Br radicals in the tropical troposphere: a GEOS-Chem perspective

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CONTRASTATTREX/CAST STM (October 22nd)

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Why do we care about bromine in the (sub) tropical troposphere?

- Role of Br in tropical troposphere still unclear
- Increasing evidence for significant bromine radical activity in the tropical troposphere
- Tropospheric bromine chemistry affect:
  - **Trop. O_3:** GHG; air pollution; OH precursor => CH_4.
  - **NO_x:** O_3 precursor.
  - **Hg:** Pollutant; Neurotoxin; Bio accumulate.
  - **DMS:** Sulfate precursor.

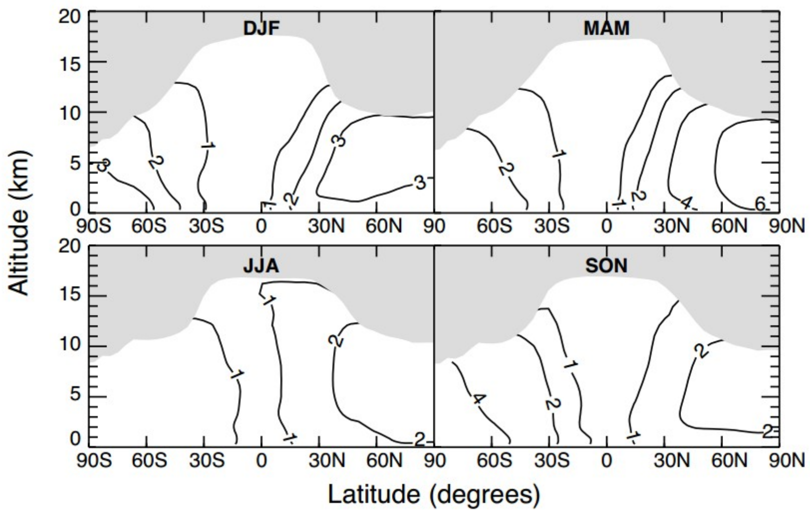


Fig. 6. Decrease in tropospheric ozone (nmol mol^{-1}) from bromine chemistry. The figure shows zonal seasonal mean differences between GEOS-Chem simulations including vs. not including bromine chemistry. Shading indicates the stratosphere.

Parrella et al. ACP (2012)

Why do we care about bromine in the (sub) tropical troposphere?

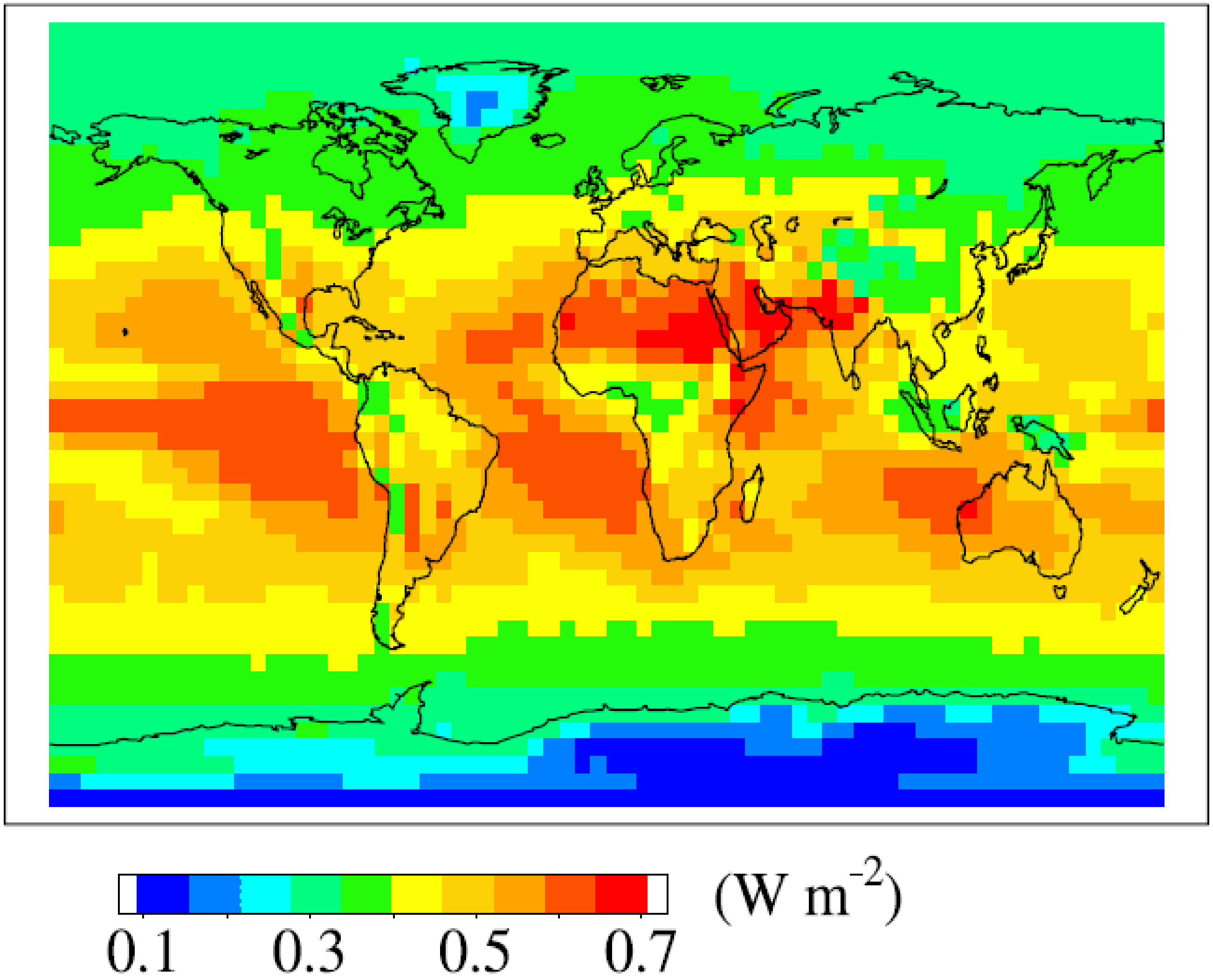
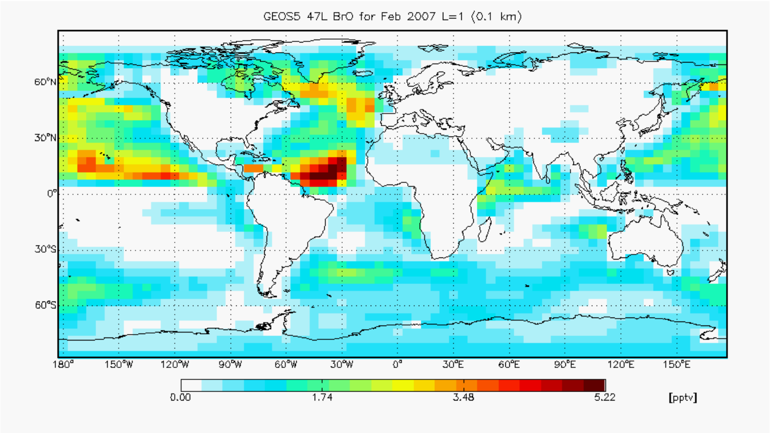


Fig. 3 of Mickley et al. (2004): Change in forcing due to uniform 18 ppb increase to pre-industrial tropospheric ozone.

Overview of the GEOS-Chem Chemical Transport Model

- **Global 3-D model of the troposphere**
- **Offline Stratospheric Bry from GEOSCCM**
- **Driven by meteorological data**
  - GEOS-5 model
- **Contains ~80 transported species:**
  - Ox (O_3, HO_2 ...)
  - NOx (NO, NO_2, HNO_3)
  - Br (Br, BrO, Br_2, $CHBr_3$ ...)
  - Etc ...
- **Contains ~10^2 chemical reactions:**
  - gas phase
  - Photolysis
  - heterogeneous (surface)
  - Emissions
  - Wet and dry deposition

