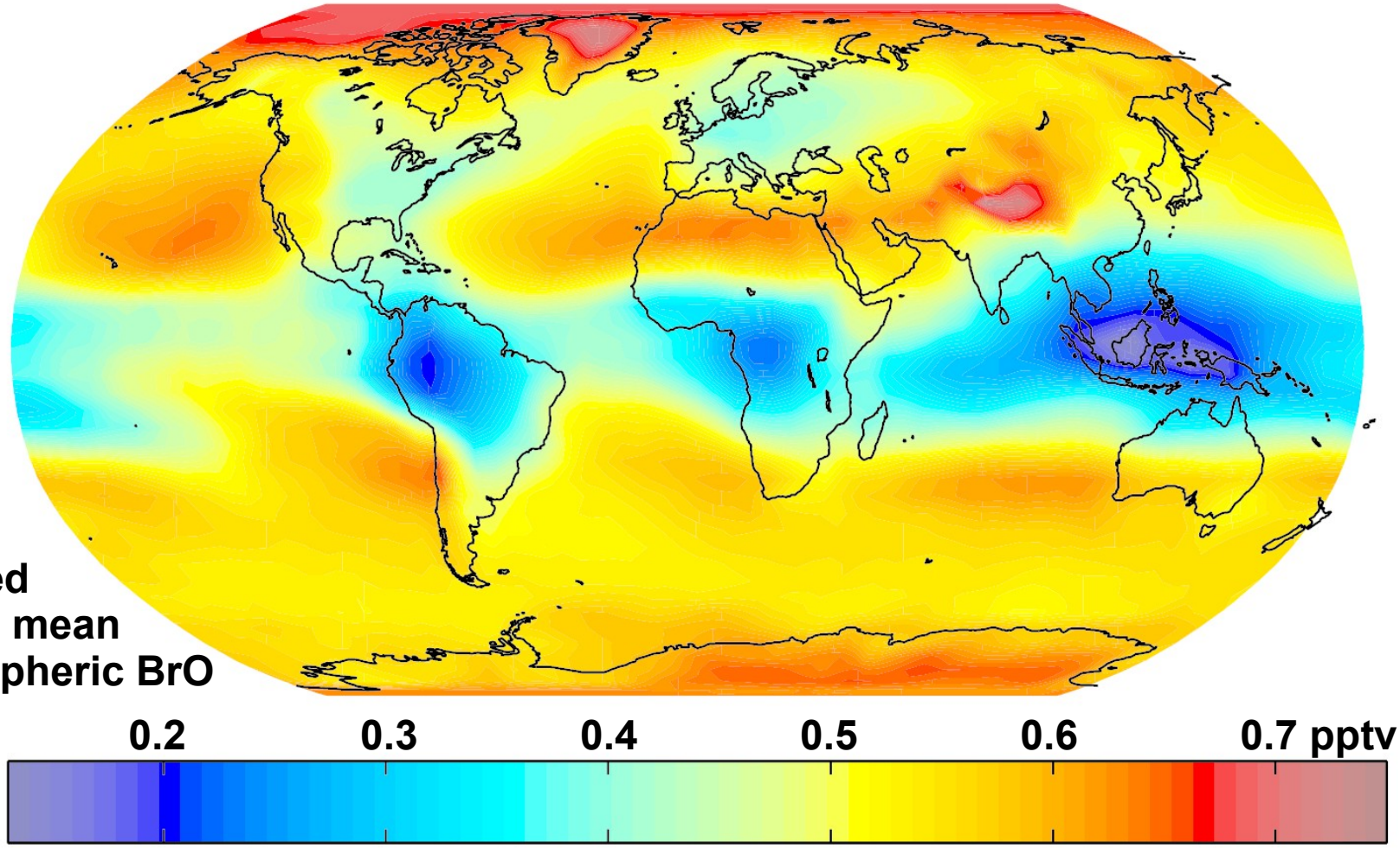
Halogen chemistry in GEOS-Chem: Accounting for elevated BrO levels



