Current Status of VSL Halogen Chemistry in CESM 2.2: How Changes in Tropospheric SAD Fields Impact on Halogen Recycling and Washout?

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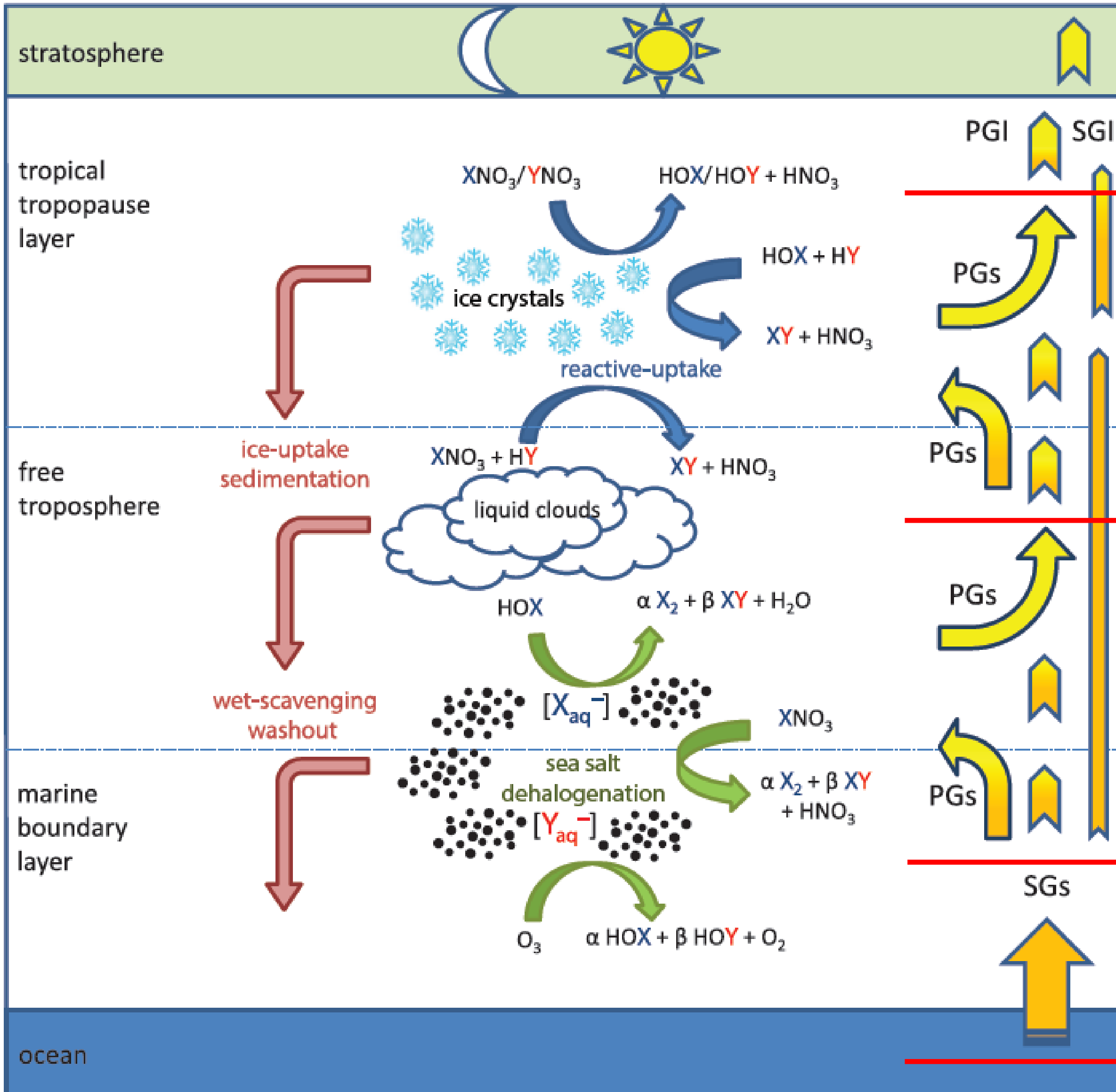
Boulder, CO, February 2021

Outline

- **Description (Technical + Historical) of VSL Halogen implementation in CAM-Chem**
  - ***Focused mostly on "processes/reactions" than in "impacts/implications"***
  - ***Main porpoise of highlighting main routines & namelist options for the non-VSL CAM-Chem user***
- **All developments performed in CAM4 (CESM1)**
  - ***Evaluate how changes on SAD & MET fields between CESM1 and CESM2 impact on tropospheric halogen abundances***
- **Distinction between Simplified vs. Full VSL approaches**
  - ***Describe the implementation of new sources, sinks and re-partitioning***
  - ***Evaluate spatial and vertical changes of tropospheric distributions***
  - ***Highlight major difficulties found for the het. Recycling implementation***

Very Short-Lived (VSL) Halogens

Box 1-3. WMO 2018



4 **Het. Recycling Ice-scavenging (change in partitioning)**

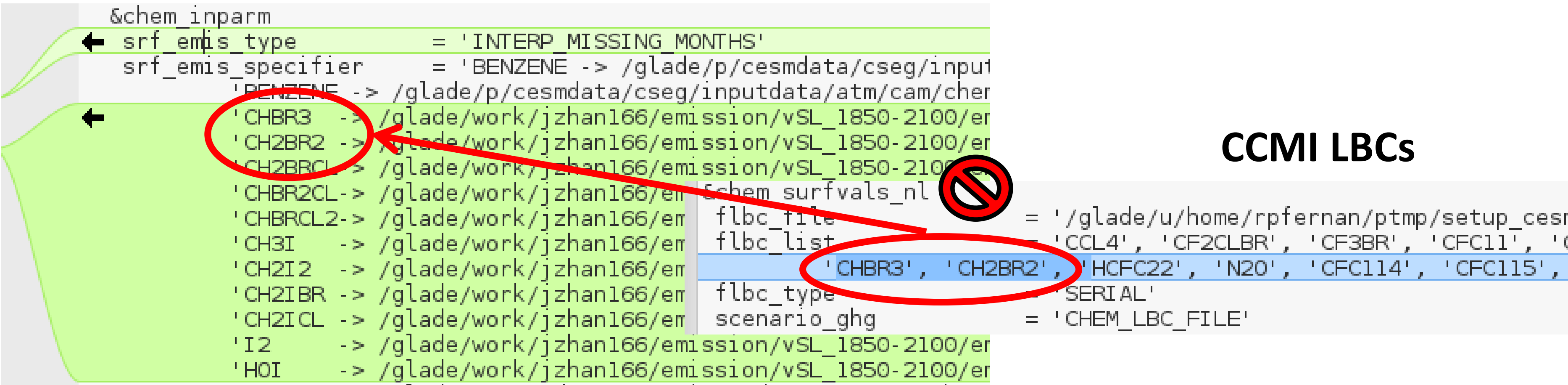
3 **Washout & wet-scavenging (net sink)**

2 **Sea-Salt Recycling (net source)**

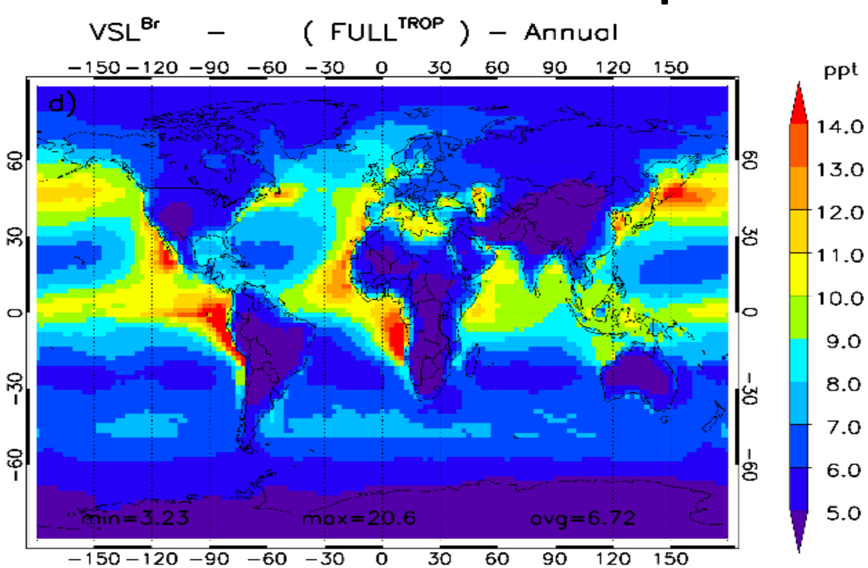
1 **Oceanic VSL emissions (on-line vs fff-line)**