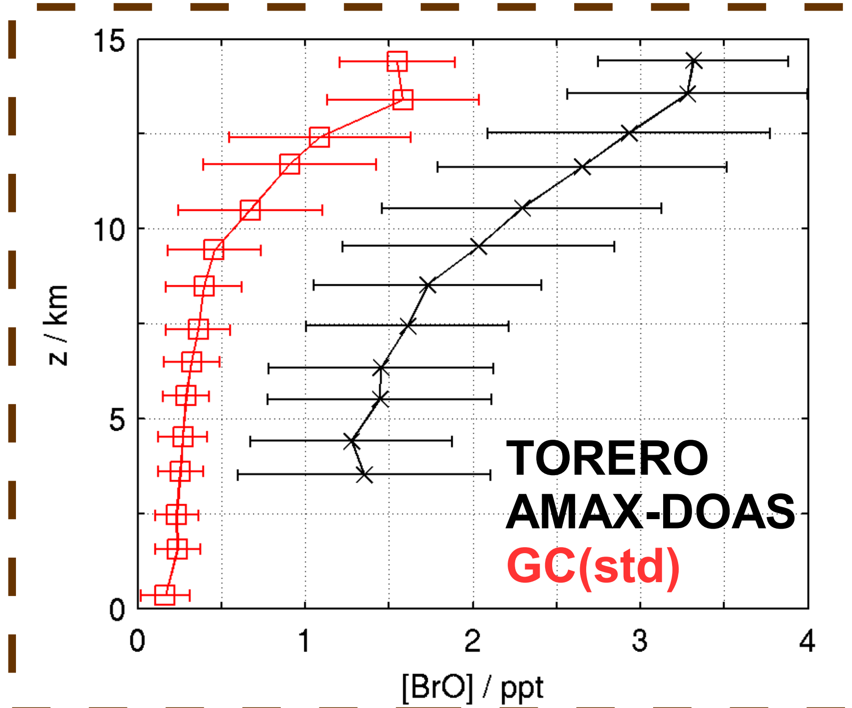


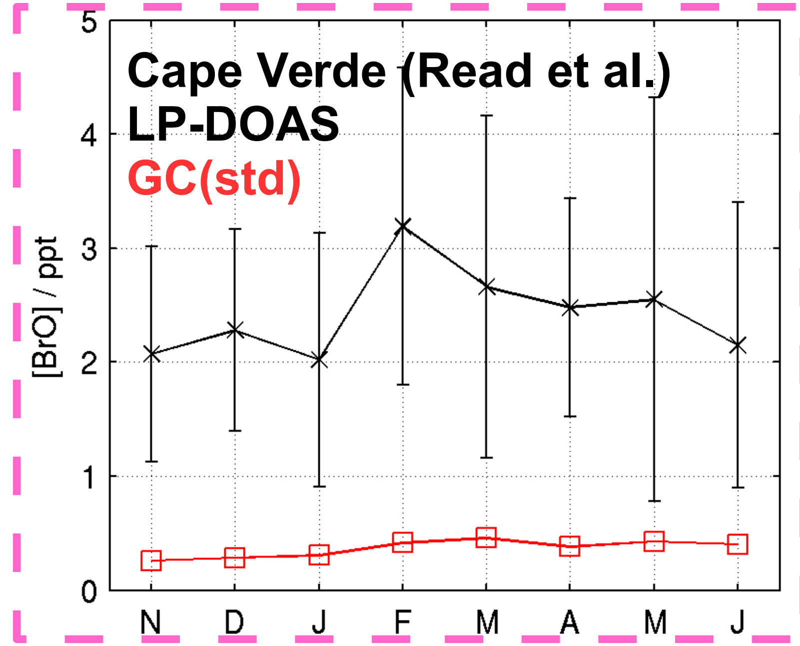
Daytime surface BrO from GEOS-Chem with new halogen chemistry mechanism.

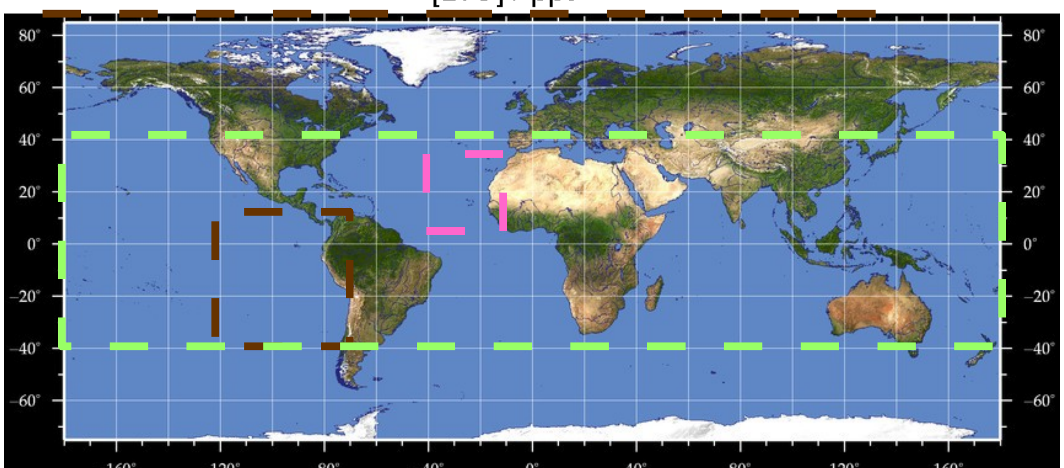
Main points:

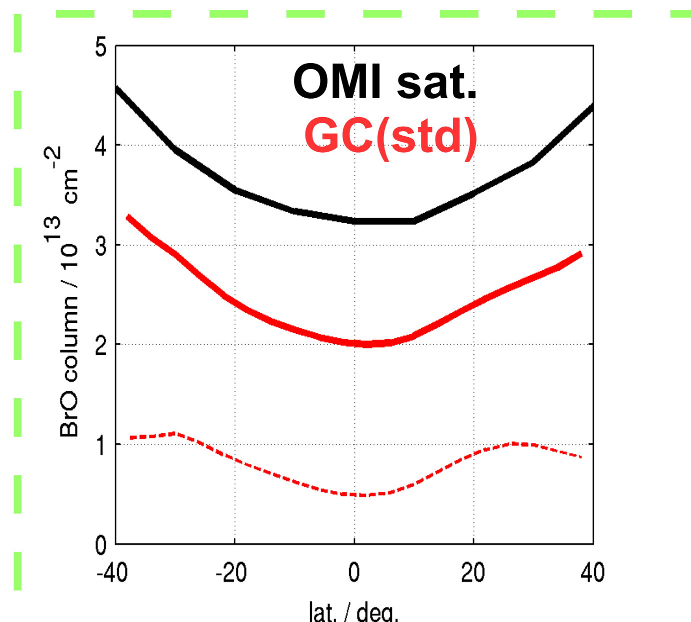
1. Standard GEOS-Chem(v9-02) simulation cannot reconcile observed high levels of BrO in the tropics
2. Multi-phase bromide oxidation in sea salt aerosols and clouds enhance BrO in the MBL and FT
3. BrO in the tropical UT is highly sensitive to LS inorganic bromine (Bry)
4. GEOS-Chem bromocarbon sources are consistent with observation in and outside the tropics