Modeled Annual mean Tropospheric BrO

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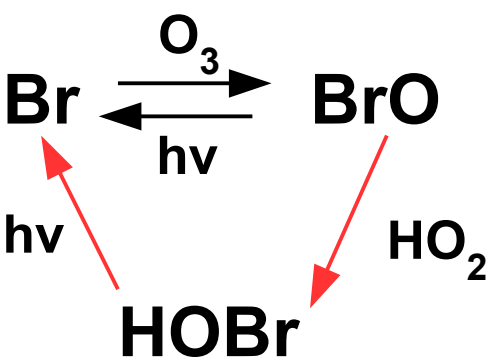
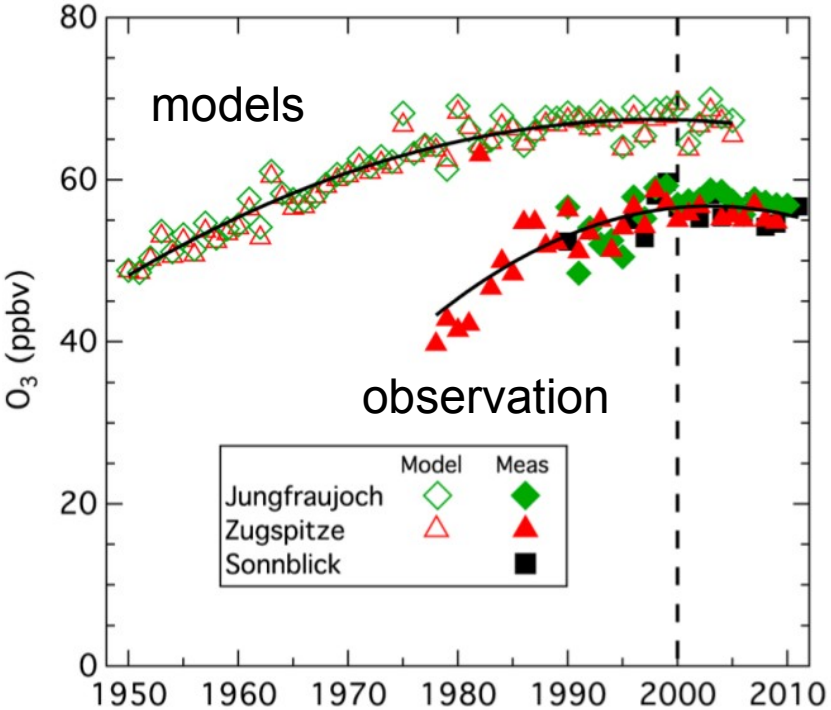
Acknowledgments: **HU ACMG:** D. Jacob, L. Hu, H. Horowitz; **TORERO:** R. Volkamer, S. Wang; **CAST:** M. Le Breton; **NASA:** Q. Liang; **HS CfA:** K. Chance, G. Abad; **MIT:** S. Eastham; **Danish Foundation for Independent Research**.

New observations point to pptv levels of inorganic bromine in the troposphere

- Bromine catalyze ozone destruction: Low levels (BrO ~ 1 pptv = 10^{-12}) are enough to cause significant ozone loss.
- But the role of bromine chemistry in the troposphere is still unclear.
- Tropospheric bromine sources include: Sea salt, bromocarbons, stratosphere.
- Parrella et al. (2012; GC v9-02) showed a 6.5 % decrease in global tropospheric ozone by bromine.
- New observations point to even higher levels of BrO and HOBr.