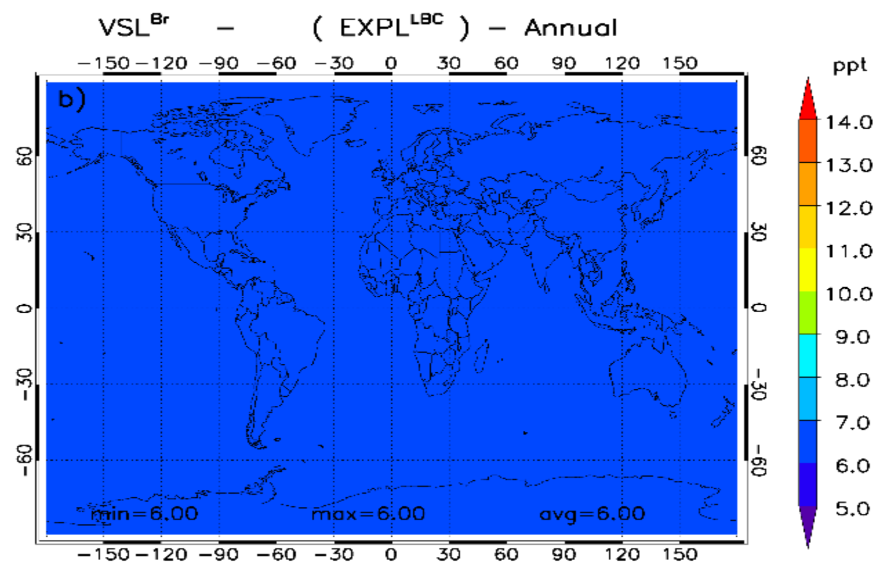
1. Surface Emissions (VSL SGs)

user_nl_cam + mo_srf_emissions.F90



Full CAM-Chem-VSL Setup ← **CCMI Setup (VSL)**





Chl-a dependent emissions for 6 VSLs

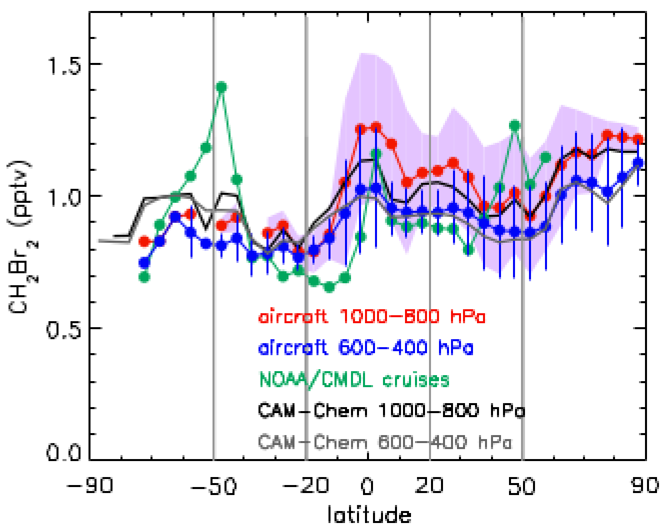
1.2 ppt ($CHBr_3$ + CH_2Br_2) = 6 ppt VSL^{Br}

1. Surface Emissions (VSL SGs)

user_nl_cam + mo_srf_emissions.F90

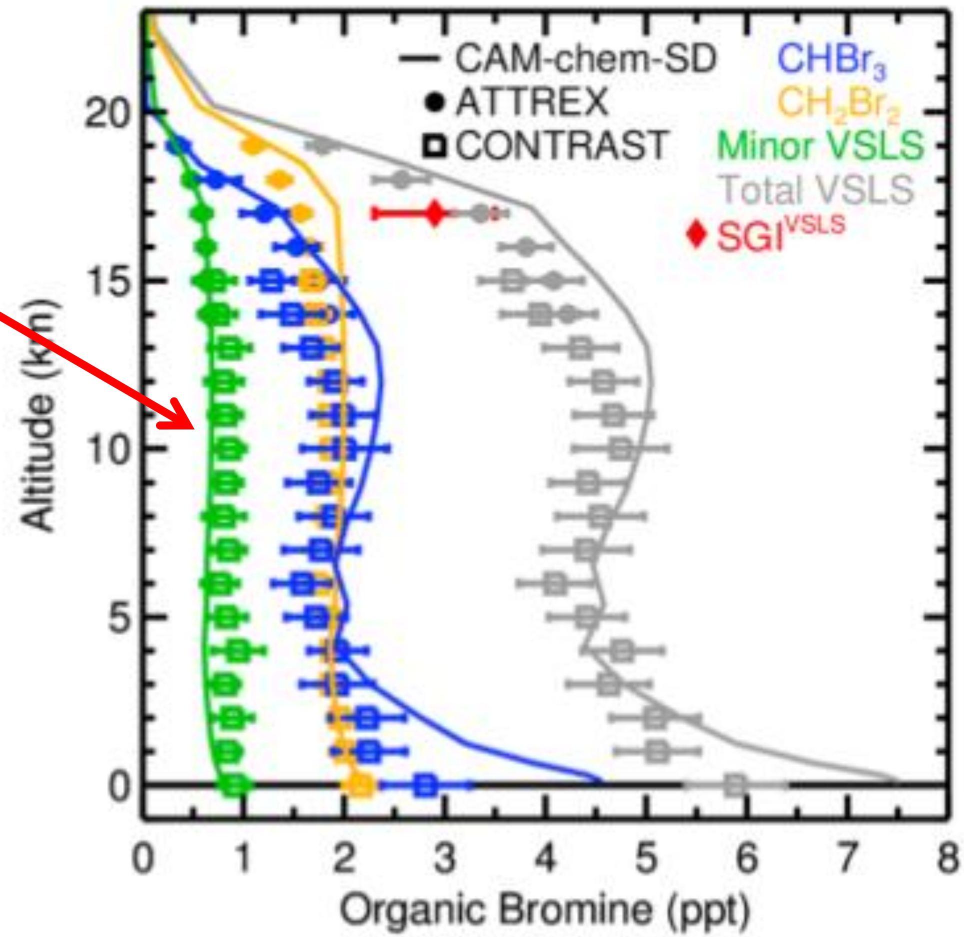
```
&chem_inparm
 srf_emis_type          = 'INTERP_MISSING_MONTHS'
 srf_emis_specifier     = 'BENZENE -> /glade/p/cesmdata/cseg/input
          'BENZENE -> /glade/p/cesmdata/cseg/inputdata/atm/cam/cher
          'CHBR3   -> /glade/work/jzhan166/emission/vSL_1850-2100/er
          'CH2BR2  -> /glade/work/jzhan166/emission/vSL_1850-2100/er
          'CH2BRCL -> /glade/work/jzhan166/emission/vSL_1850-2100/er
          'CHBR2CL-> /glade/work/jzhan166/emis
          'CHBRCL2-> /glade/work/jzhan166/emis
          'CH3I    -> /glade/work/jzhan166/emis
          'CH2I2   -> /glade/work/jzhan166/emis
          'CH2IBR  -> /glade/work/jzhan166/emis
          'CH2ICL  -> /glade/work/jzhan166/emis
          'I2      -> /glade/work/jzhan166/emis
          'HOI     -> /glade/work/jzhan166/emis
```

