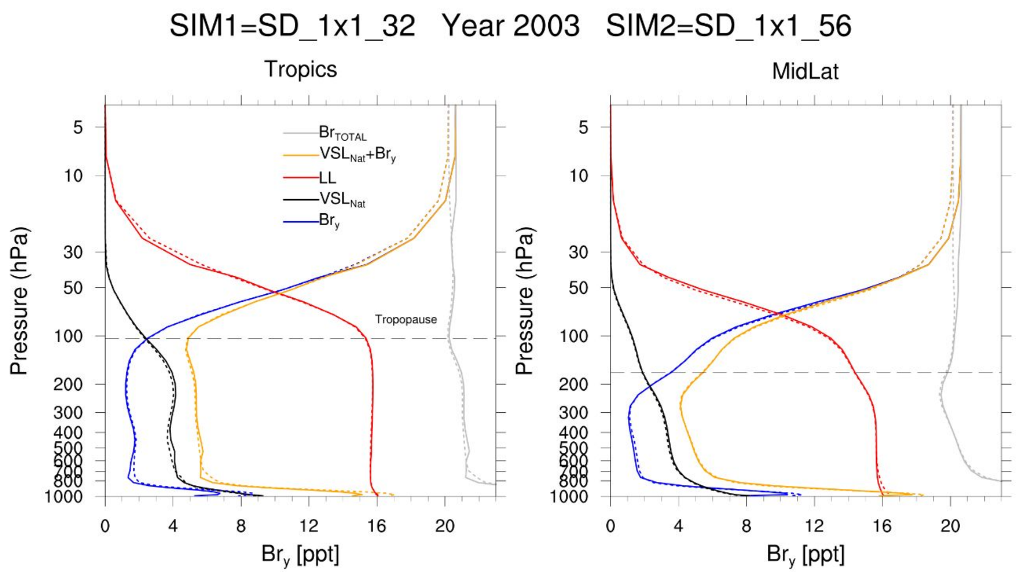
Difference in PGI for Br_y < 0.3 pptv

Total Br profile for FR does not show a marked decrease at the tropopause

Despite the SGI + PGI difference between NDG and FR is aprox. 0.4 pptv, the Br_y difference at the top of the model is 0.8-1.0 pptv, and presents large LL differences in the middle stratosphere. Why?

Is there any Upper Boundary condition in CESM2 affecting stratospheric Br_y abundance/partitioning?

Evaluating CESM2-SLH setup: Vertical Resolution



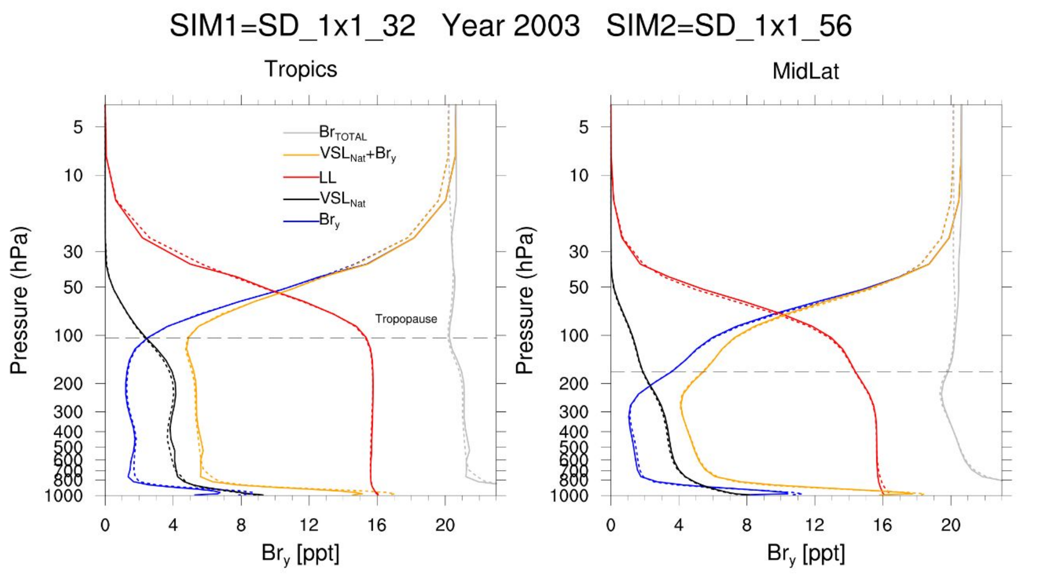
SD_32L vs. SD_56L for Bromine

Changes in reactive transport for different vertical resolutions was evaluated with a 1°x1° SD approach.