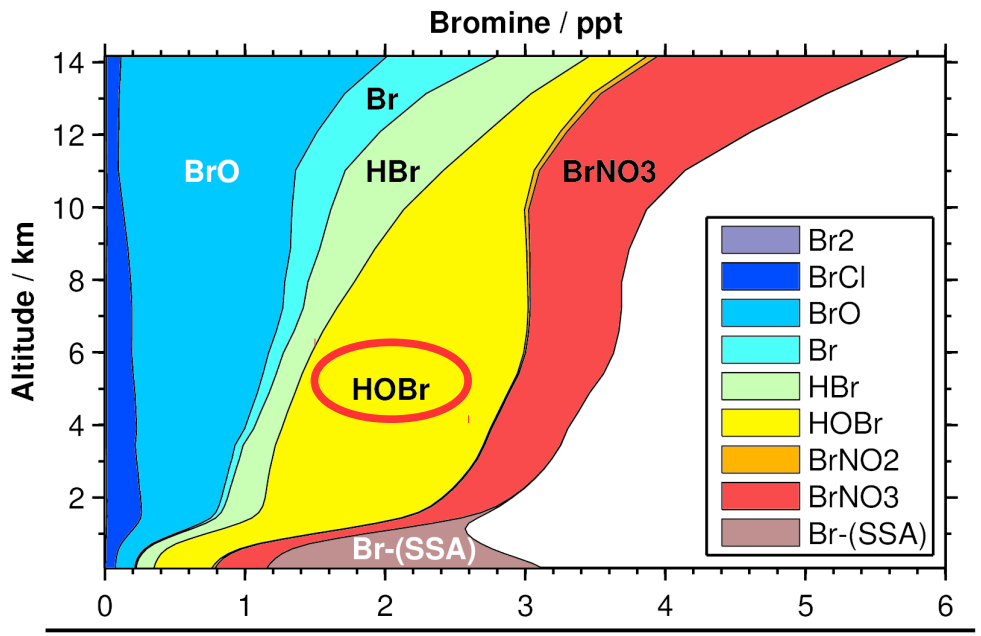


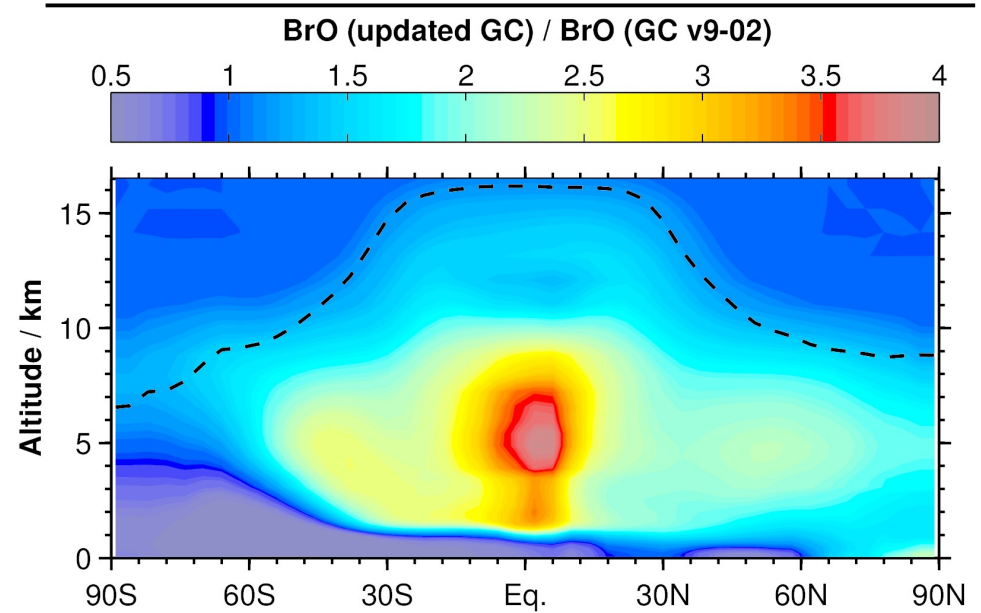


Parrish et al (2014)

An updated GC halogen mechanism: Chlorine and multiphase Br^- cycling

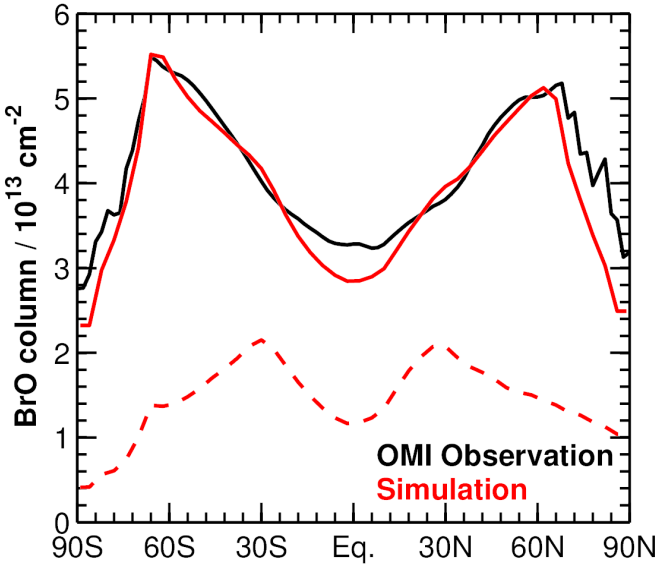
- New multiphase mechanism
  - Br^- oxidation by HOBr, $ClNO_3$ and ozone
  - Br^- oxidation on sea salt, sulfate and clouds (liq + ice)
- Added mechanism for tropospheric chlorine radicals and reservoirs
- Bromocarbon emissions validated against HIPPO, CARIBIC and TORERO observations
- HOBr is now dominant inorganic Br reservoir (HBr in GC v9-02)
- BrO increased by 50% on average and up to 300% in tropics compared to GC v9-02.