Full CAM-Chem-VSL Setup



Ordoñez et al., ACP, 2012

Wales et al., JGR, 2018



1. Surface Emissions (Iodine)

user_nl_cam + mo_srf_emissions.F90 + mo_iodine_emissions.F90 + seq_drydep_mod.F90

```
&chem_inparm
 srf_emis_type          = 'INTERP_MISSING_MONTHS'
 srf_emis_specifier     = 'BENZENE -> /glade/p/cesmdata/cseg/input
        'BENZENE -> /glade/p/cesmdata/cseg/inputdata/atm/cam/cher
        'CHBR3   -> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CH2BR2  -> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CH2BRCL-> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CHBR2CL-> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CHBRCL2-> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CH3I    -> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CH2I2   -> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CH2IBR  -> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'CH2ICL  -> /glade/work/jzhan166/emission/vSL_1850-2100/er
        'I2      -> /glade/work/jzhan
        'HOI     -> /glade/work/jzhan
```

$$\left[I^-_{aq}\right] = 1.46\times 10^6 \times \exp\left(\frac{-9,134}{SST}\right)$$

$$F_{HOI} = [\mathrm{surf.O_3}]\times\left\{4.15\times 10^5\times\left(\frac{\sqrt{\left[I^-_{aq}\right]}}{ws}\right) - \left(\frac{20.6}{ws}\right) - 23,600\times\sqrt{\left[I^-_{aq}\right]}\right\}$$

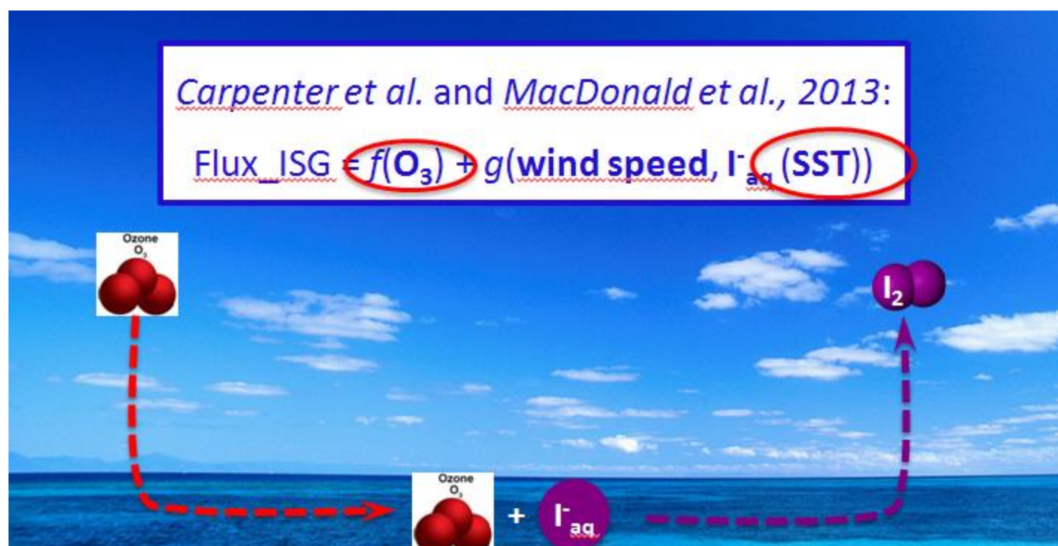
Offline I2 + HOI source
mo_srf_emissions.F90

↓

Forced to zero

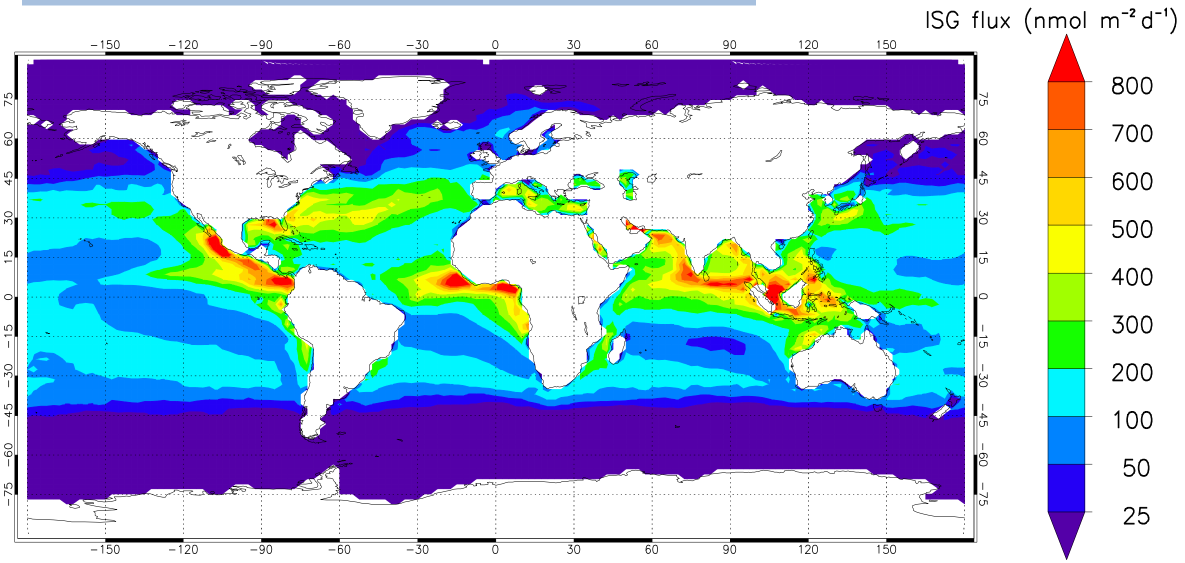
↓

Compute iodine flux online
mo_iodine_emissions.F90



1. Surface Emissions (Iodine)

Prados-Roman et al., ACP, 2015



CESM1
Iodine Flux
~ 1.9 Tg I yr^{-1}

↑

CESM2
Iodine Flux
~ 3.7 Tg I yr^{-1}

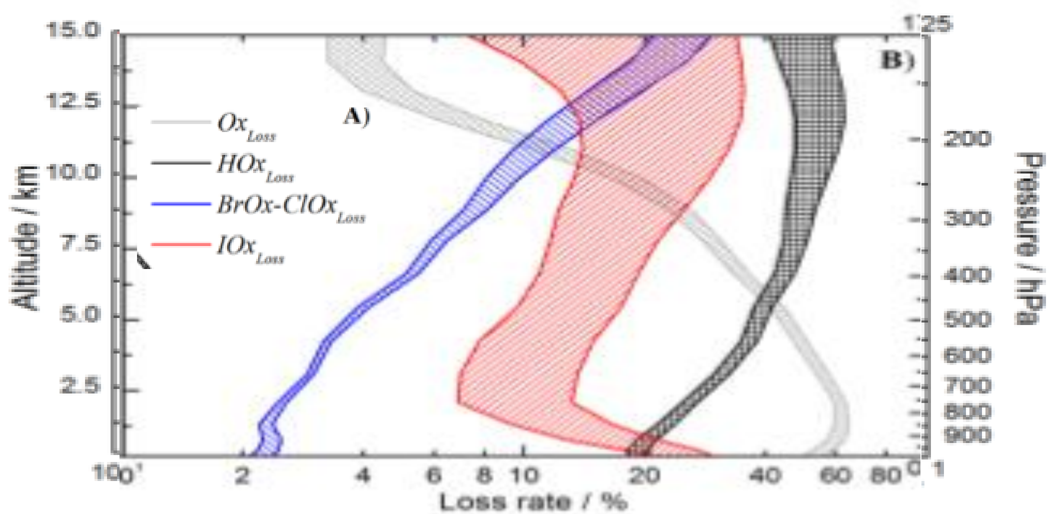
Offline I2 + HOI source
mo_srf_emissions.F90

↓

Forced to zero 🚫

↓

Compute iodine flux online
mo_iodine_emissions.F90



Saiz-Lopez et al., ACP, 2014

2. Sea-Salt Recycling (SSA-dehalogenation)

chem_mech.in + mo_usrrxt.F90

```
[usr_TERPNIT_aer]        TERPNIT   -> HNO3
*********************************
*** Sea Salt Aerosol (SAD_SSLT)
*********************************
[het_ss_0]              BRONO2   -> 0.65*BR2 + 0.35*BRCL
[het_ss_1]              BRNO2   -> 0.65*BR2 + 0.35*BRCL
[het_ss_2]              HOBR   -> 0.65*BR2 + 0.35*BRCL
[het_ss_3]              CLONO2   -> CL2
[het_ss_4]              CLNO2   -> CL2
[het_ss_5]              HOCL   -> CL2
[het_ss_6]              IONO2   -> 0.5*IBR + 0.5*ICL
[het_ss_7]              INO2   -> 0.5*IBR + 0.5*ICL
[het_ss_8]              HOI   -> 0.5*IBR + 0.5*ICL
```