Std. GC simulation cannot reconcile high obs. BrO in tropical troposphere

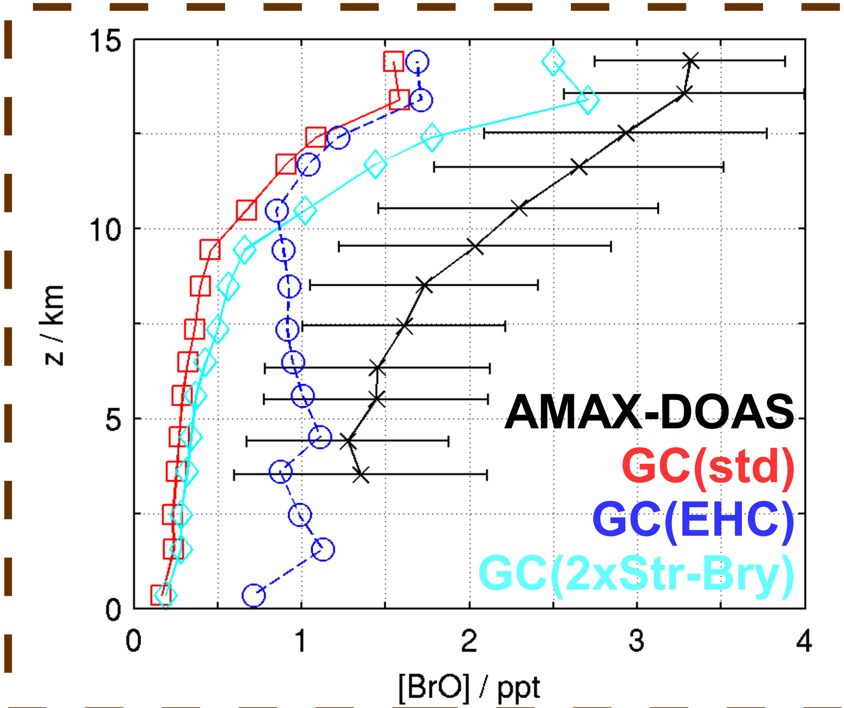


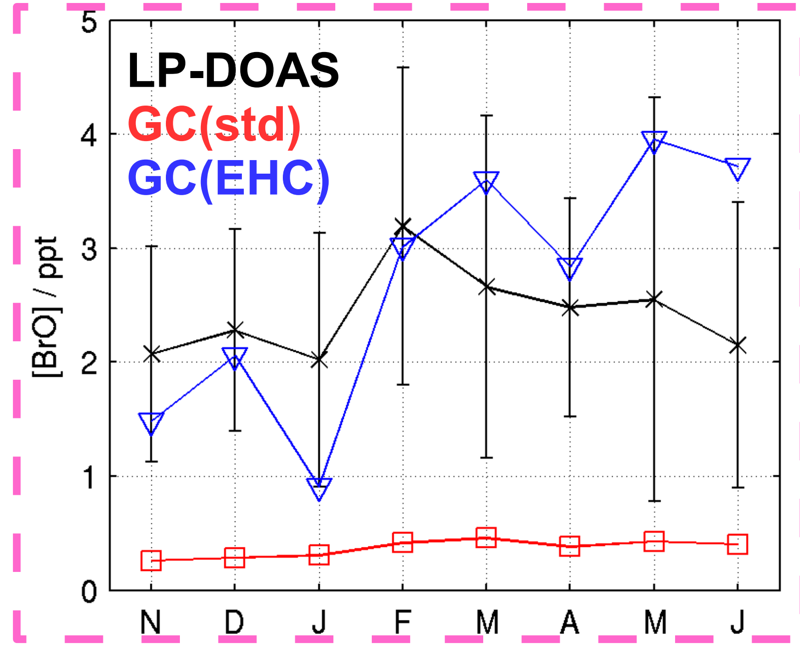


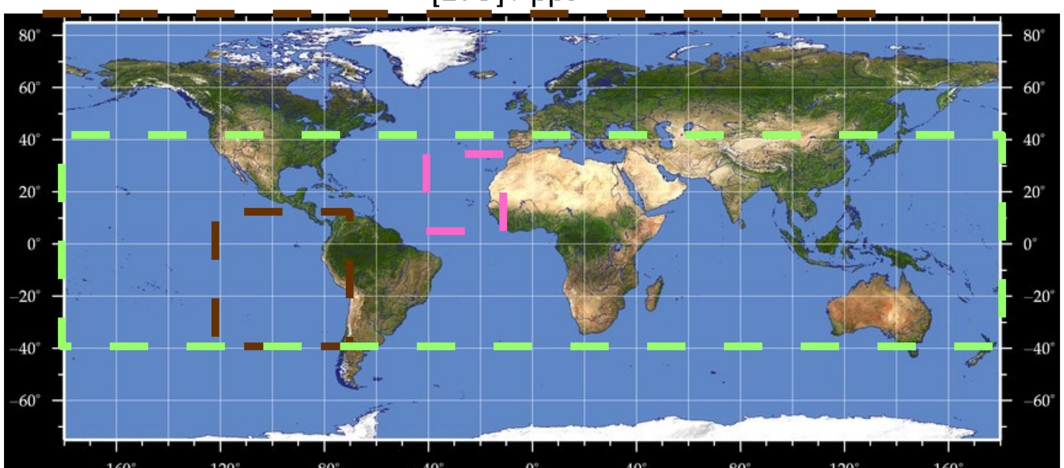


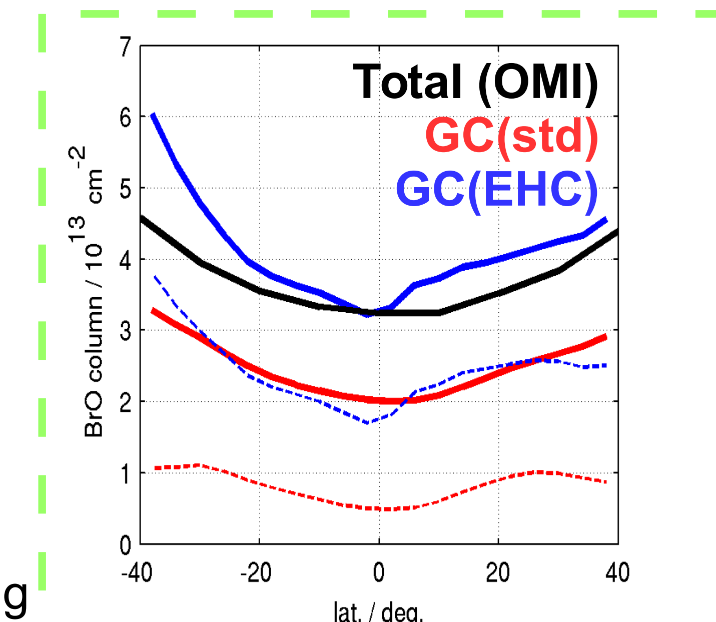


Multi phase chemistry and increased Bry input from strat. can reconcile obs.