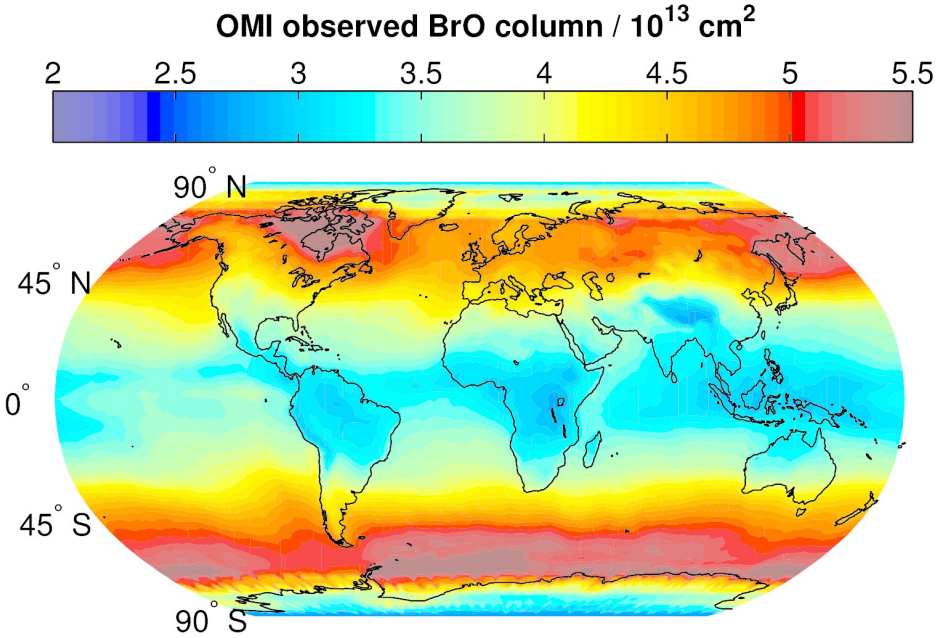


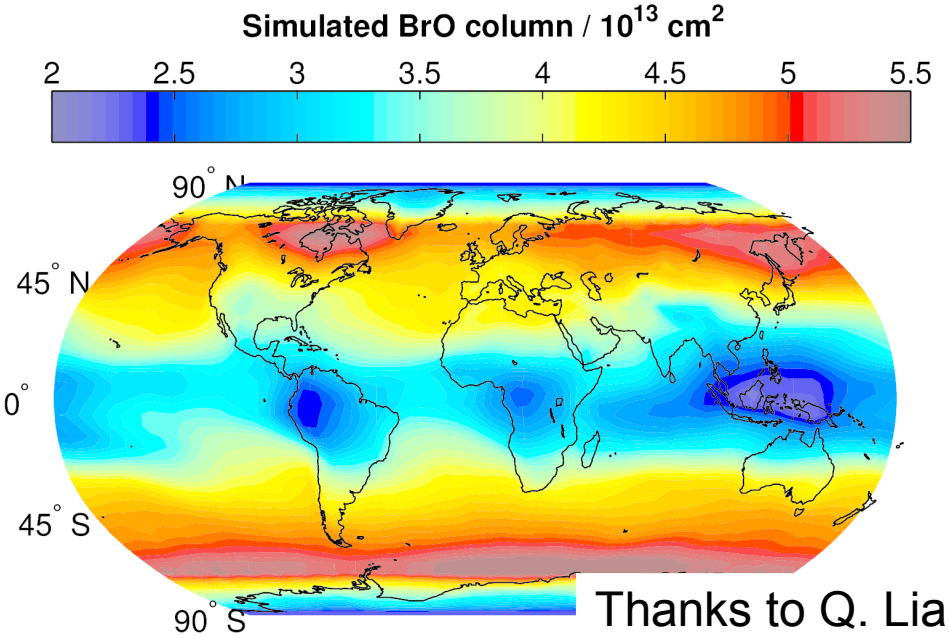


Simulated BrO column density agree with OMI and GOME-2 satellite observations

- Good agreement with OMI total (strat + trop) BrO column observations
- Model low bias in polar regions
- Tropospheric BrO account for between 25% and 55% of the total BrO column in tropics and at mid-latitudes
- Excessive heterogeneity in tropics