Non-stoichiometric
Net source of Br and Cl
Change Partitioning I

mo_usrrxt.F90

```
!  CESM2-VSL.003 - CC2x2_nocap_gd4 (meands gammas divided by 4
   real(r8), parameter :: gamma_brono2_ss    = 0.012_r8   !
   real(r8), parameter :: gamma_brno2_ss     = 0.012_r8
   real(r8), parameter :: gamma_hobr_ss      = 0.048_r8   !
```

```
!rpf (Feb 17, 2013): introduce logical c
if (press_lev < 300._r8) then
   logical_sslt = 0.0_r8
else
   logical_sslt = 1.0_r8
endif

sad_sslt_eff(i,k) = sad_sslt_mask * DF
```

Free Regime Approximation

v_d

$$F_{ssa} = v_d \times \gamma_i \times SAD_{ssa} \times DF(Lat,t)$$

Sea-salt aerosol

Br^- / Cl^-

$BrONO_2 \rightarrow 0.65\ Br_2 + 0.35\ BrCl$

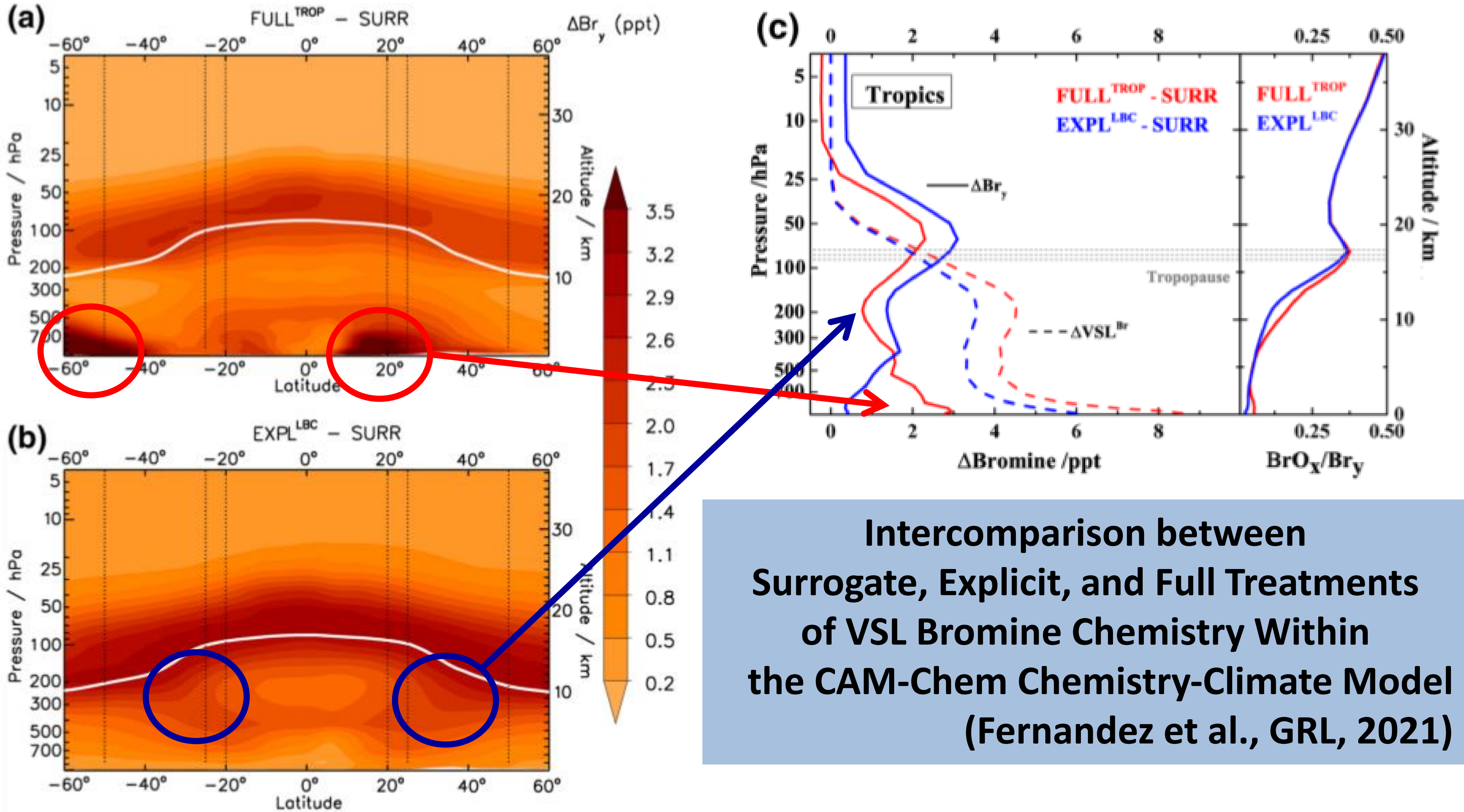
$BrNO_2 \rightarrow 0.65\ Br_2 + 0.35\ BrCl$

$HOBr \rightarrow 0.65\ Br_2 + 0.35\ BrCl$

MBL

Do not keep track of halide content on aged Sea-Salt !!!
(infinite halide reservoir)

2. Sea-Salt Recycling (SSA-dehalogenation)

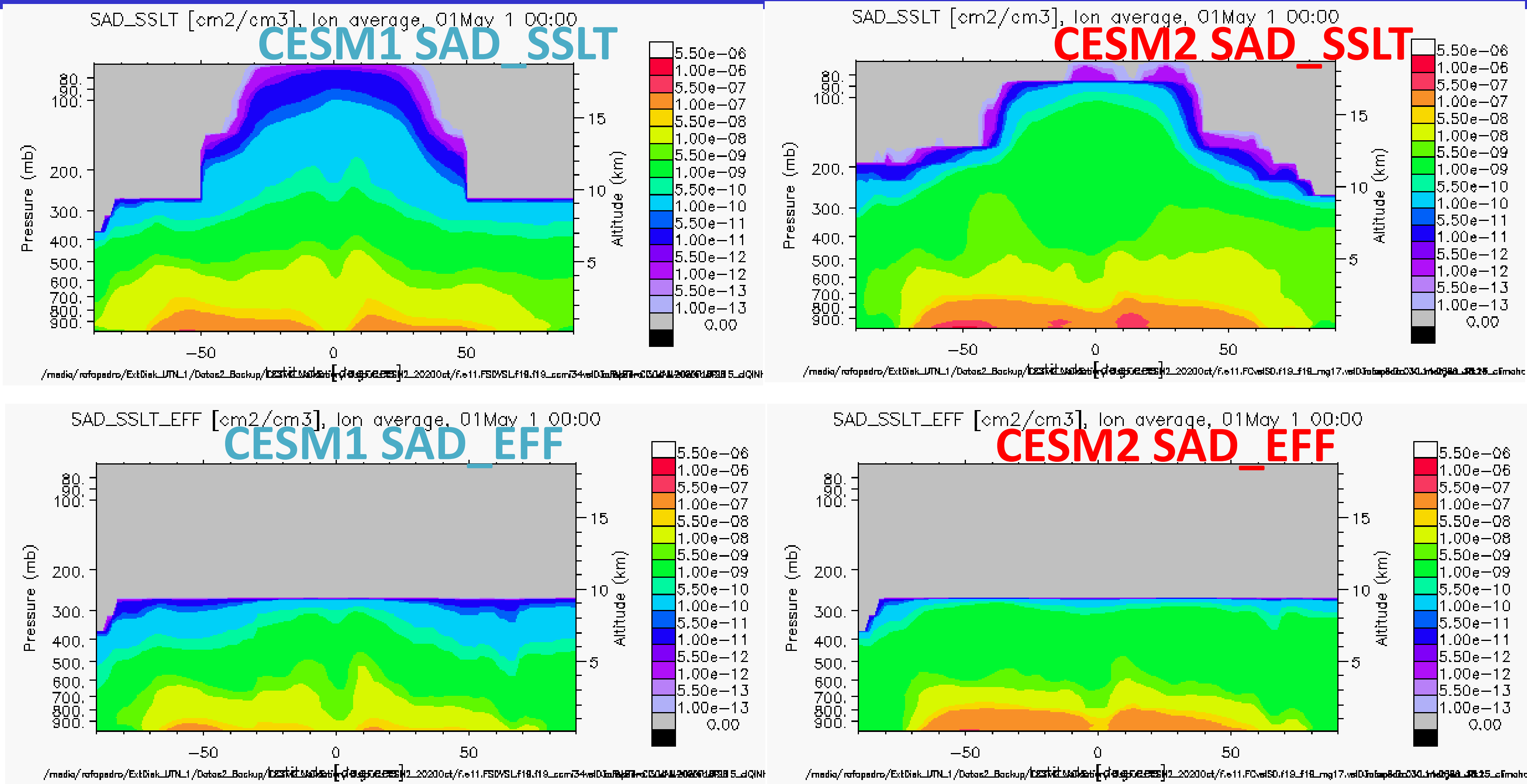


Intercomparison between Surrogate, Explicit, and Full Treatments of VSL Bromine Chemistry Within the CAM-Chem Chemistry-Climate Model (Fernandez et al., GRL, 2021)