There are no significant differences between 32L and 56L neither in the troposphere nor in the stratosphere

Tropical peak at 30 hPa arises due to stratospheric stabilization

Evaluating CESM2-SLH setup: Vertical Resolution



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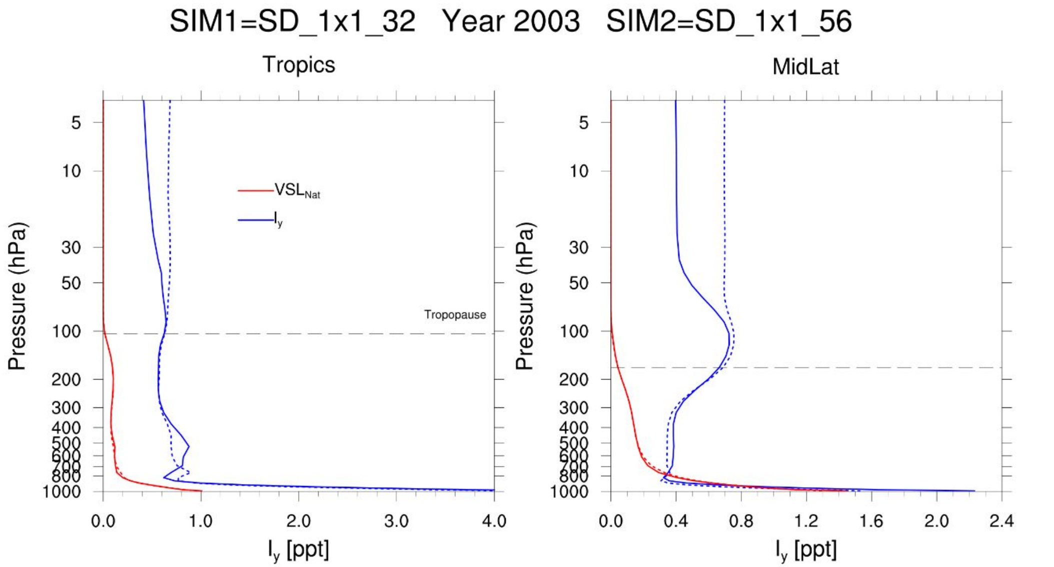
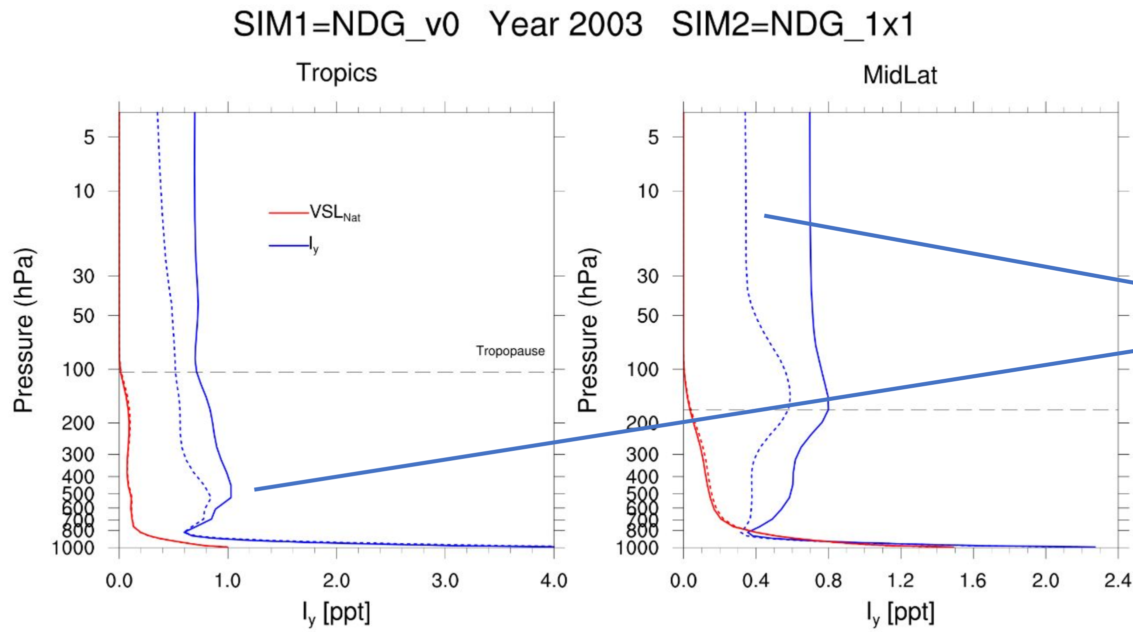