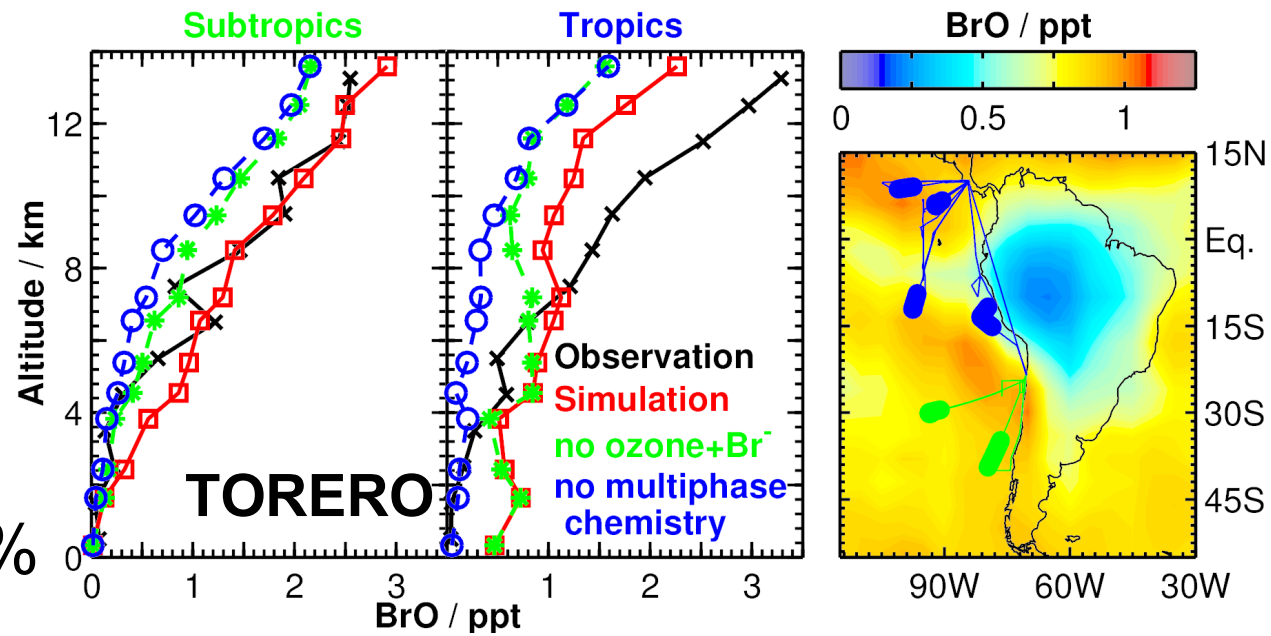


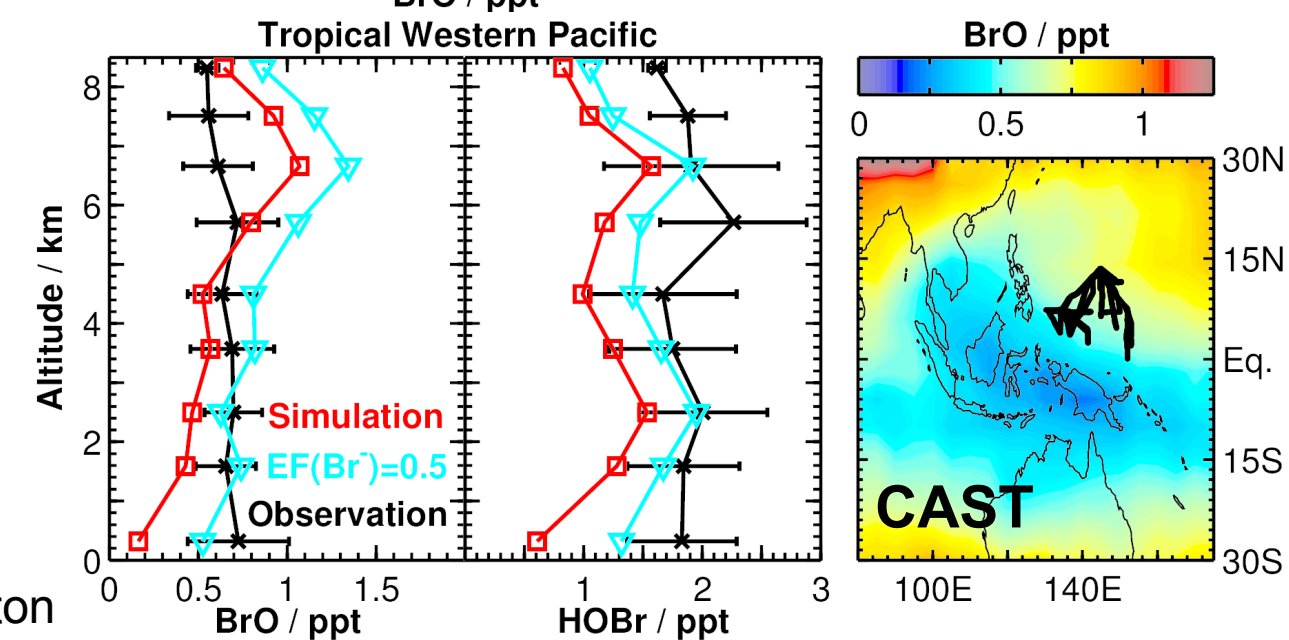


Thanks to Q. Liang

Simulated BrO and HOBr consistent with recent aircraft observations

- Model BrO low bias in tropical upper troposphere.
- Oxidation of Br^- by ozone enhance BrO 30% to 100% in subtropics.
- High levels of HOBr in tropics consistent with model HOBr being dominant Br_y reservoir

