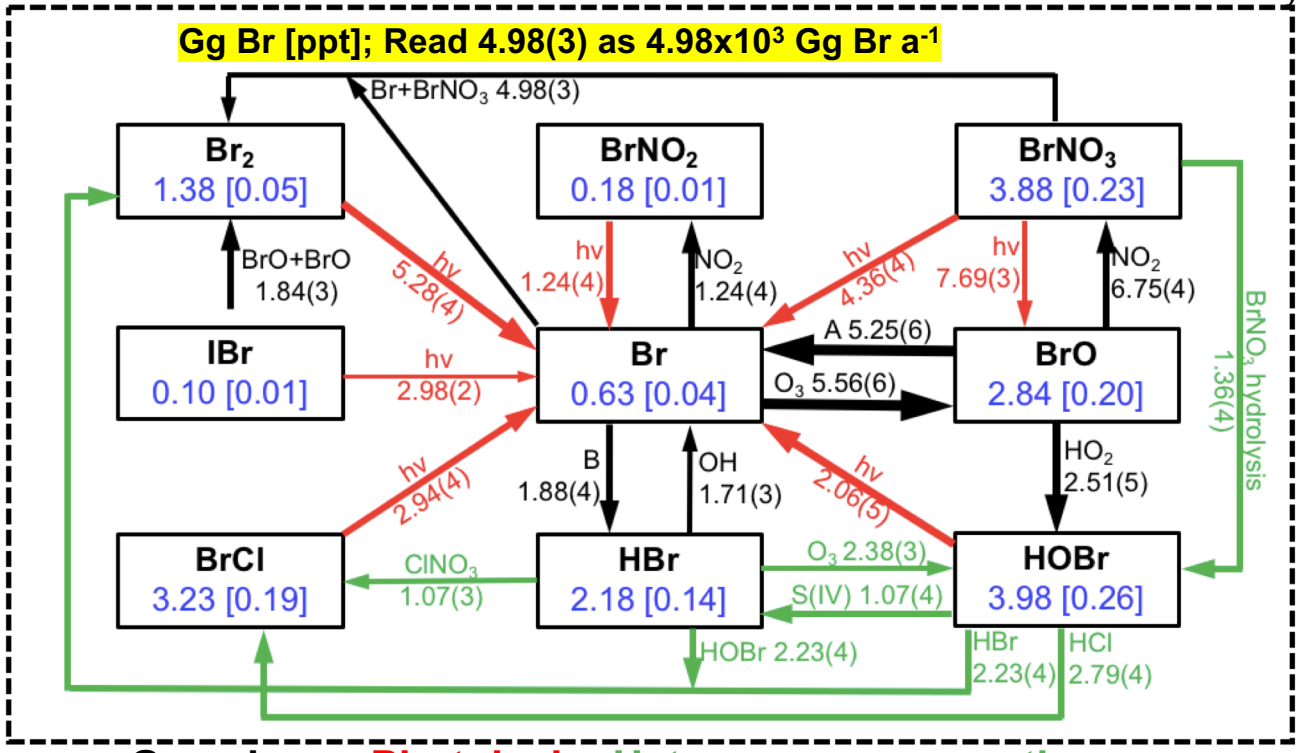
Modeling of tropospheric halogen (Cl-**Br**-I) chemistry: cycling, debromination, and impact

Global annual mean inventory of tropospheric inorganic bromine (Br_y)



Gas phase; Photolysis; Heterogeneous reactions

Results based on one-year simulation (v1102-d, 2012, 4x5, MERRA2)