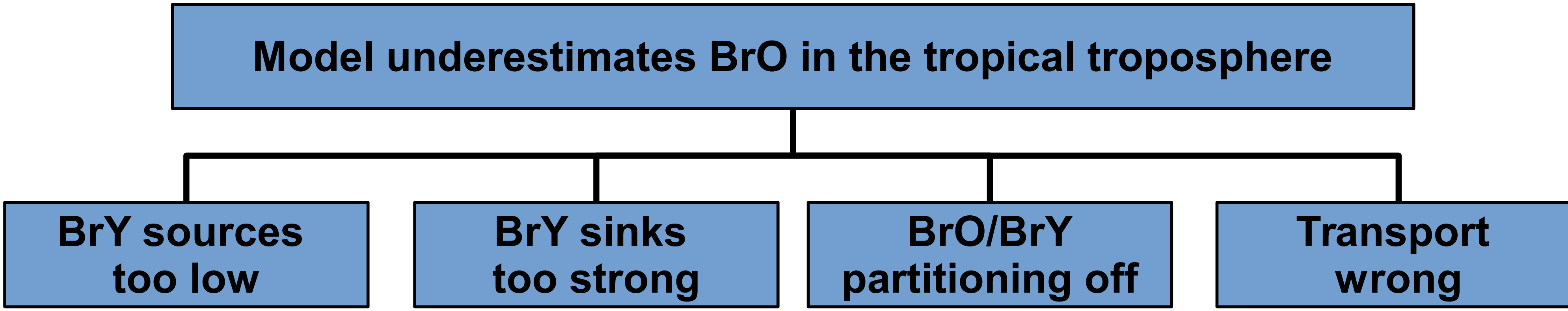


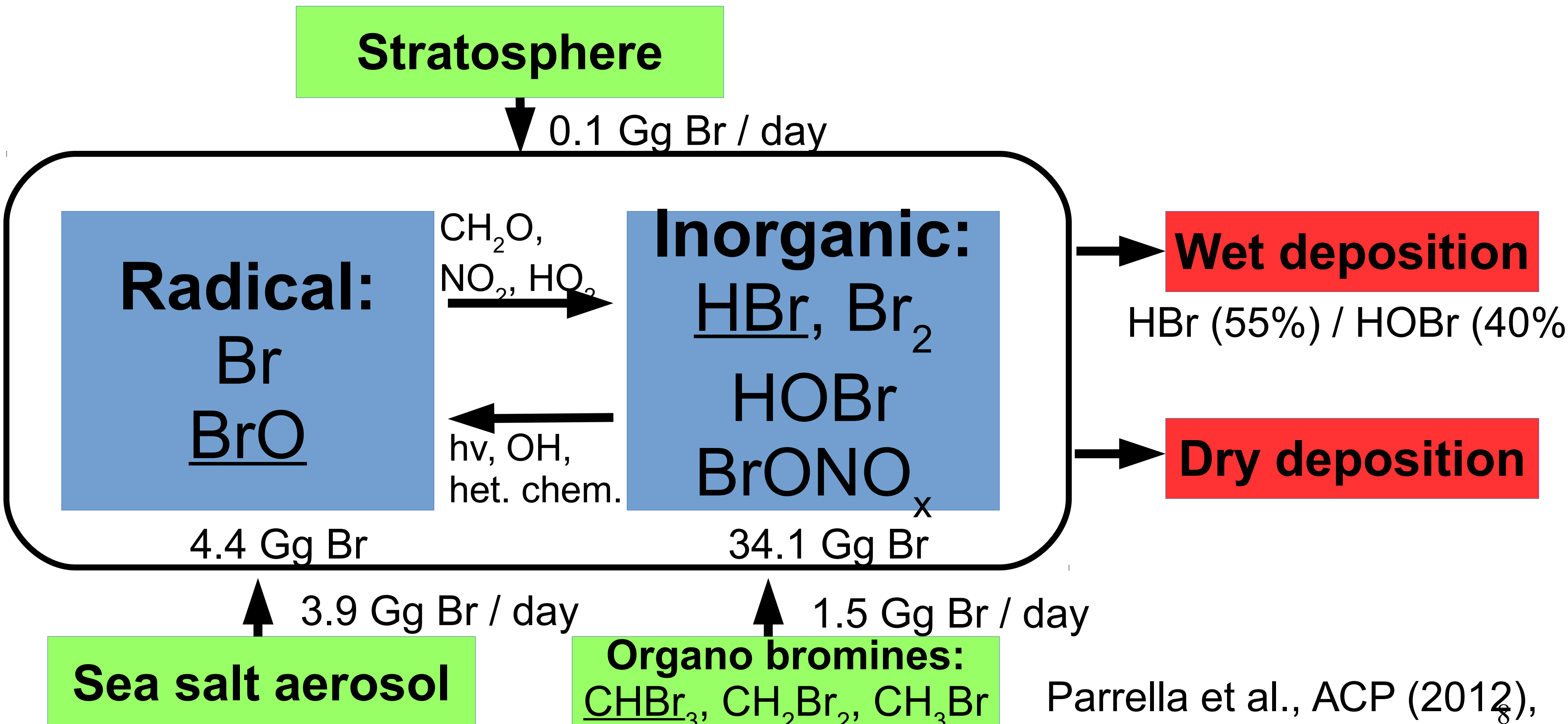






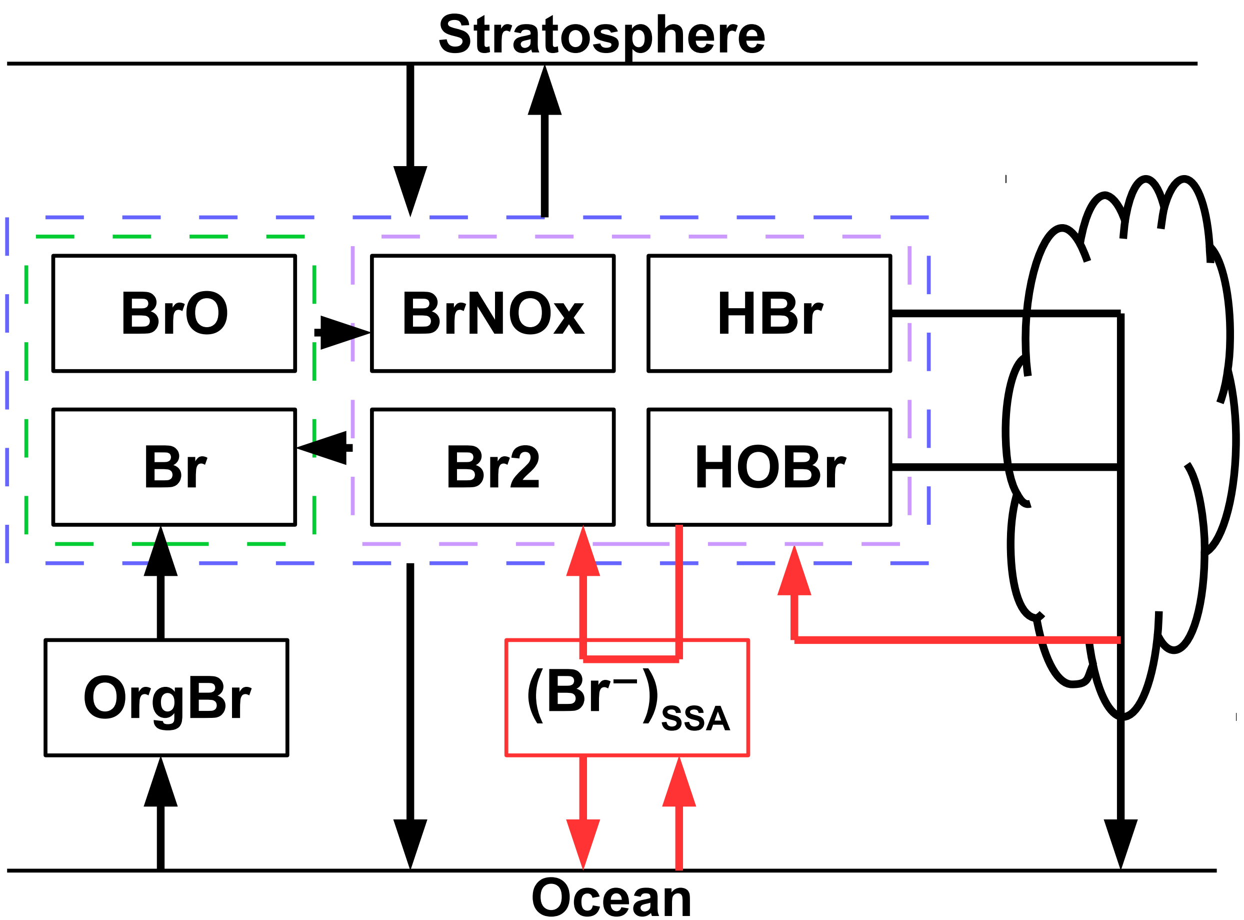
BrO column figure credit: Qing Liang





Parrella et al., ACP (2012),
Ann. mean budget
GC(v9-01-3)/GEOS-5

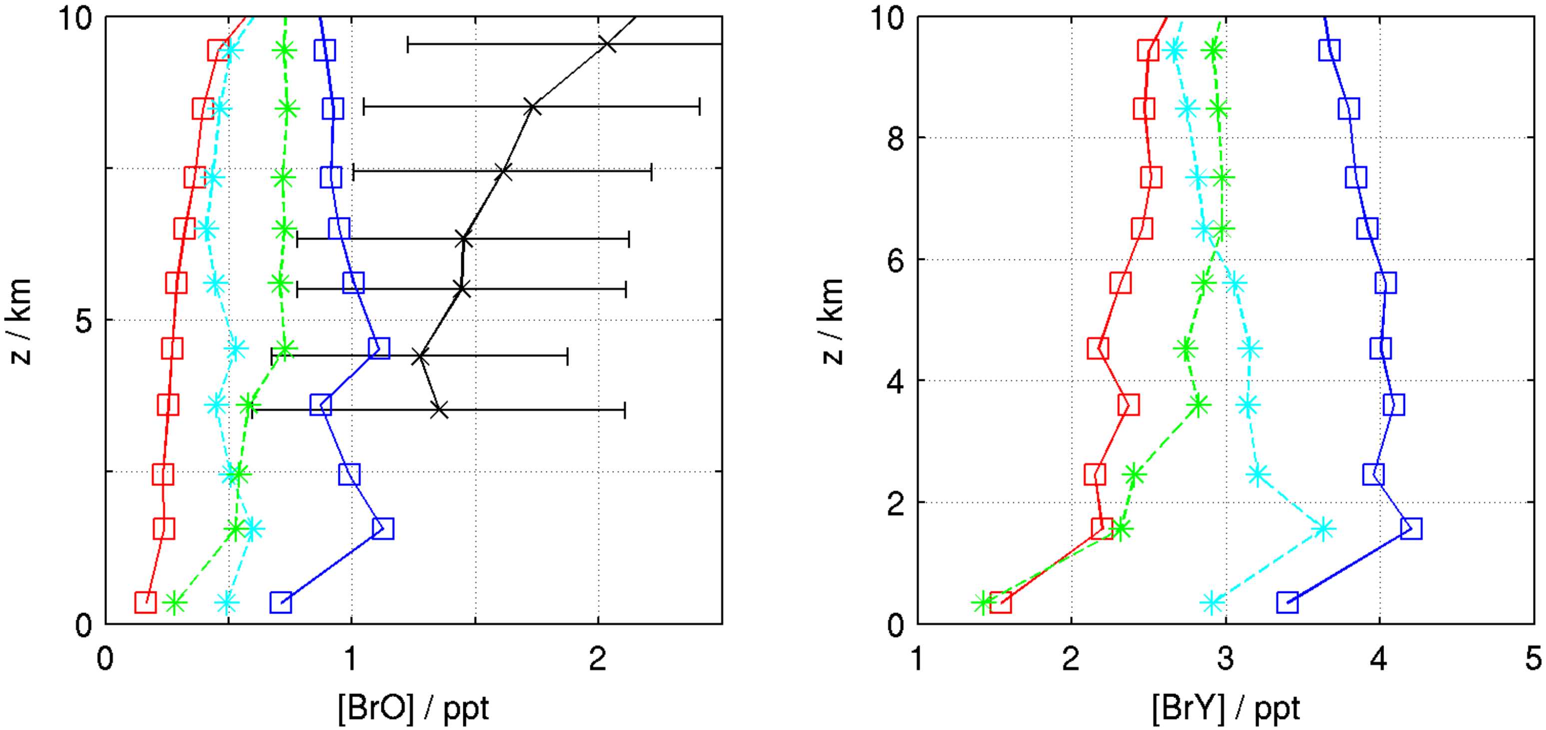
Updated GC halogen heterogeneous chemistry mechanism (EHC)