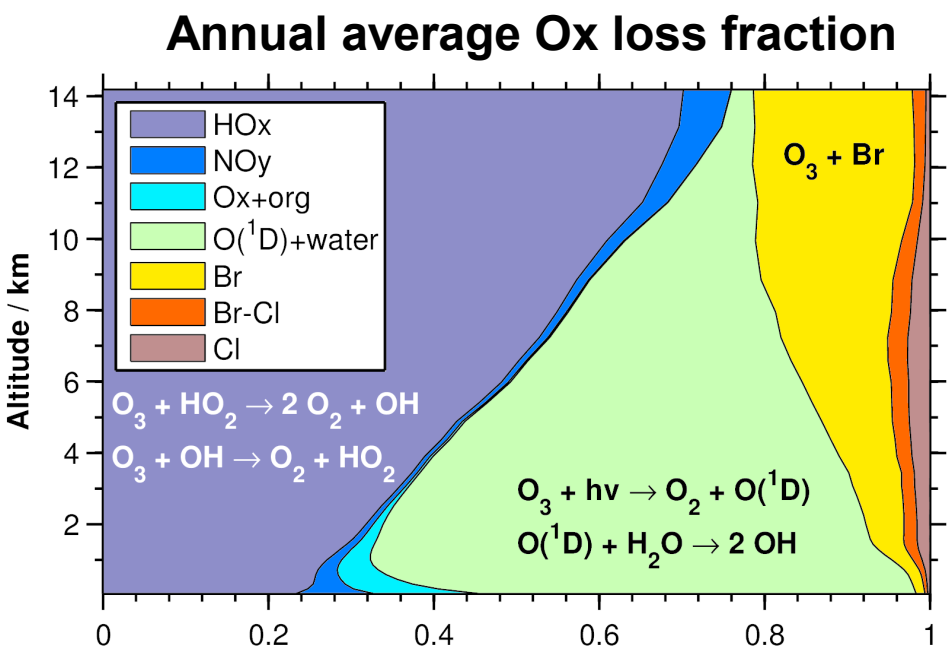


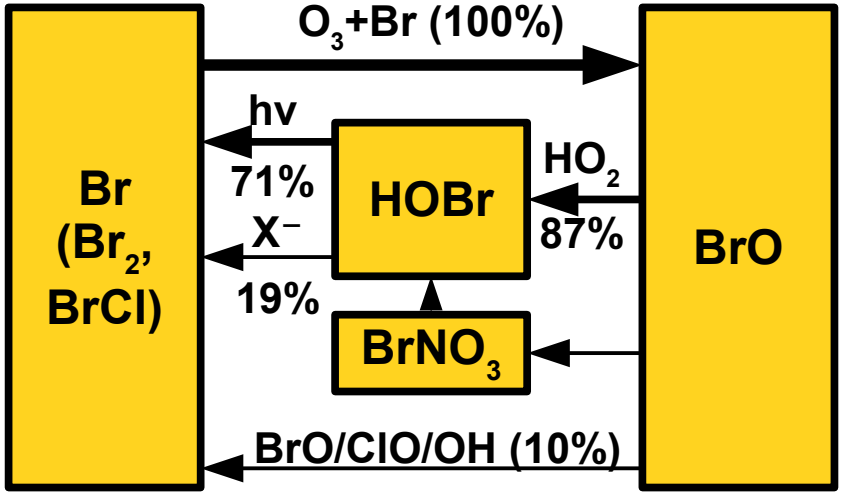


Thanks to R. Volkamer and M. Le Breton

Halogen chemistry (Br,Cl) drive 20% of Ox loss in the upper troposphere

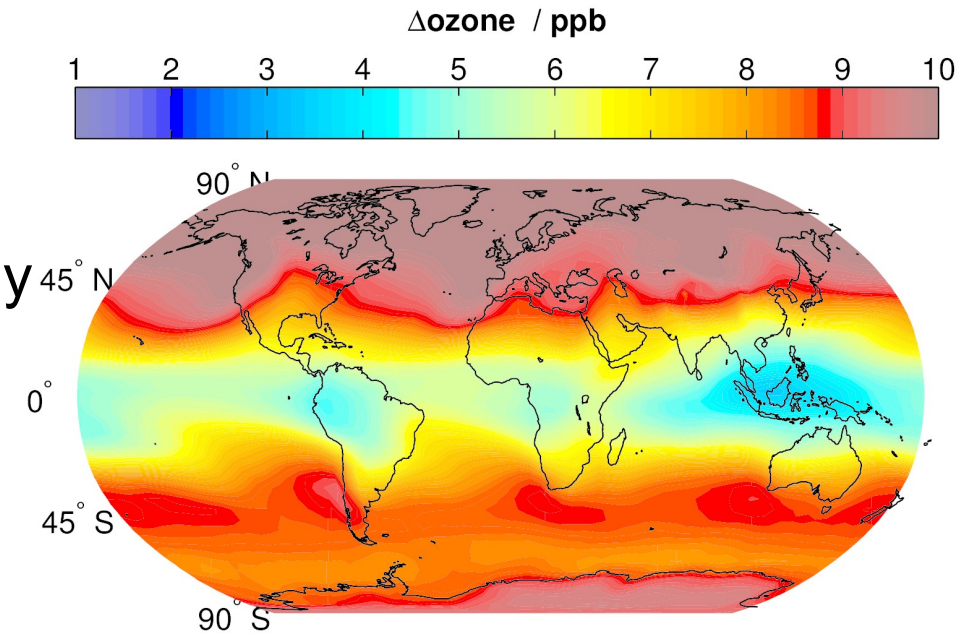
- Halogen Ox loss mainly due to inorganic bromine cycles
- Cycling of HOBr is dominant halogen Ox loss mechanism
- Br-Cl cross coupling via HOBr+Cl⁻ accelerates HOBr cycling and drive ~15% of halogen Ox loss
- Contribution from iodine not considered (Tomás Sherwen)