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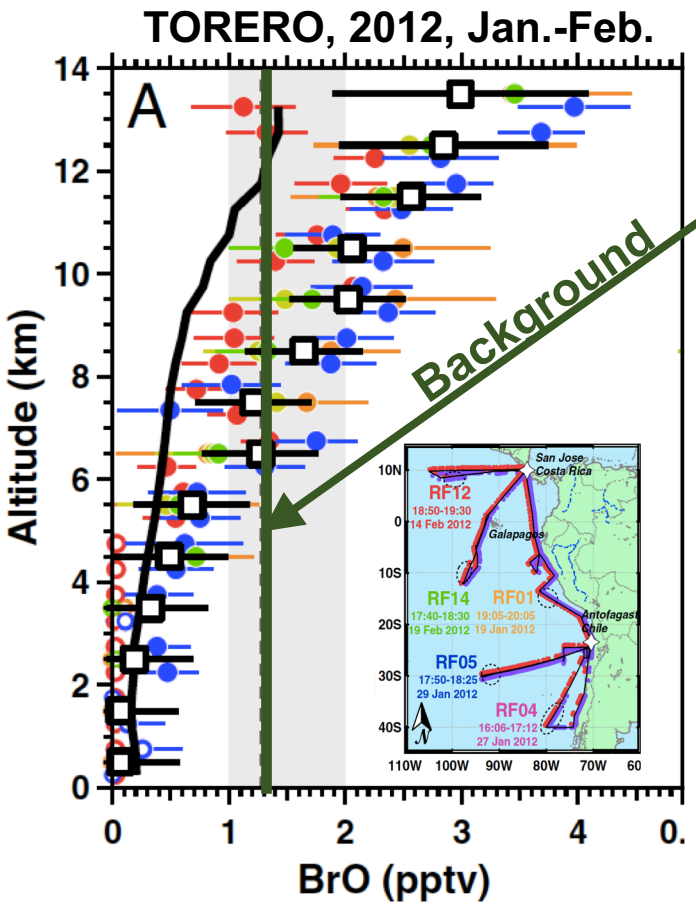
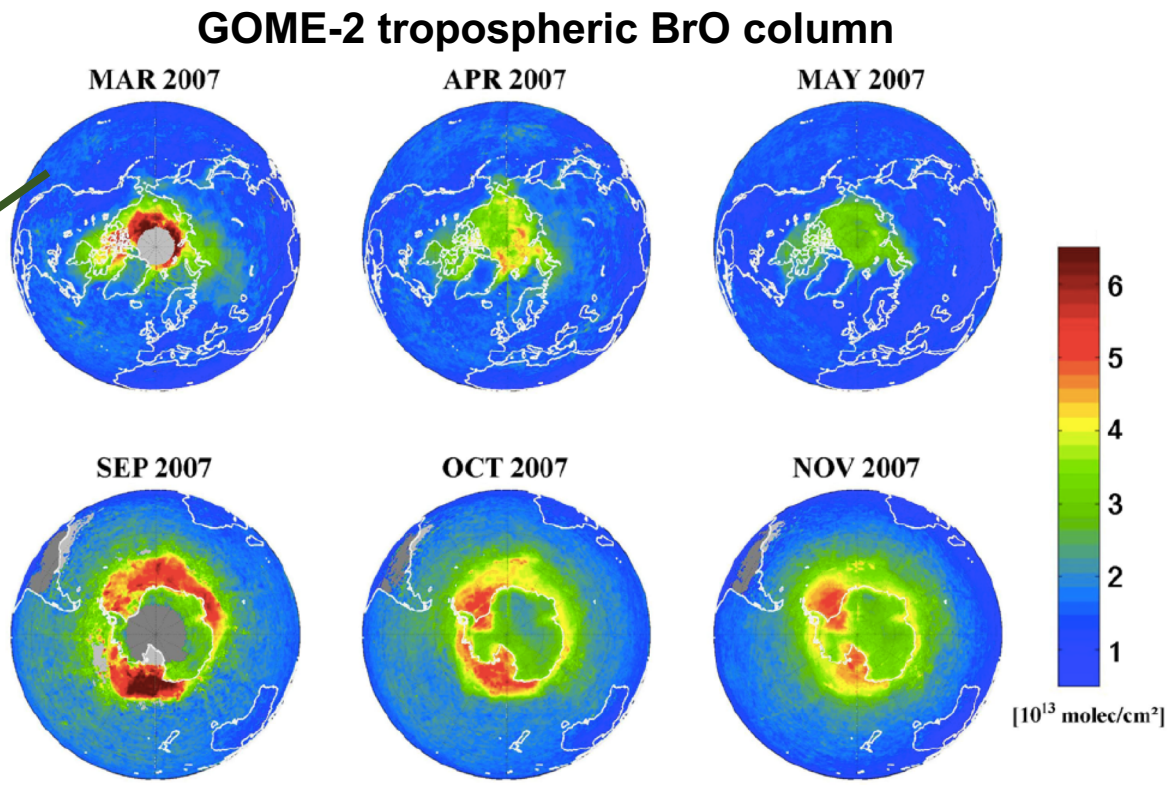
Increasing evidence for widespread bromine in the troposphere