- On going work (Further obs. constraints needed!)
- Multi phase reactions on liq. and ice clouds (GEOS-5 IWC / LWC)
- Multi-phase reaction on hydrophilic aerosol
- Explicit (chem. driven) SSA debromonation
- Online reactive uptake coefficients
- IUPAC recommendation (Ammann et al. 2013)
- Update also incl. Chlorine

$$\gamma(T, \text{radius}, \text{pH}, [Br^-], \text{air density}) = 1/(\ 1/\Gamma_{diff} + 1/\alpha + 1/\Gamma_{rxn})$$

Multi phase HBr recycling on liquid cloud droplets enhance Lower FT BrO

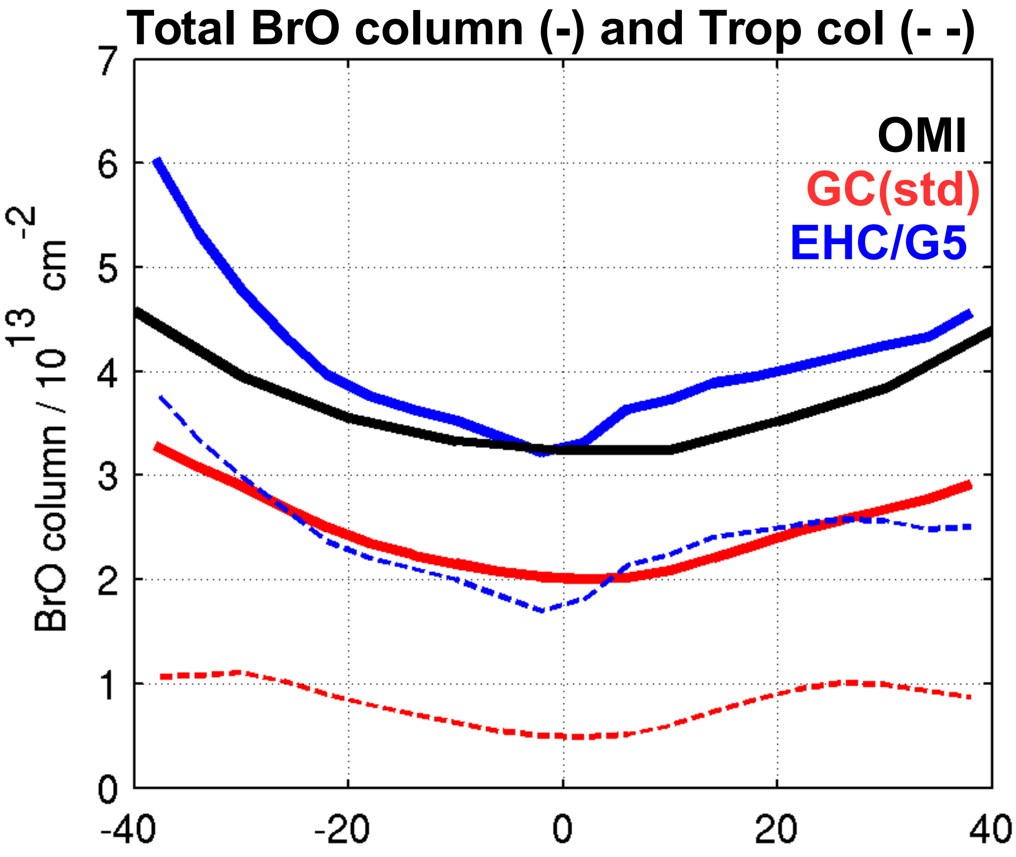


Average along all 17 TORERO RFs

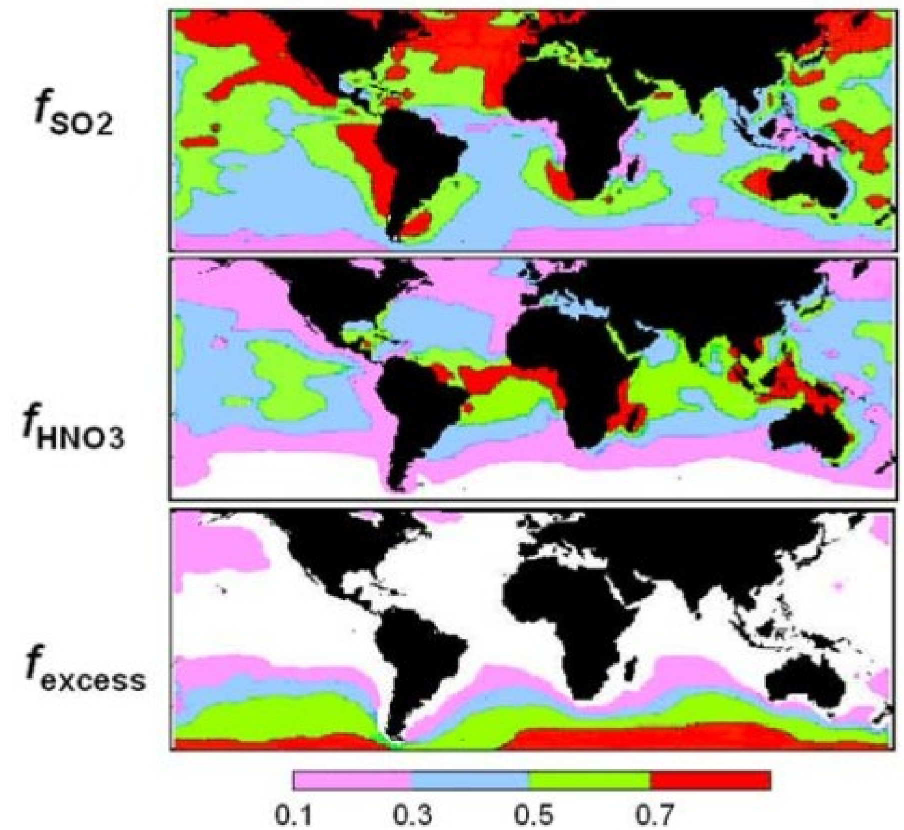
Obs. (AMAX-DOAS)
GC(std)
GC(EHC)
GC(EHC) alkaline SSA
GC(EHC) no HBr recycling on clouds

- Multiphase chemistry (**GC(EHC)**) enhance LT BrO by a factor of ~4
- Multiphase chemistry (**GC(EHC)**) only enhance LT Bry by about ~2
- Sensitive to SSA-Bry emissions throughout the FT (note gap between green and blue)
- Results very sensitive to recycling of HBr (and HCl) on liquid cloud droplets

Multi-phase recycling of HBr enhance the tropospheric BrO column in tropics



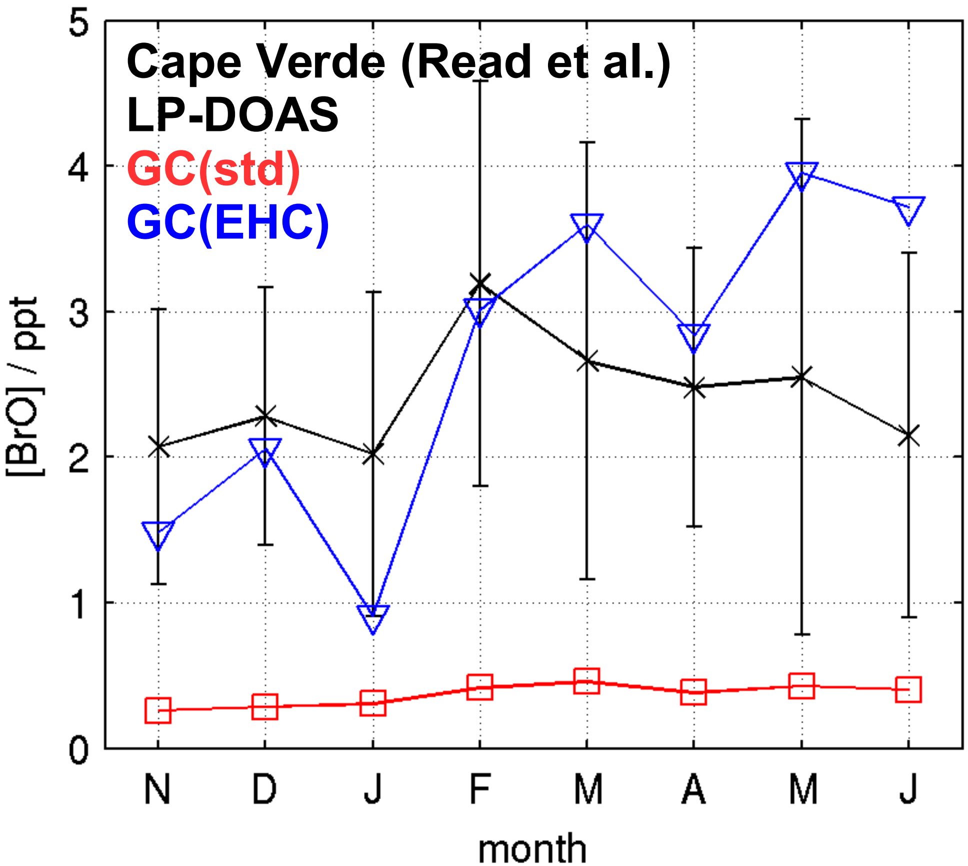
OMI credit: K. Chance, R. Suleiman (Q. Liang)