Bry enhancements below 500 hPa are > 2 times larger for FULL respect to EXPL

The omission of Bry ice-scavenging within the EXPL approach results in an infinite tropospheric lifetime of bromine atoms released in the upper troposphere

2. Sea-Salt Recycling (CESM1 vs. CESM2)

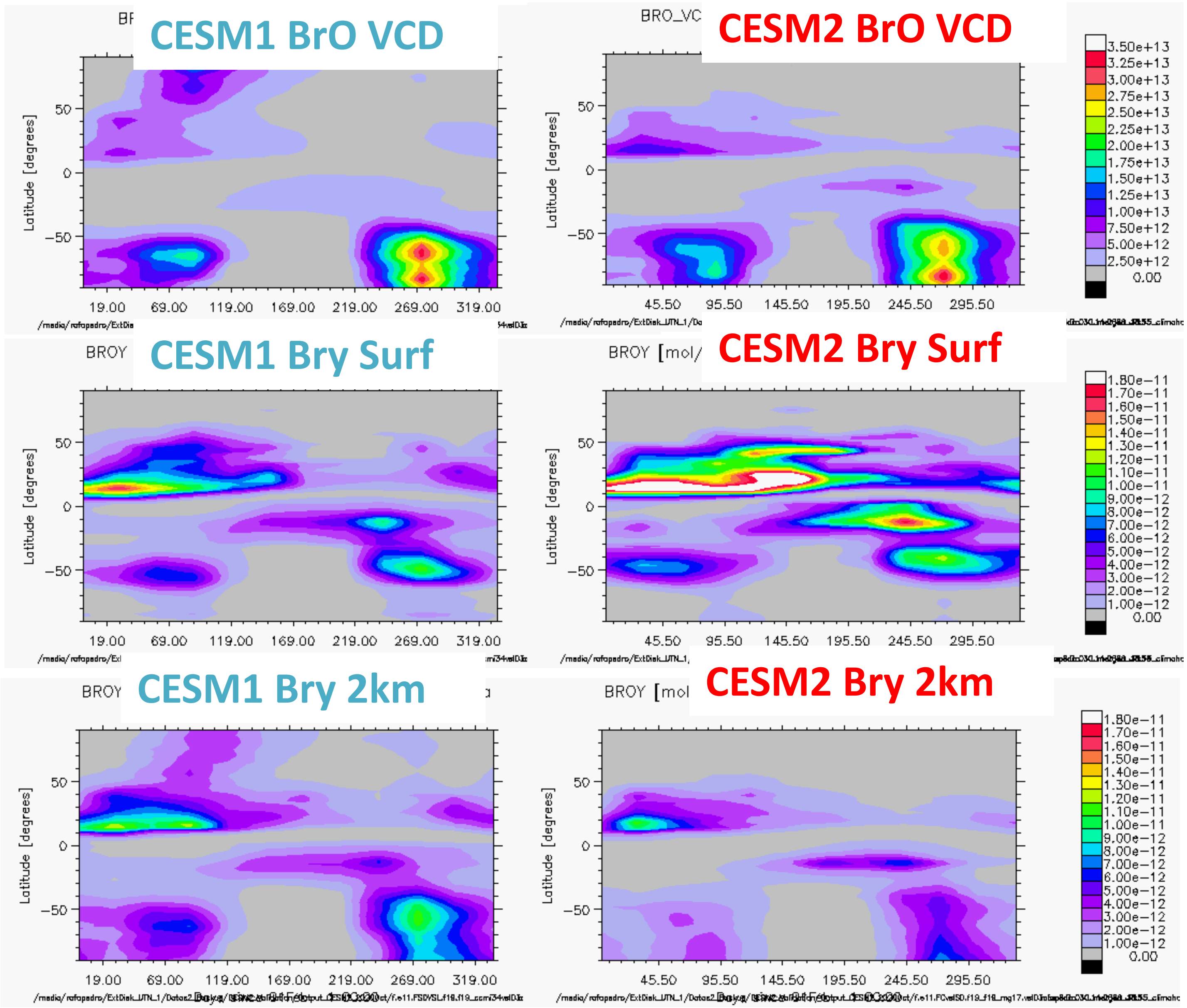


SAD levels in CESM2 are more than 5 times larger than in CESM1

We implemented 2 approaches for reducing the recycling efficiency:

- **a. SAD CAP**
- **b. Reduce gamma efficiency**

2. Sea-Salt Recycling (CESM1 vs. CESM2)



Tropospheric BrO
CESM1 ≈ CESM2
Seasonality over the Southern Ocean

Surface Bry
CESM1 < CESM2

Free Trop Bry
CESM1 > CESM2

3. Washout on liquid and ice clouds

user_nl_cam + chem_mech.in + mo_neu_wetdep.F90 + mo_usrrxt.F90 + seq_drydep_mod.F90

```
&wetdep_inparm
 gas_wetdep_method              = 'NEU'
 gas_wetdep_ice_uptake_list ='HOI','IONO2','HI','BRONO2', 'HNO3'
 gas_wetdep_list              = 'HOI', 'ALKNIT', 'ALKOOH', 'BC
        'BIGALK', 'BIGENE', 'BR2', 'BRCL', 'BRNO2', 'BRONO2', '
```

NEU routine not mapped to HNO3

↓

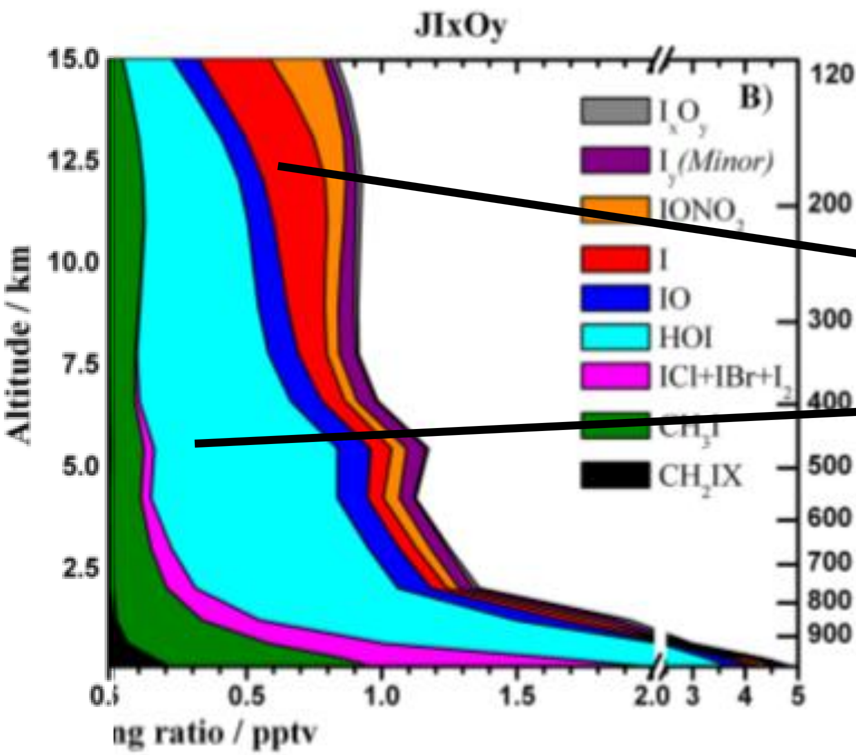
Too efficient washout For inorganic iodine

↓

washout of HOI & IONO2 Controls Iy burden

↓

Replace NEU scheme by FR Aprox.