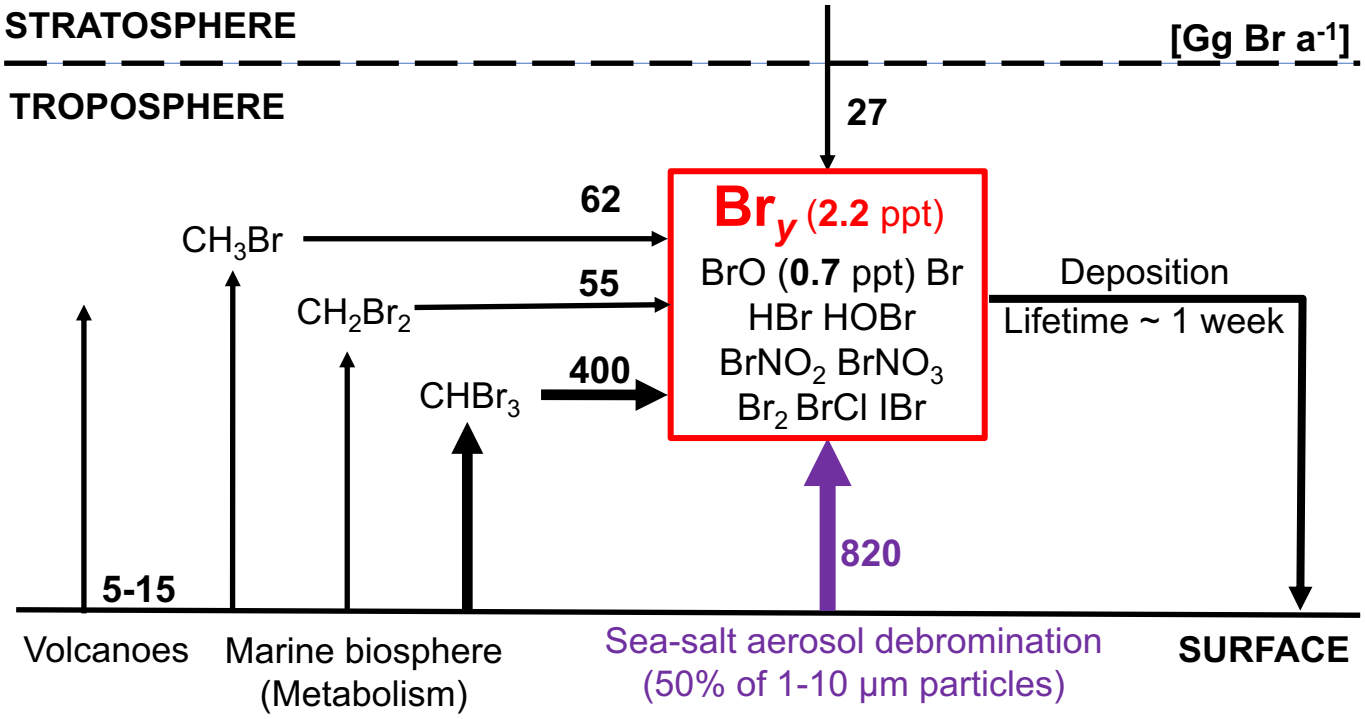
- Tropospheric daytime BrO background: ~1ppt

- Bromine radicals (Br and BrO) play important roles in tropospheric chemistry by:
  - depleting ozone and OH
  - oxidizing elemental mercury and VOCs

Probably impact your work!