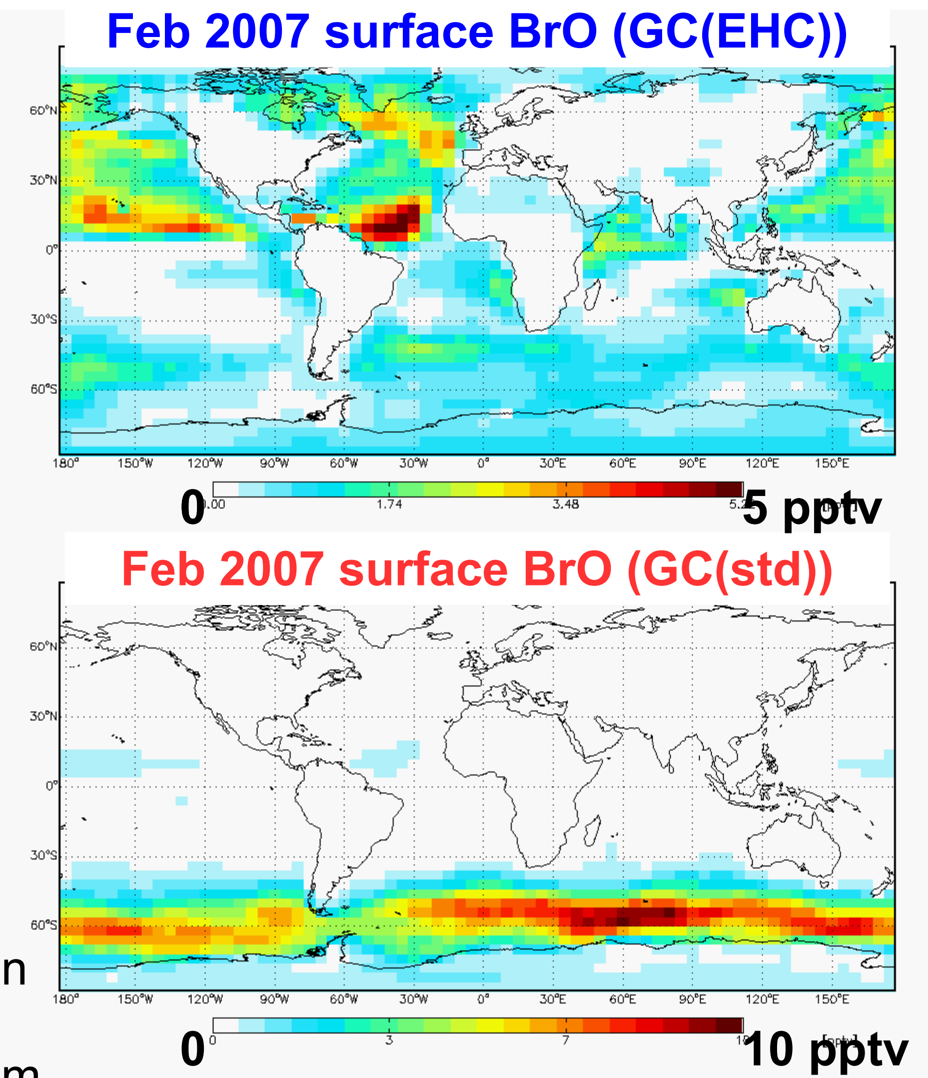


SSA alkalinity (Alexander et al. 2005)

- **EHC/G-5 tropospheric BrO column larger than stratospheric column**
- **EHC/G-5 BrO column too large in S. Mid-lat.**
- **SSA excess alkalinity would prevent debromonation in S. ocean**

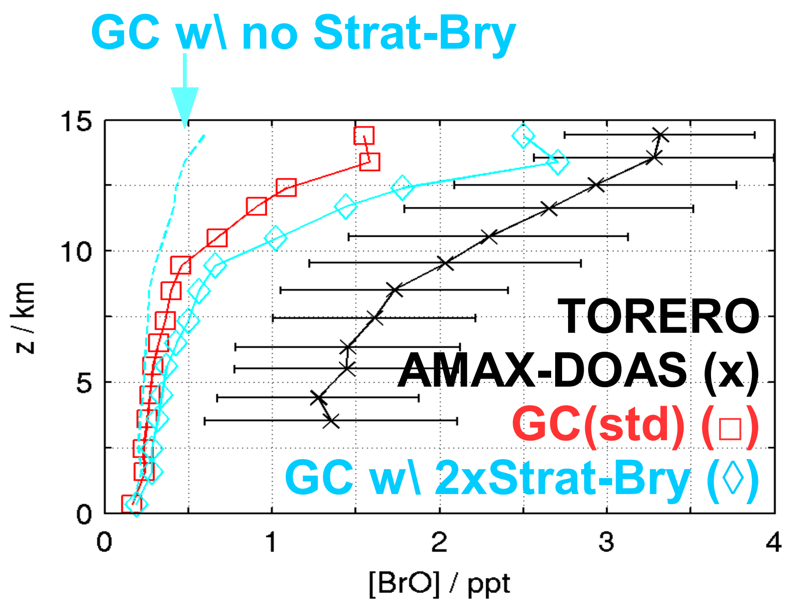
Extensive BrO “plume” over the tropical Atlantic ocean

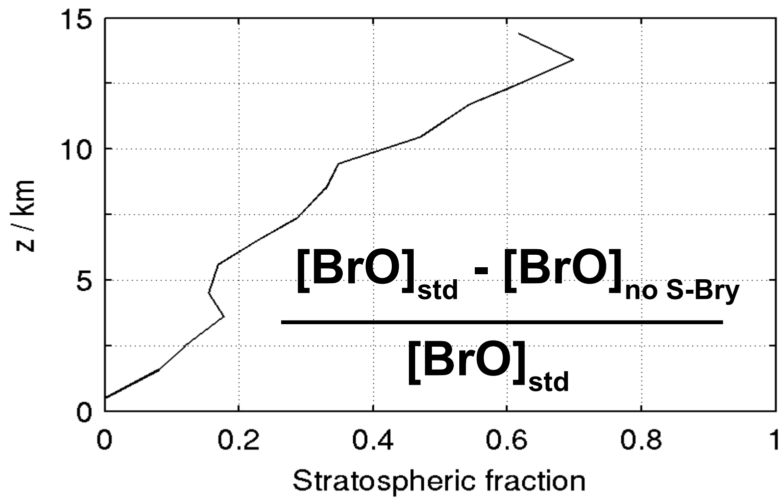




- Shift MBL SSA-Br emissions away from S. Ocean
- Shift reflect sensitivity to “seed” Bry initiating debromonation, temperature and other phys/chem conditions.
- Model SSA bromide depletion consistent with obs.