SD_32L vs. SD_56L for Iodine

Iodine and chlorine variations due to changes in the vertical resolution are also negligible.

Differences at the top of the model appear because ic for 32L neglected halogen chemistry.

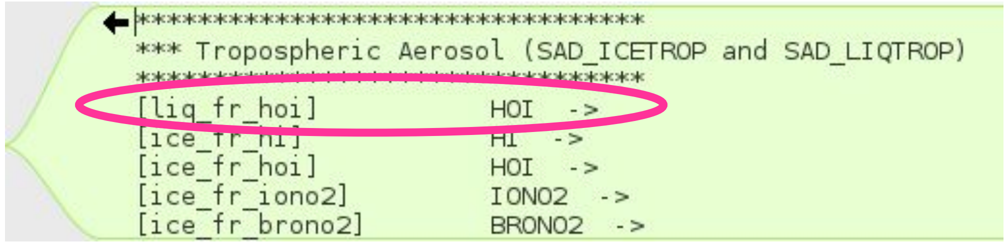
Evaluating CESM2-SLH setup: Spatial Resolution

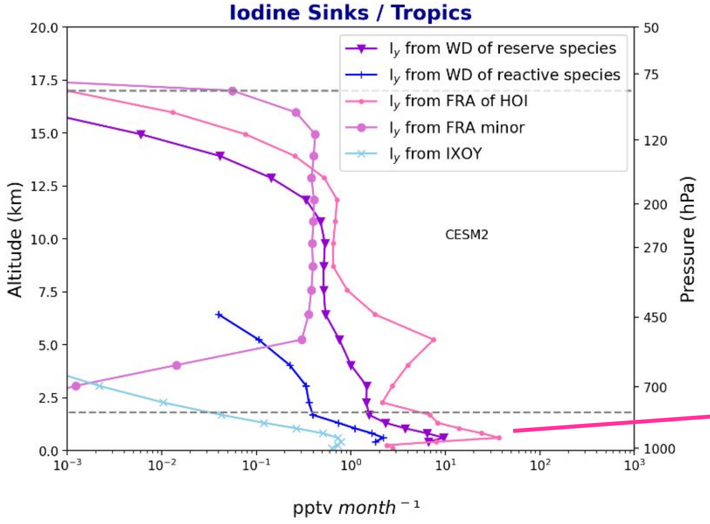


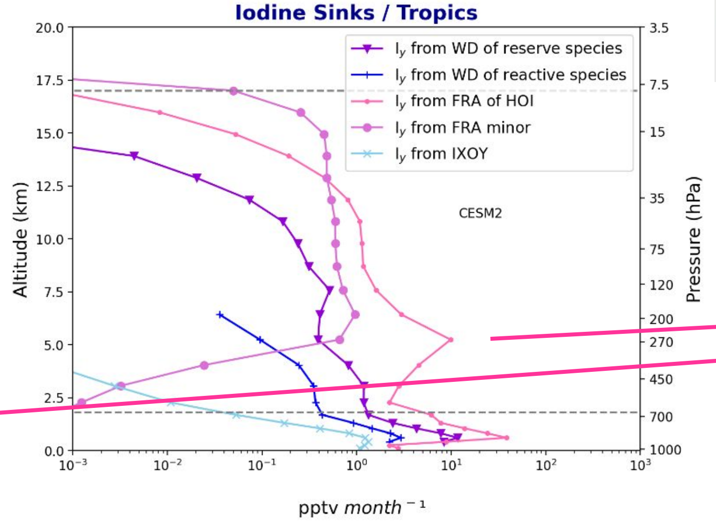
NDG_f19(2°x2.5°) vs. NDG_f09(1°x1°) for Iodine

Changes in spatial resolution significantly modifies iodine vertical profiles from the LT and upwards.

Stratospheric iodine injection is reduced aprox. by half for NDG_f09, which affects UT and LMS ozone impacts







The Free Regime Approximation (FRA) scheme is sensitive to the spatial resolution

Changes in spatial resolution significantly modifies iodine washout efficiency in the LT

Conclusions

1. **Short-Lived Halogen chemistry has been included into CESM2**
   - ***Tropospheric and Stratospheric distributions of halogens are consistent with previous studies, although some minor differences remain.***
   - ***Tropospheric abundance and stratospheric injection are sensitive to changes in the model setup, particularly increasing the spatial resolution to f09 (1°x1°) and using nudging (NDG) setup.***

2. **Importance of marinating support to low-resolution configurations for climate studies**
   - ***Allow to perform more sensitivities when developing new mechanisms***
   - ***Note of caution on SLH abundance when changing model resolution***