Saiz-Lopez et al., ACP, 2014

```
*****************************************
*** Tropospheric Aerosol (SAD_ICETROP and SAD_LIQTROP)
*****************************************
[liq_fr_hoi]          HOI   ->
[ice_fr_hi]           HI    ->
[ice_fr_hoi]          HOI   ->
[ice_fr_iono2]        IONO2  ->
[ice_fr_brono2]       BRONO2  ->
```

4. Tropospheric Ice Recycling (Br and Cl)

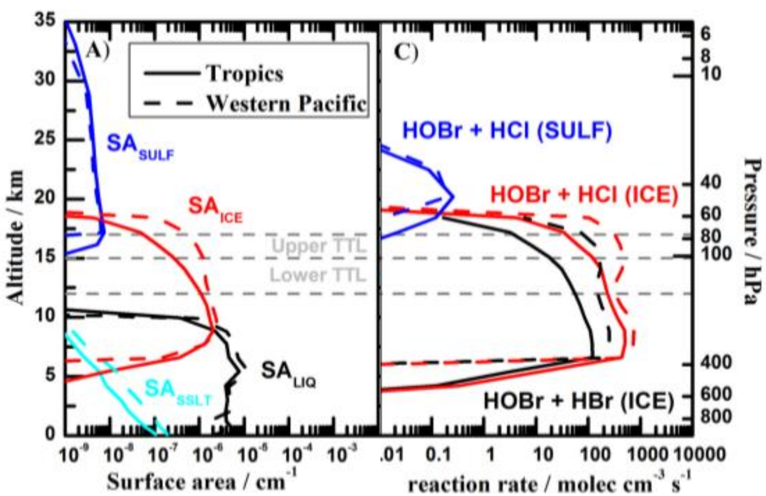
user_nl_cam + chem_mech.in + mo_usrrxt.F90 + mo_sadtrop.F90

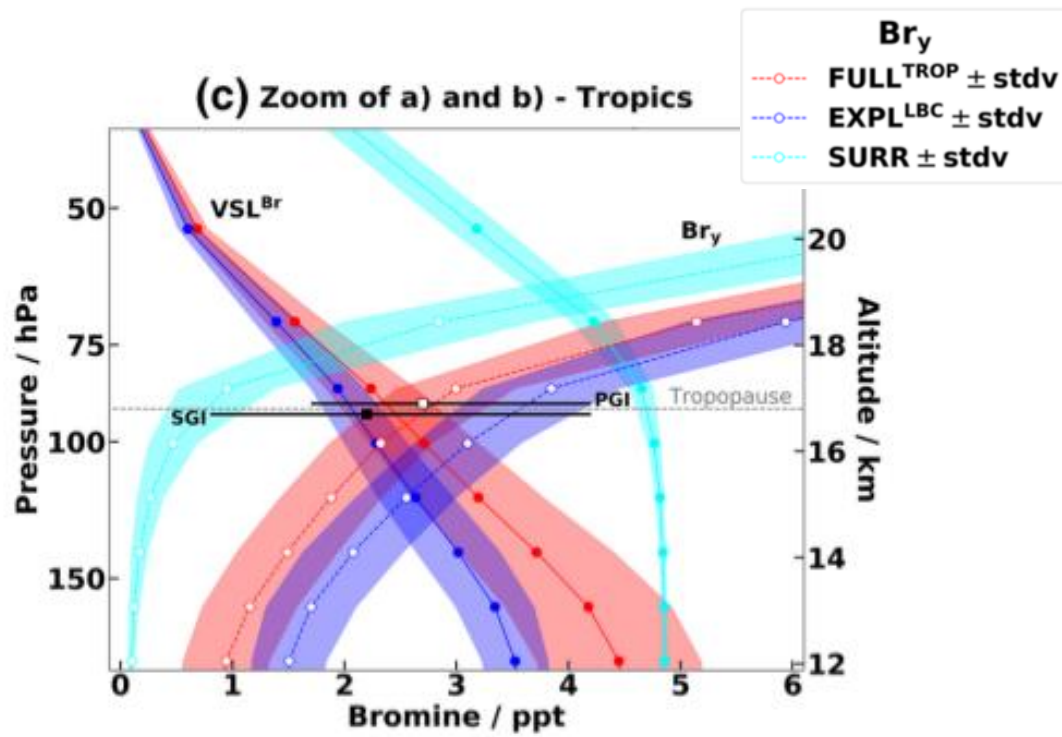
```
*********************************
*** Tropospheric Aerosol (SAD_ICETROP and SAD_LIQTROP)
*********************************
[ice_trp_cl_1]        CLONO2 -> HOCL + HNO3
[ice_trp_br_1]        BRONO2 -> HOBR + HNO3
[ice_trp_hbr_5]       HOCL + HBR  -> BRCL + H2O
[ice_trp_hcl_5]       HOCL + HCL  -> CL2 + H2O
[ice_trp_hbr_6]       HOBR + HBR  -> BR2 + H2O
[ice_trp_hcl_6]       HOBR + HCL  -> BRCL + H2O
```

Based on strato_rates.F90
On tropospheric ice-crystals

↓

Change in partitioning
Halogen reactivation





Fernandez et al., ACP, 2014
Fernandez et al., GRL, 2021

4. Tropo & Strato Recycling (Iodine)

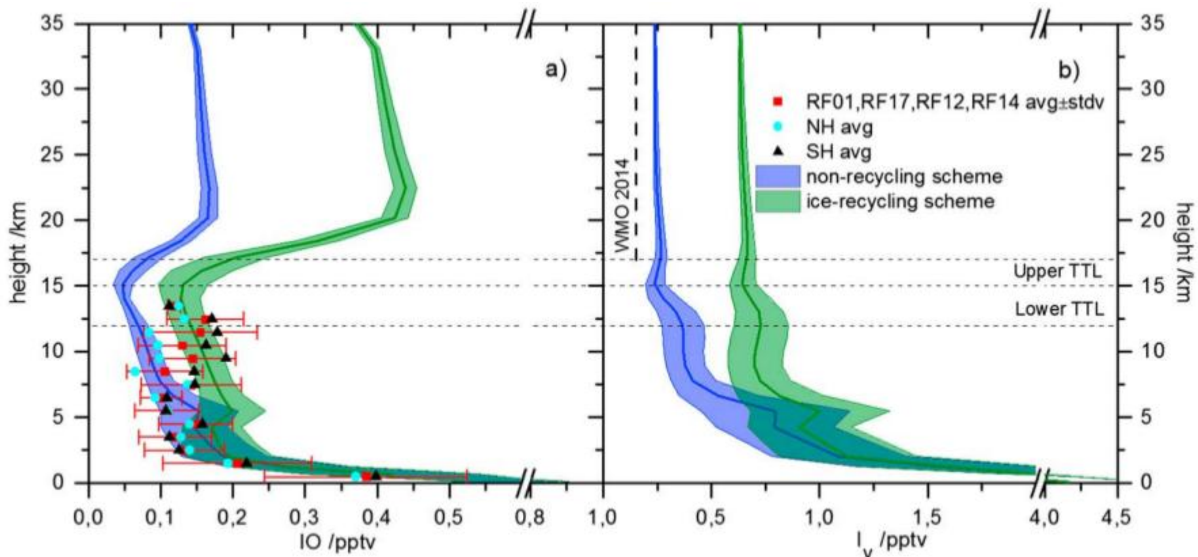
user_nl_cam + chem_mech.in + mo_usrrxt.F90 + mo_sadtrop.F90

```
*********************************
*** Stratospheric Aerosol
*********************************
[slf_str_i_1]           IONO2 -> HOI + HNO3
[slf_str_i_2]           HOI + HCL -> ICL + H2O
[slf_str_i_3]           HOI + HBR -> IBR + H2O
[slf_str_i_4]           HOI + HI   -> I2 + H2O
[slf_ipart_1]           IONO2 -> IPART
[slf_ipart_2]           HOI + HCL -> IPART
...
```

Based on strato_rates.F90
Mapped to Br and Cl
SULF, NAT, ICE SAD

Increase lifetime against washout

Compatible with Inorganic Iodine stratospheric injection Iy < 0.75 pptv



Saiz-Lopez et al., GRL, 2015

Table 1-5. Summary of estimated VSL source gas injection (SGI) and product gas injection (PGI) contributions to stratospheric halogens (based on observations and model results).