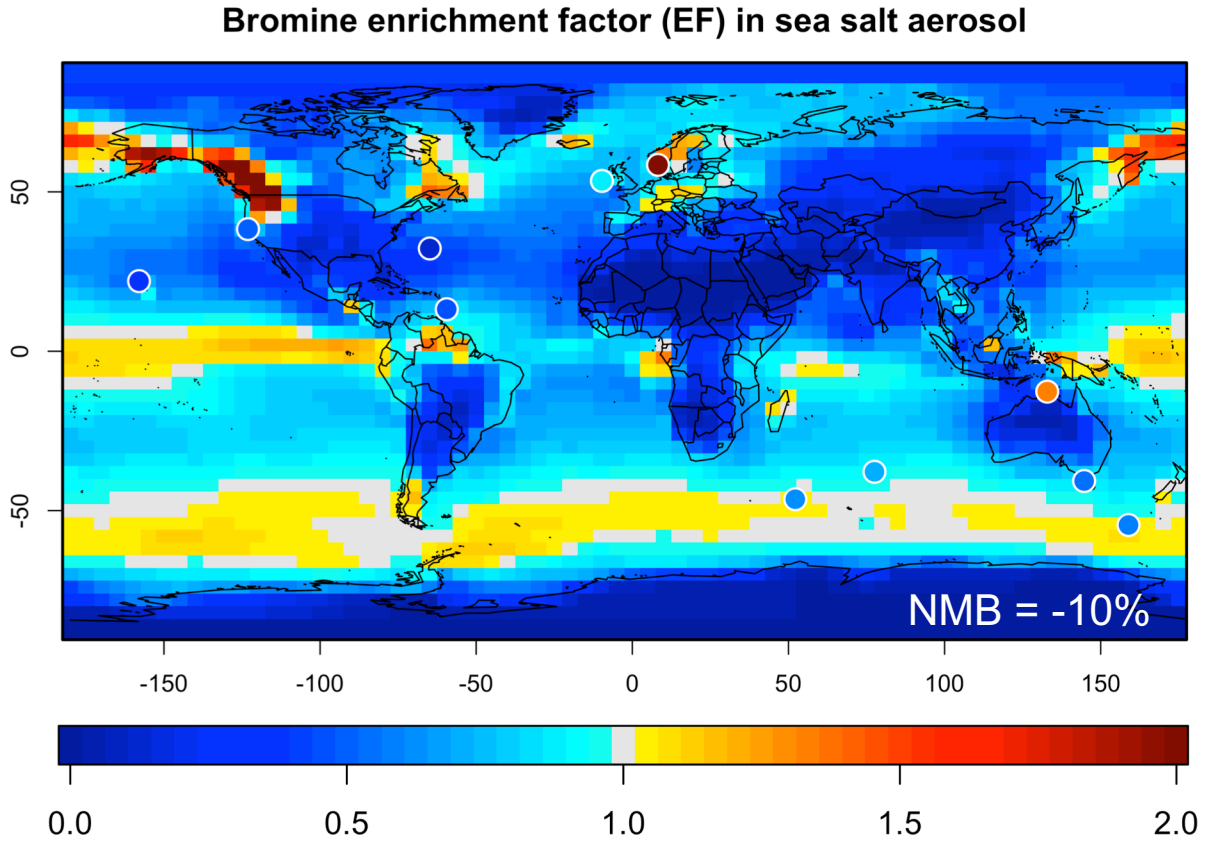
[Theys et al. 2011; Wang et al., 2015]

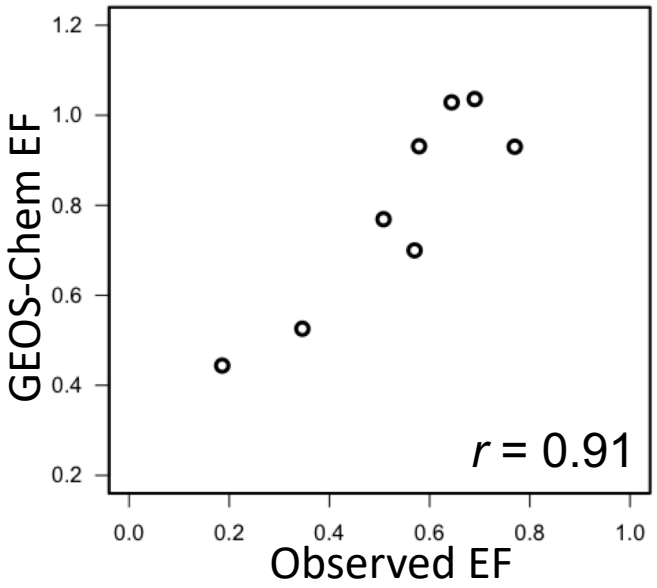
Global tropospheric budget for inorganic halogen (Br_y)