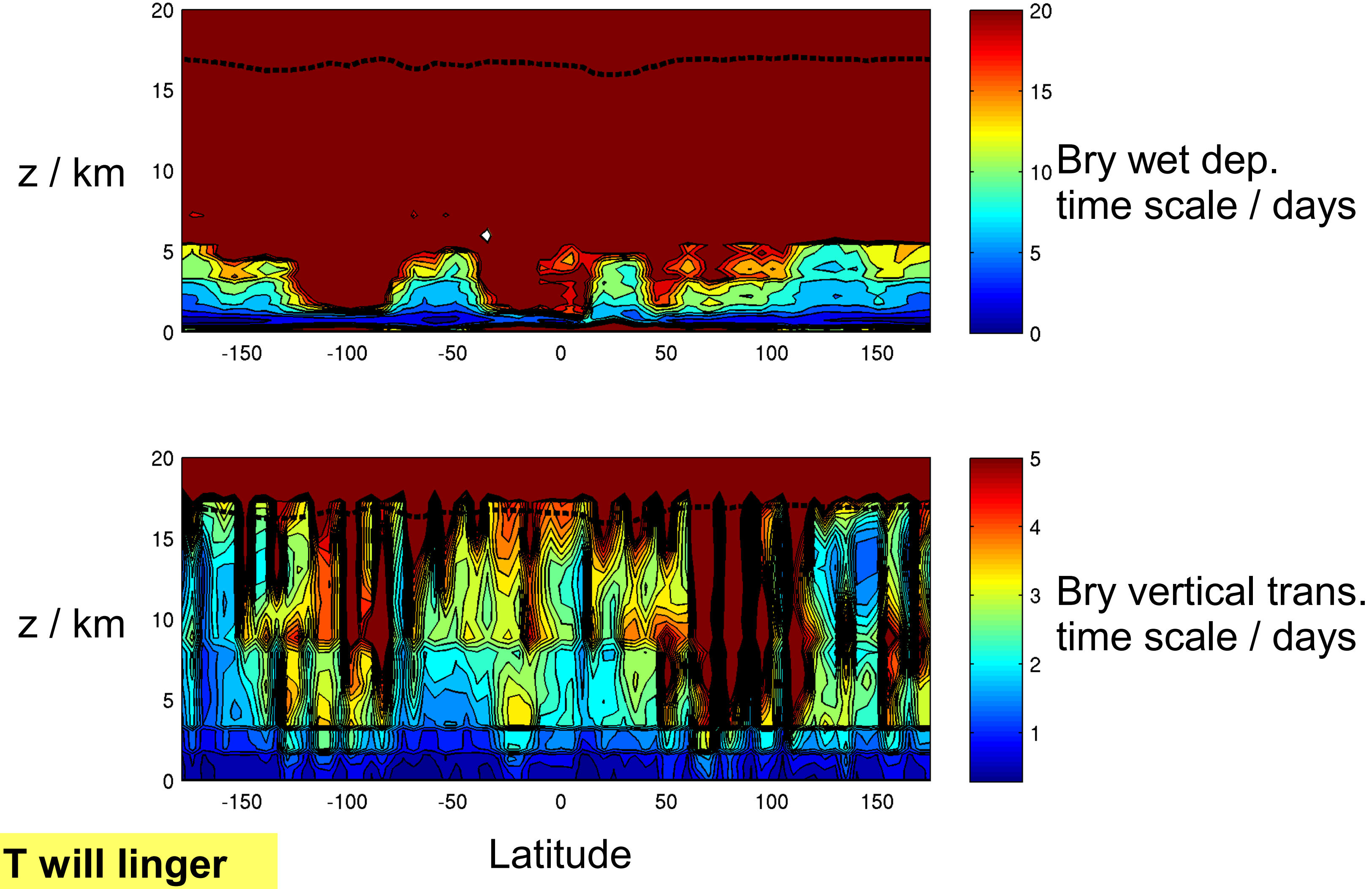
TORERO UT BrO is highly sensitive to changes in Stratospheric Bry





- **Model sensitivity to changes in strat Bry and Strat-Trop Exchange evaluated by increasing strat Bry by a factor 2**
- **TORERO RF04 and RF05 suggests model Bry in LS is underestimated by 25% to 75%**
- **MLS CO obs. indicate GC/GEOS-5 vertical velocities underestimated in tropics.**
- **40 – 70% of UT (10-15 km) BrO derived from input of stratospheric Bry**
- **Large gap between model and obs. remain below the UT which is not affected by increased Strat. Bry flux.**

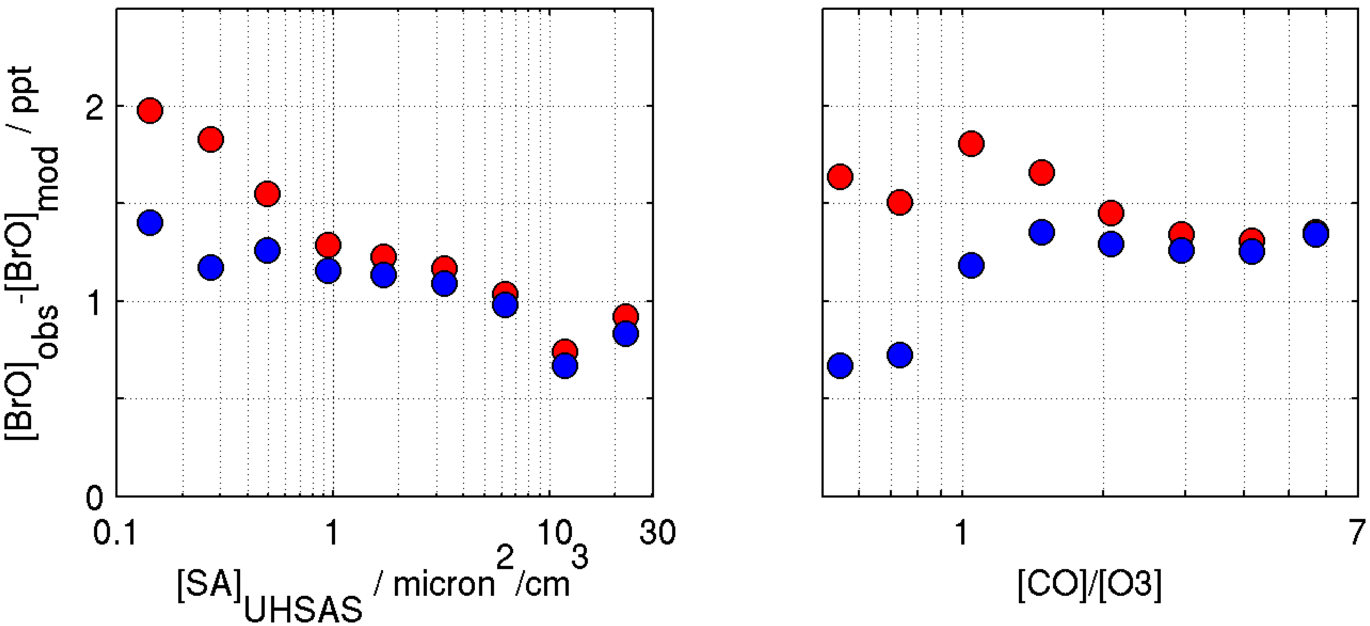
Why is Bry input from the stratosphere important? Point of entry matters!



- **Bry injected in UT will linger**
- **Bry injected in PBL will be washed out**

GC/GEOS-5 (Feb 2006; 22S - 22N)

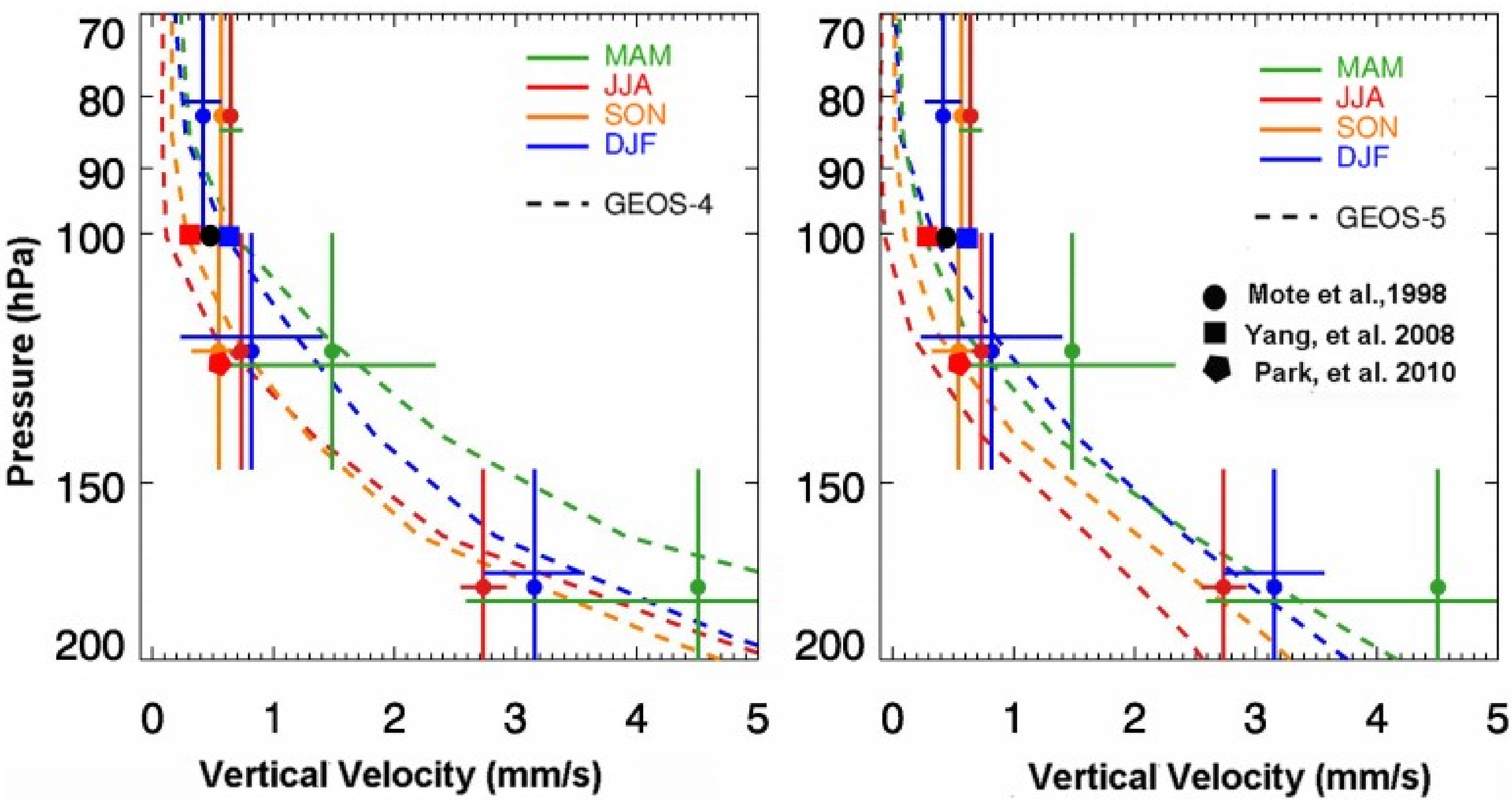
Obs. - Mod. deviation correlated to stratospheric influence signatures