VSLS Best Estimate (ppt)	SGI[1]	PGI[2]	Total (SGI + PGI)[3]
Chlorine	92 (75–110)	25 (8–50)	115 (75–160)
Bromine	2.2 (0.8–4.2)	2.7 (1.7–4.2)	5 (3–7)
Iodine	0–0.1	0–0.7	0–0.8

Table 1-5. WMO 2018

4. Tropo & Strato Recycling (Iodine)

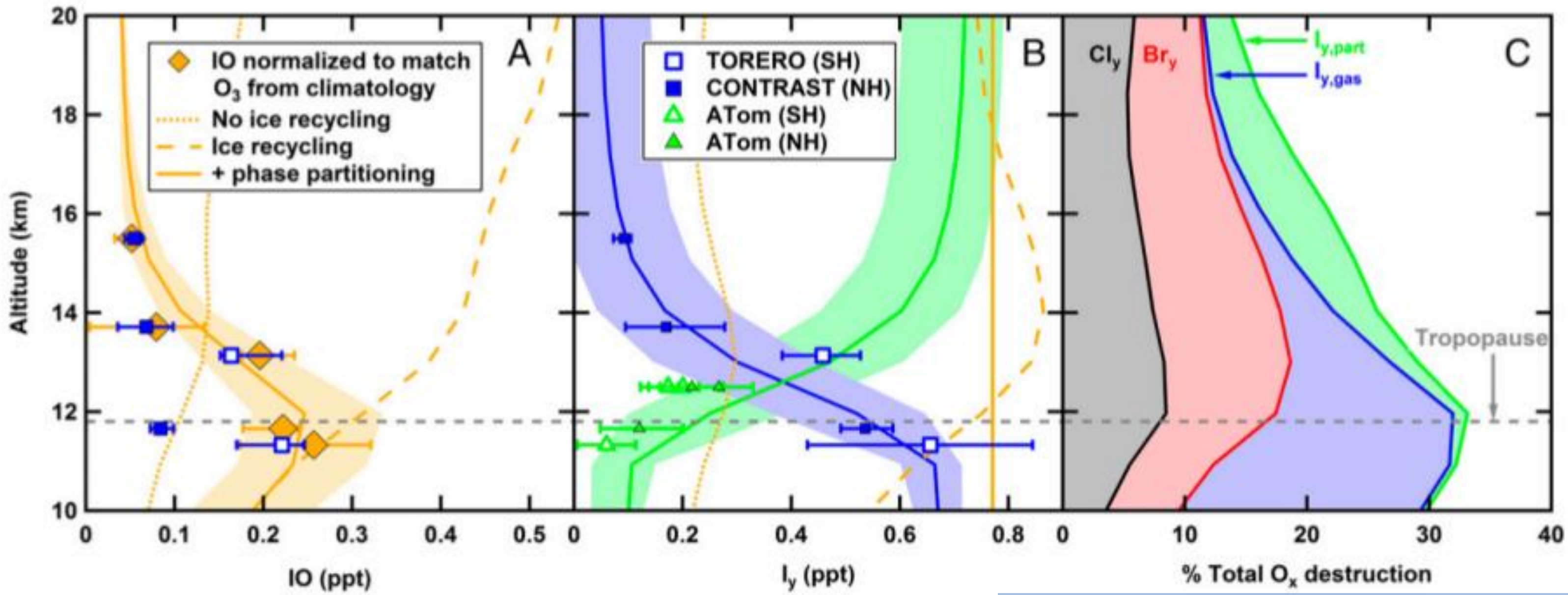
user_nl_cam + chem_mech.in + mo_usrrxt.F90 + mo_strato_rates.F90

```
*********************************
*** Stratospheric Aerosol
*********************************
[slf_str_i_1]          IONO2 -> HOI + HNO3
[slf_str_i_2]          HOI + HCL -> ICL + H2O
[slf_str_i_3]          HOI + HBR -> IBR + H2O
[slf_str_i_4]          HOI + HI -> I2 + H2O
[slf_ipart_1]          IONO2 -> IPART
[slf_ipart_2]          HOI + HCL -> IPART
...
[ice_str_i_1]          IONO2 -> HOI + HNO3
[ice_str_i_2]          HOI + HCL -> ICL + H2O
[ice_str_i_3]          HOI + HBR -> IBR + H2O
[ice_str_i_4]          HOI + HI -> I2 + H2O
[ice_ipart_1]          IONO2 -> IPART
[ice_ipart_2]          HOI + HCL -> IPART
```

Formation of Particulate Iodine
Iy_gas → Iy_part

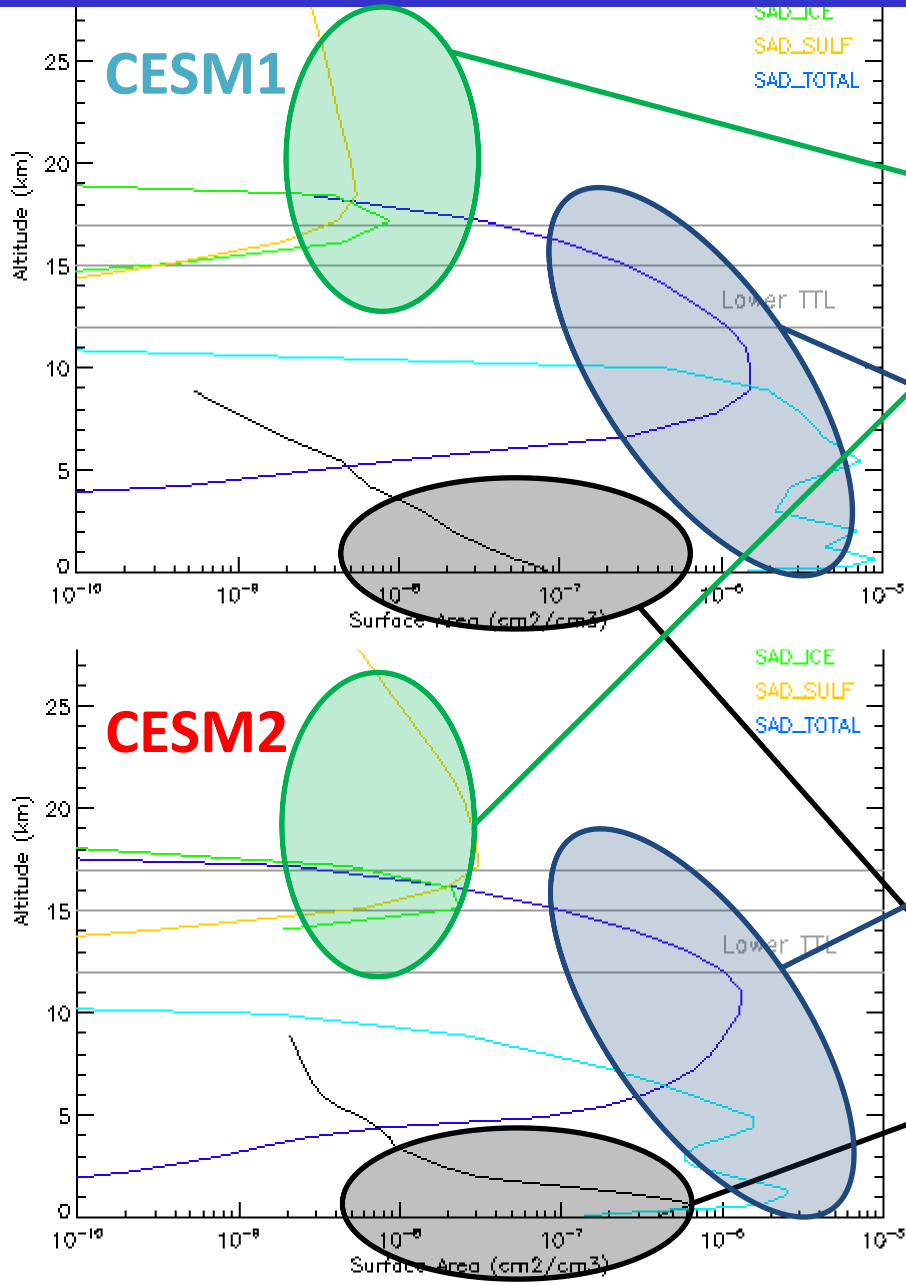
↓

Phase change of iodine species
Uptake by stratospheric aerosols



Koenig et al., PNAS, 2020

SAD fields: CESM1 vs CESM2



Tropical mean (20ºN – 20ºS)