CONTACT

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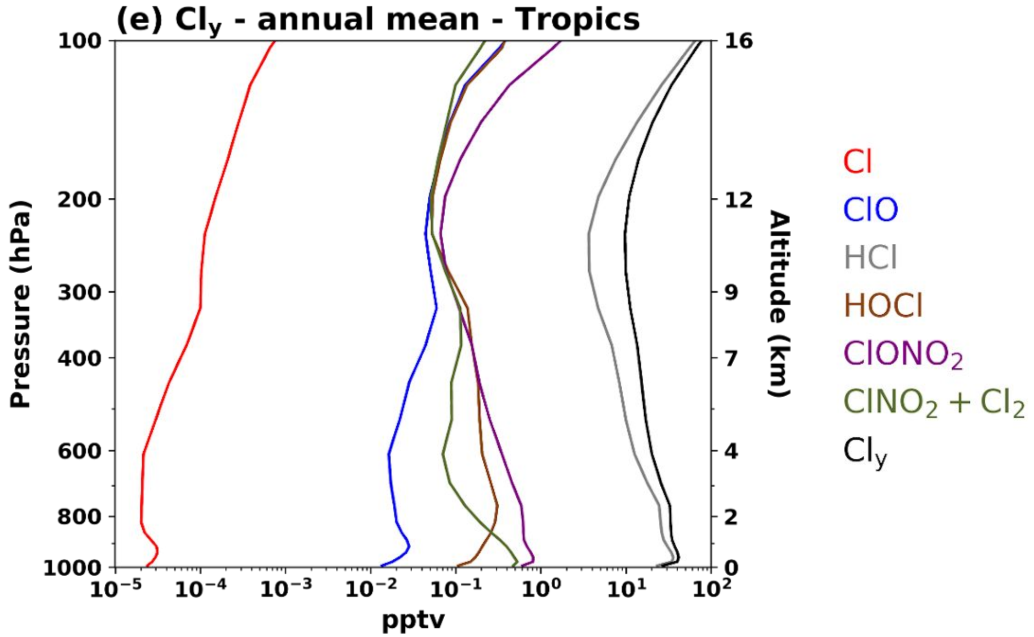
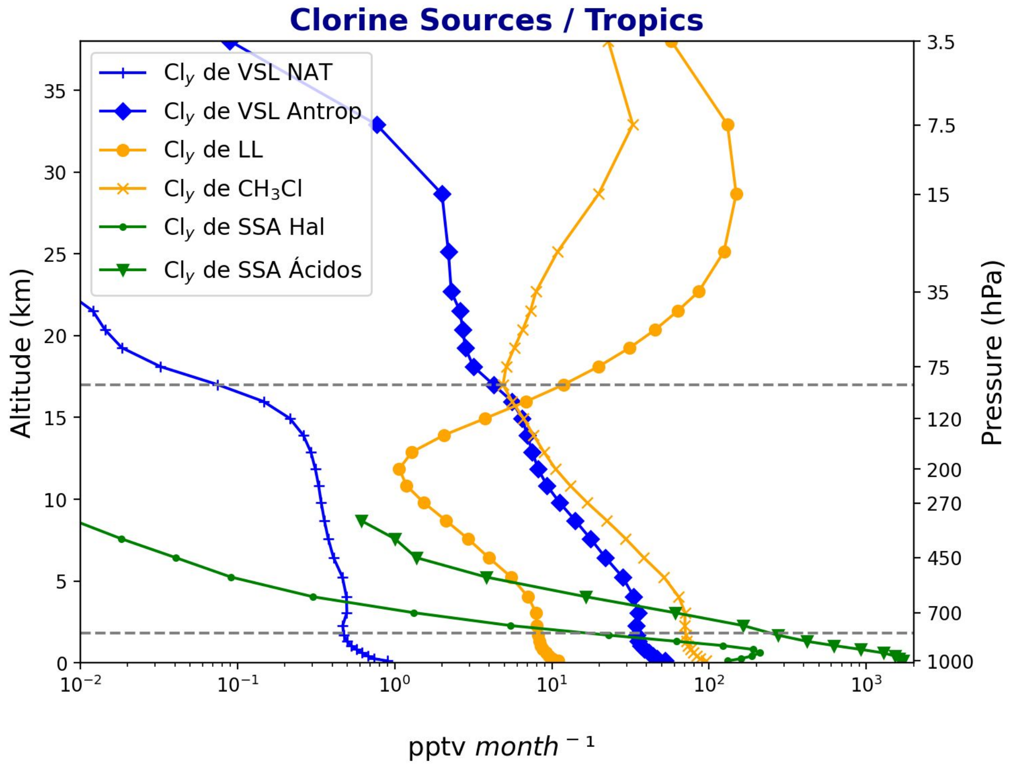
Chlorine in CESM2: Sources and Partitioning





- HCl dominates Cl_y partitioning in the UT and controls washout and PGI.
  - Reactive chlorine (Cl, ClO) are minor species □ smaller impacts w.r.t. Br/I
- Acid-driven SSA-dehalogenation is the dominant source in the MBL (>80%).
- Photo-degradation of CH_3Cl (LL) controls the release of Cl_y in the FT, surpassing Cl atom source from all Anthro VSL^{Cl} together
  - Note CH_3Cl are imposed as LBC and possess a natural contribution
- Anthro VSL^{Cl} contribute to tropospheric Cl burden (~35%), SGI and PGI
  - Natural VSL^{Cl} are negligible

GLOBAL (90°N-90°S)	Clorine Sources (Gg/yr)							
	Nat VSL	Anthropogenic VSL		Long Lived (LL)		SSA	Total Cl	Perc
		CH_2Cl_2	Minor VSL	CH_3Cl	CFCs HCFCs	Cl_y		
Photolysis	54.0	0.02	1.11	0	7.53	0	62.66	**0.3**
OH + O¹D	11.60	590	758	2298	251	0	3908.6	**16.5**
Cl	0	1.83	3.46	23.6	0	0	28.89	**0.1**
SSA HAL	0	0	0	0	0	2285	2285	**9.7**
SSA ACID	0	0	0	0	0	17318	17318	**73.4**
Total Cl	65.6	591.85	762.57	2321.6	258.53	19603	23603,15	**100**
Percentage	**0.3**	**2.5**	**3.2**	**9.8**	**1.1**	**83.1**		
Percentage	**1.6**	**14.8**	**19.1**	**58**	**6.5**	--		

35%