- Global source of tropospheric halogens is mainly natural and from the oceans
  - Bromoform ($CHBr_3$) is major source in the free troposphere
  - *Conundrum*: Sea salt aerosol (SSA) is the dominant global source, but caused too high BrO in previous model studies

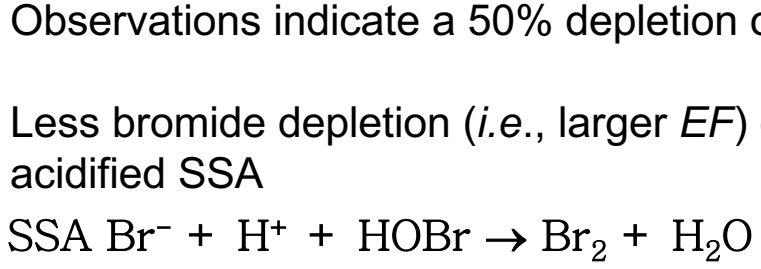
Modeling of sea salt aerosol (SSA) debromination





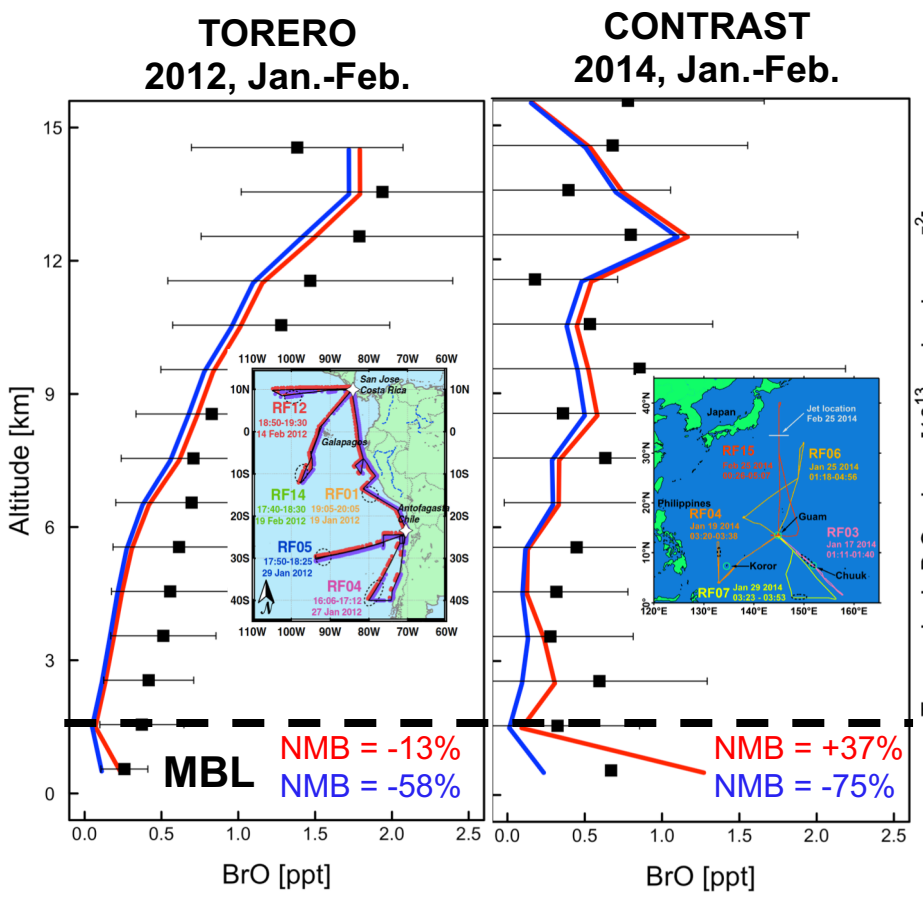
$$EF(\mathrm{Br}) = \frac{\left(\frac{[\mathrm{Br}^-]}{[\mathrm{Na}^+]}\right)_{\mathrm{SSA}}}{\left(\frac{[\mathrm{Br}^-]}{[\mathrm{Na}^+]}\right)_{\mathrm{Sea\ water}}}$$