SAD_SULF & SAD_ICE
CESM2 > CESM1

SAD_ICETROP
CESM1 ≈ CESM2

SAD_LIQTROP
CESM1 > CESM2

SAD_SSLT
CESM2 >> CESM1

Conclusions

❖**VSL Halogen Chemistry is now included in CESM 2.2**

- ❖***Tuning was required for heterogeneous processes due to changes in SAD, mostly on SAD SSLT and Liquid Clouds***
- ❖***Washout efficiency and uptake for soluble reservoir species is performed both using NEU routine and the FR Approx. approach.***
- ❖***Both Halogen SGs and PGs show equivalent spatial and vertical distributions as in CAM4-Chem (CESM1)***
- ❖***Tropospheric Burden and Impacts are sensitive to changes in model spatial resolution and compsets (FR vs. SD) due to changes in SAD***
- ❖***A proper representation of atmospheric halogen impacts requires using a Full Chemical Treatment of VSL Halogens in the troposphere and stratosphere***

CONTACT

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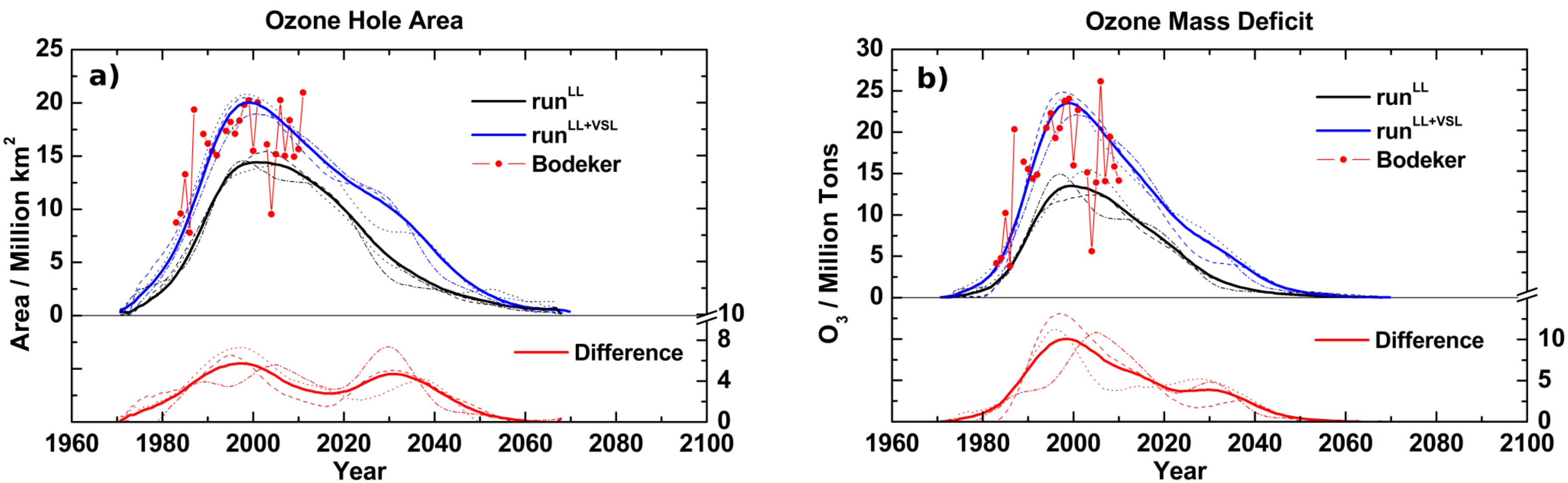
Rafael P. Fernandez rpfernandez@mendoza-conicet.gob.ar

Impact of VSL^{Br} on the OHA

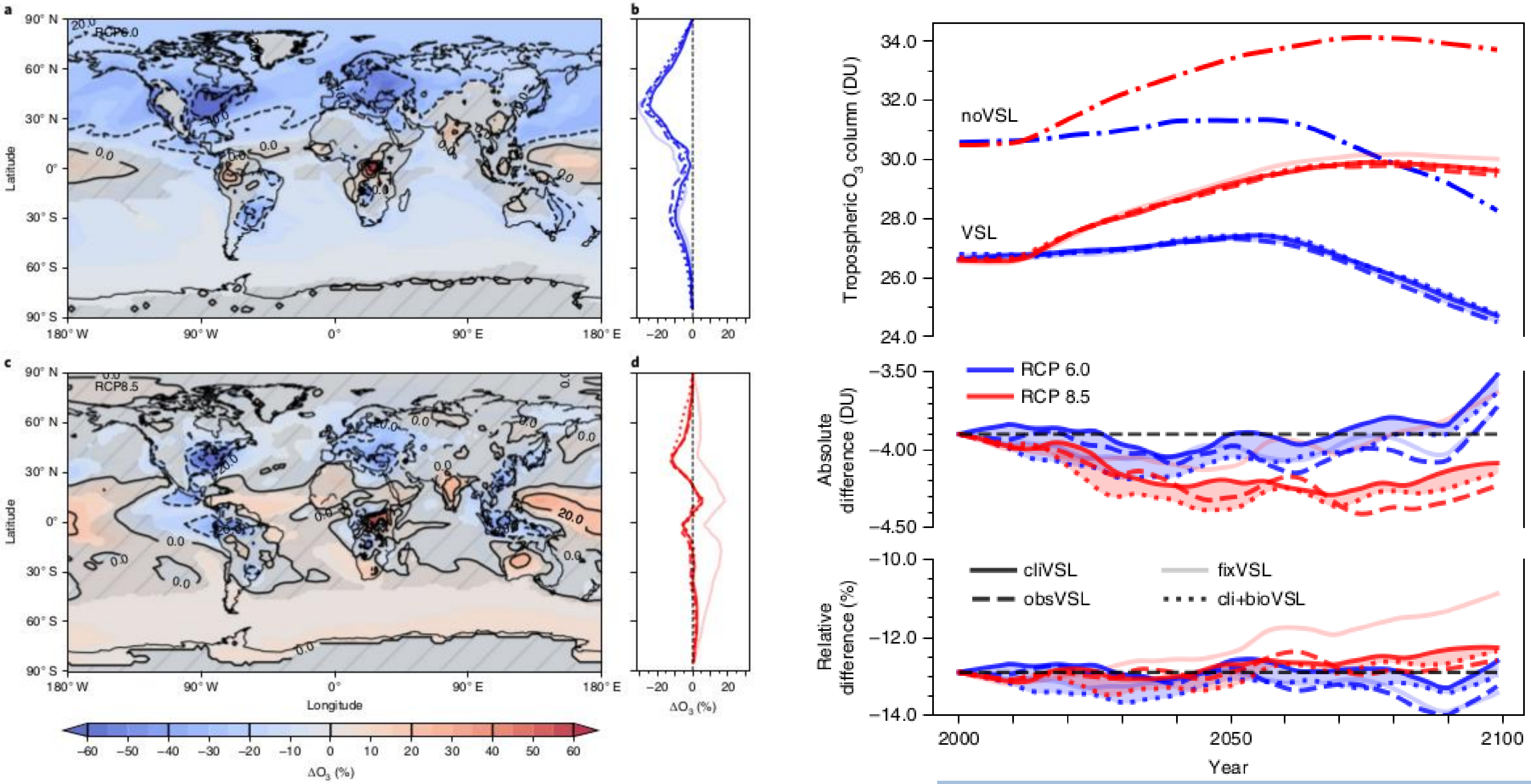


Impact of Biogenic VSL^{Br}:

- Including VSL^{Br} improves the model-measurement agreement
- The biogenic bromine-driven **OHA enlargement is ~5 million km^2**, equivalent to the current chemical healing shrinkage estimated due to the phase-out of LL^{Cl} and LL^{Br} emissions (***Solomon et al., 2016***).
- VSL^{Br} increases the max. OHA by 40% during the 2000th decade, and **doubles the ozone hole extension during 2030th decade**.

Fernandez et al., ACP, 2017

Natural Halogens Buffers Tropospheric Ozone



Iglesias-Suarez et al., NCC, 2017