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

Global annual mean inventory of tropospheric inorganic bromine (Br$_y$)

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

Bromine enrichment factor (EF) in sea salt aerosol

- 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

SSA $\text{Br}^-$ + $\text{H}^+$ + $\text{HOBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$

$EF(\text{Br}) = \frac{[\text{Br}^-]/[\text{Na}^+]}{[\text{Br}^-]/[\text{Na}^+]}_{\text{Seawater}}$

$NMB = -10\%$

$GEOS-\text{Chem} \quad r = 0.91$

$EF(\text{Br})$ data are from Sander et al. [2003] and Newberg et al. [2005]; Results based on one-year simulation (2012, 4x5, MERRA2)
BrO in the marine boundary layer are maintained at relatively low levels by adding:

\[
\text{HOBr}(aq) + \text{HSO}_3^-/\text{SO}_3^{2-} \rightarrow \text{HBr} + \text{HSO}_4^-/\text{SO}_4^{2-}
\]

\[
\text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{HBr} + \text{CH}_2\text{CHO}
\]

- Uptake of HBr by the sea salt aerosol becomes the major sink of Br\text{y}
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