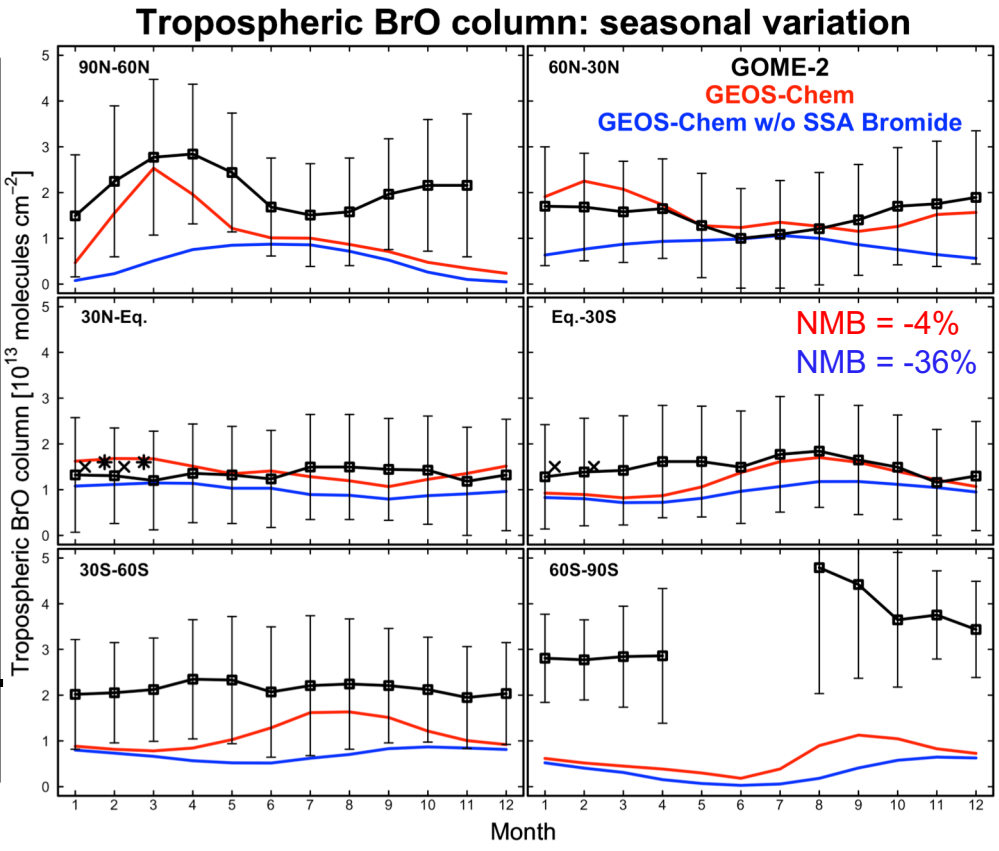
- Observations indicate a 50% depletion of bromide in SSA relative to seawater composition
- Less bromide depletion (*i.e.*, larger *EF*) over the Southern Ocean - debromination only occurs in acidified SSA



EF(Br) data are from Sander et al. [2003] and Newberg et al. [2005]; Results based on one-year simulation (2012, 4x5, MERRA2)

Observational constraints on BrO





- BrO in the marine boundary layer are maintained at relatively low levels by adding:

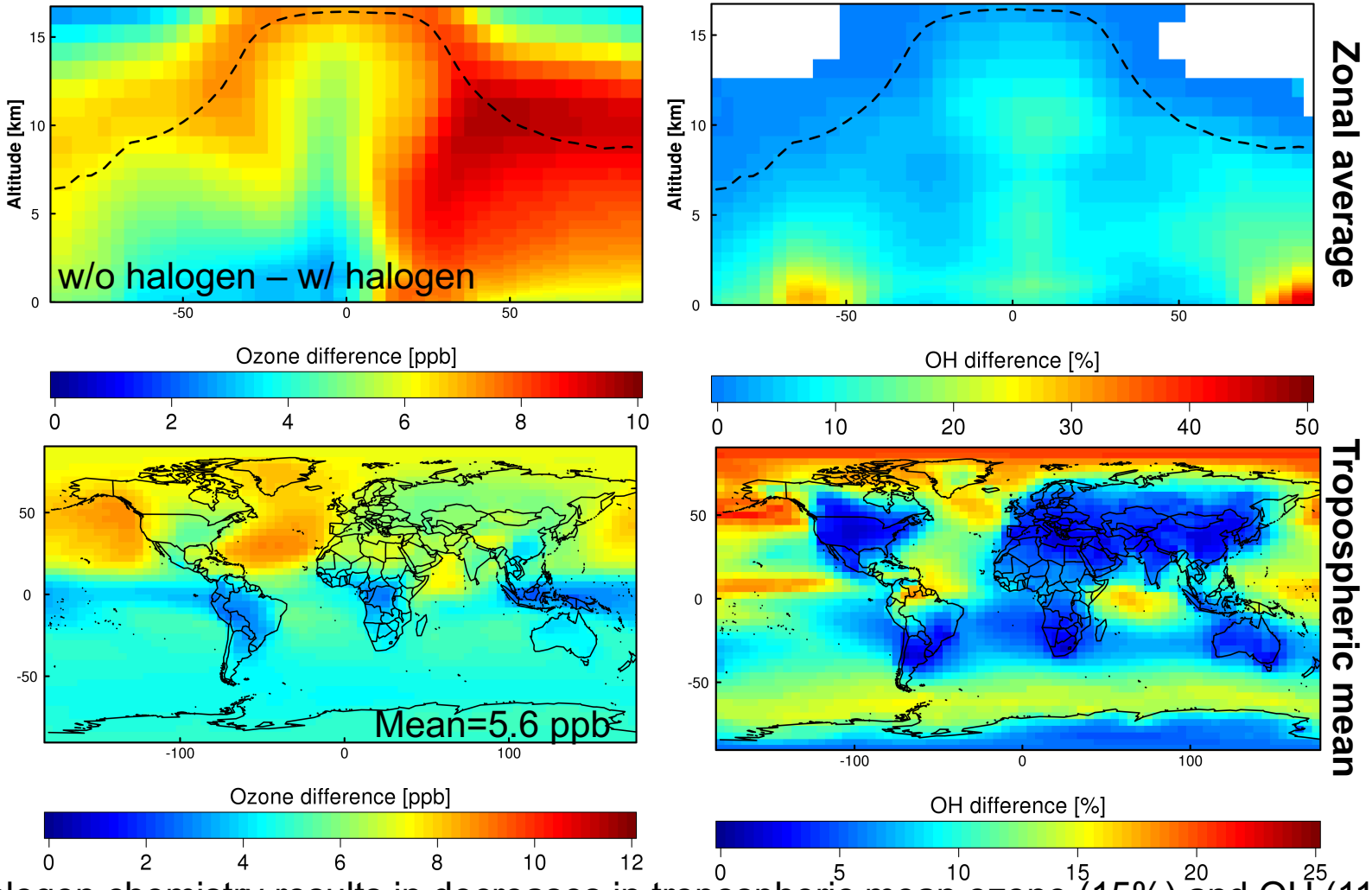
  $HOBr(aq) + HSO_3^-/SO_3^{2-} \rightarrow HBr + HSO_4^-/SO_4^{2-}$

  $Br + CH_3CHO \rightarrow HBr + CH_2CHO$

- Uptake of HBr by the sea salt aerosol becomes the major sink of Br_y

[Millet et al. 2010; Chen et al., 2017]

Effect of halogen chemistry in tropospheric ozone and OH



- Halogen chemistry results in decreases in tropospheric mean ozone (15%) and OH (11%)
- SSA debromination will be off in v11-02 because it breaks ozone

- A cycling Br_y family
- Sea salt aerosol as a source and a sink of bromine
- To make SSA debromination consistent with ozone