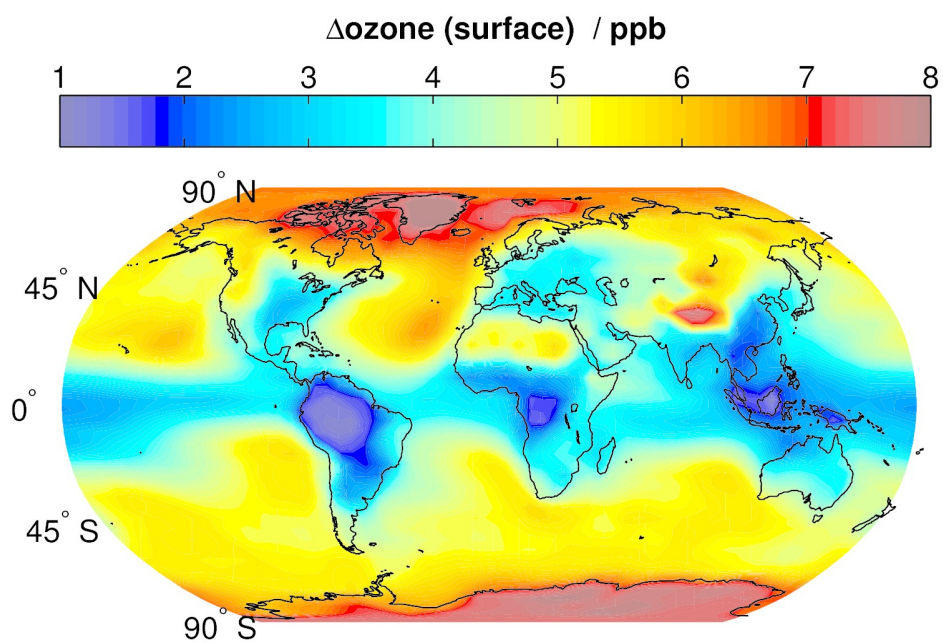




Halogen chemistry (Br and Cl) lowers tropospheric ozone by 1 to 12 ppb

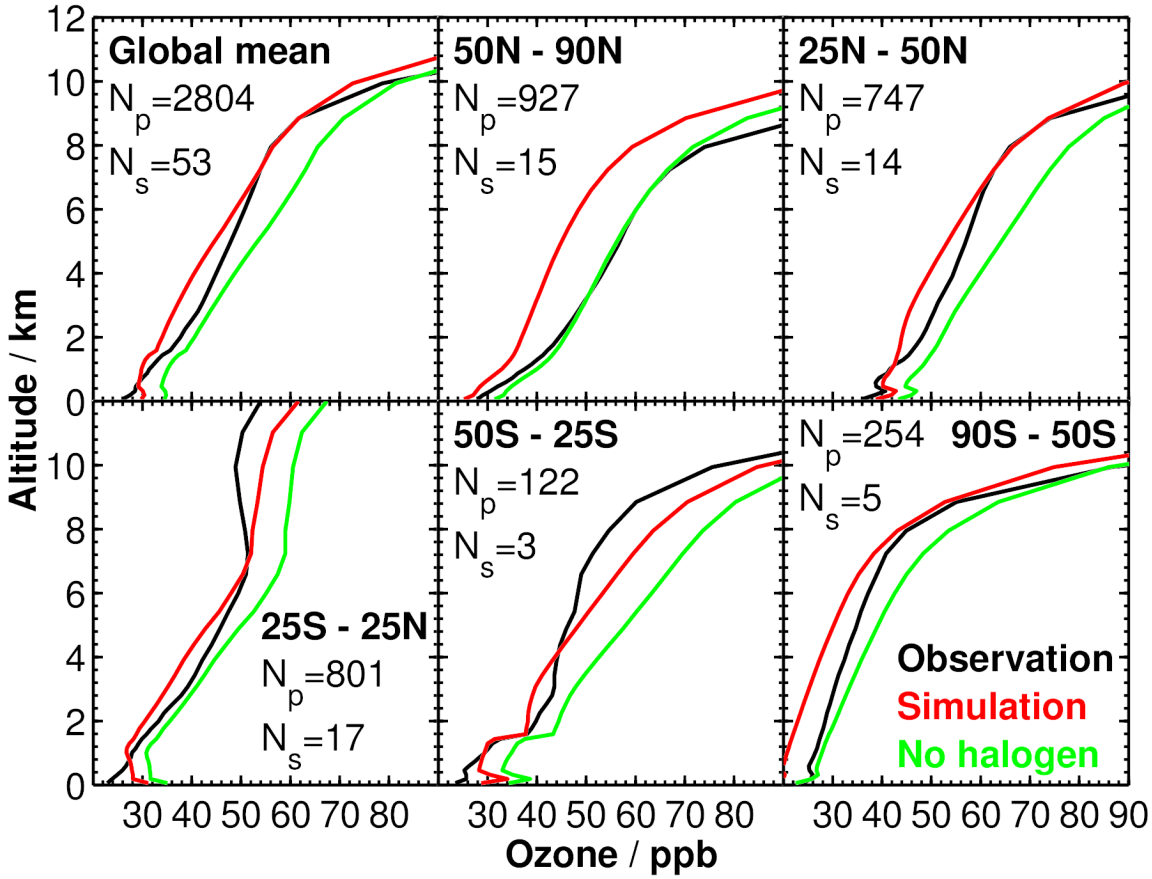
- Figure shows change in ozone: Δ(ozone) = “no halogen” – “halogen”
- Bigger ozone suppression than previously recognized, e.g. Parrella et al (2012).
- Ozone column decreases:
  - 3 to 7 ppb in Tropics
  - 6 to 10 ppb at mid-latitudes
  - >8 ppb at high-latitudes
- Surface ozone decreases 2 to 5 ppb over N. America and Europe.
- Global OH lowered 11% ...
- ... resulting in prolonged model methane lifetime from 7.1 yr to 8.0 yr in better agreement observations (9.1±1 yr)





Halogen chemistry reduce model – ozone sonde high bias

- Halogen chemistry reduce model – observation ozone bias in tropics and at mid-latitudes
- But increases ozone low bias at northern high-latitudes compared to sonde observations



Average over 53 sites and 2804 ozone sonde profiles

Thanks to Lu Hu