TORERO
AMAX-DOAS (x)
GC/G-5 (□)
GC/G-5 w\ 2xStrat-Bry (◊)

- **ΔBrO = [BrO]obs – [BrO]mod averaged across all TORERO flights**
- **GC/G-5 ΔBrO correlated with stratospheric influence tracers**
- **Correlation is weaker for model with enhanced stratospheric input**
- **Base deviation of ~1 ppt (Other process enhancing BrO)**
- **Is there any reason to suspect too low model stratospheric transport?**

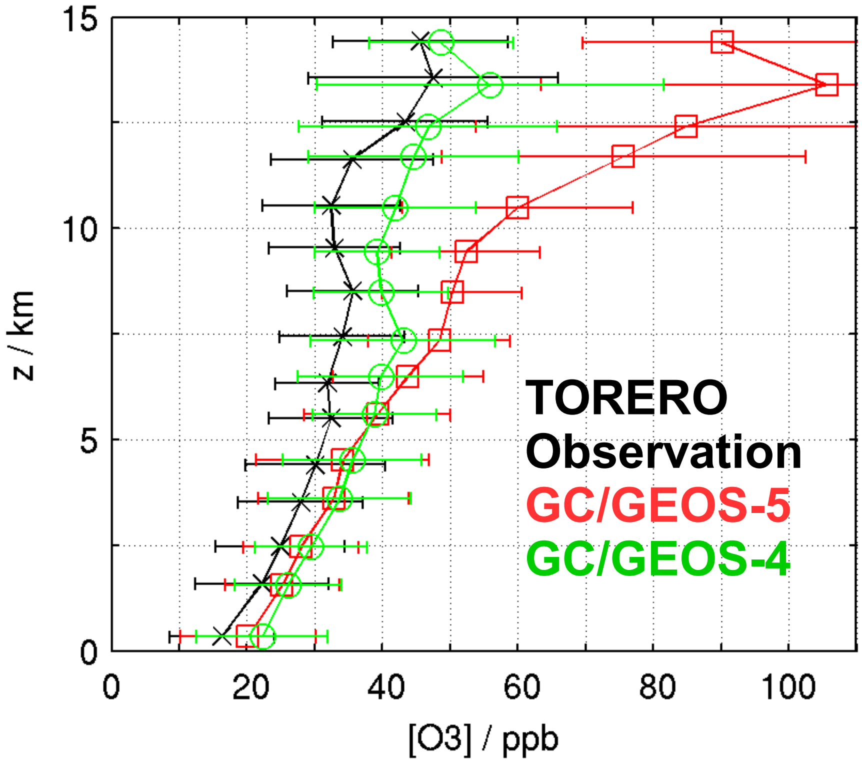
GC/GEOS-5 underestimate vertical transport near the tropical UTLS

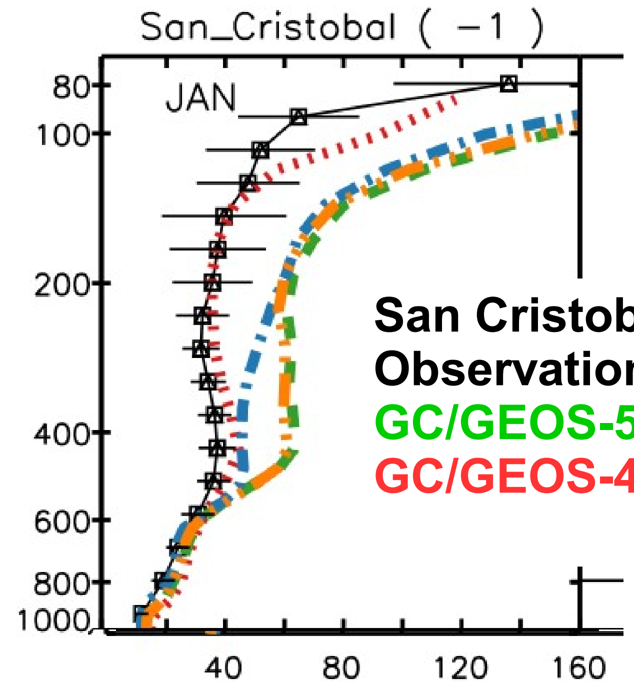


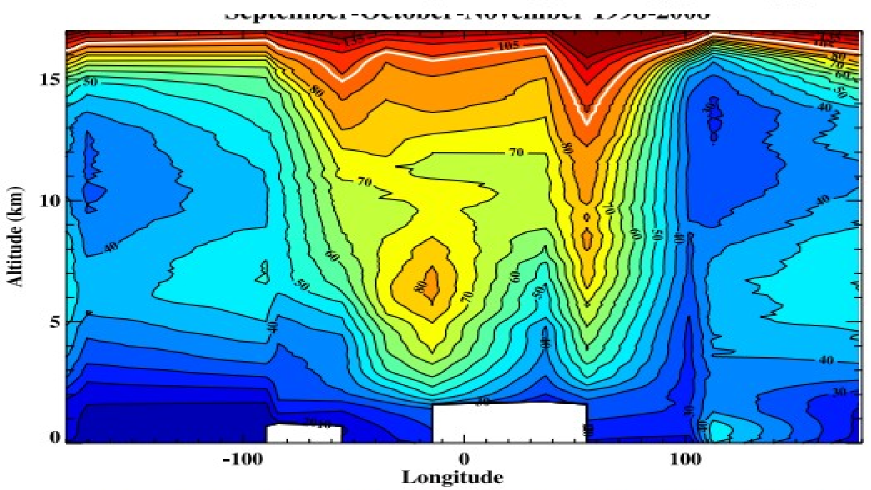
Liu et al., ACP, (2013). Vertical velocity derived from satellite CO profiles.

- **GC/GEOS-5 underestimates vertical transport near tropical UTLS**
- **GC/GEOS-4 more consistent with MLS CO derived transport**

GC/GEOS-5 underestimates convection and circulation in the tropics





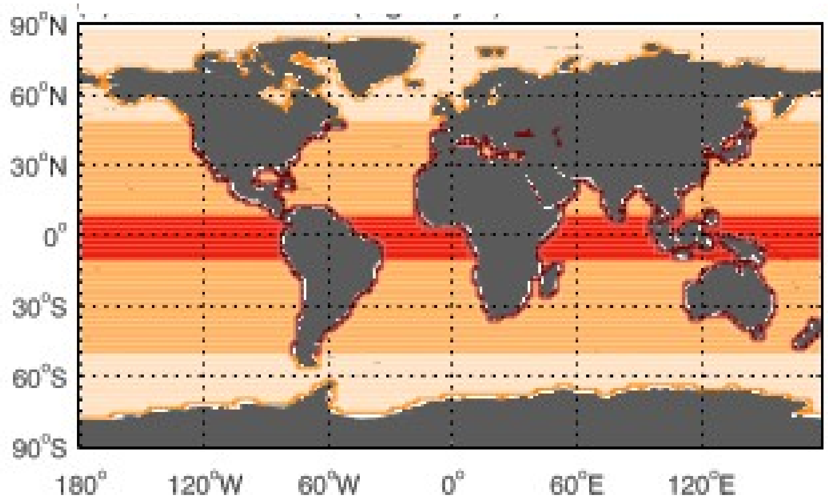


- UT ozone diluted by LT air in tropical Pacific
- GC/GEOS-5 underestimates vertical transport
- Results in high bias in GC/G-5 UT ozone

Thompson et al. (2011) O3 sonde obs. in S. Tropics

GEOS-Chem bromocarbon mixing ratios consistent with observation

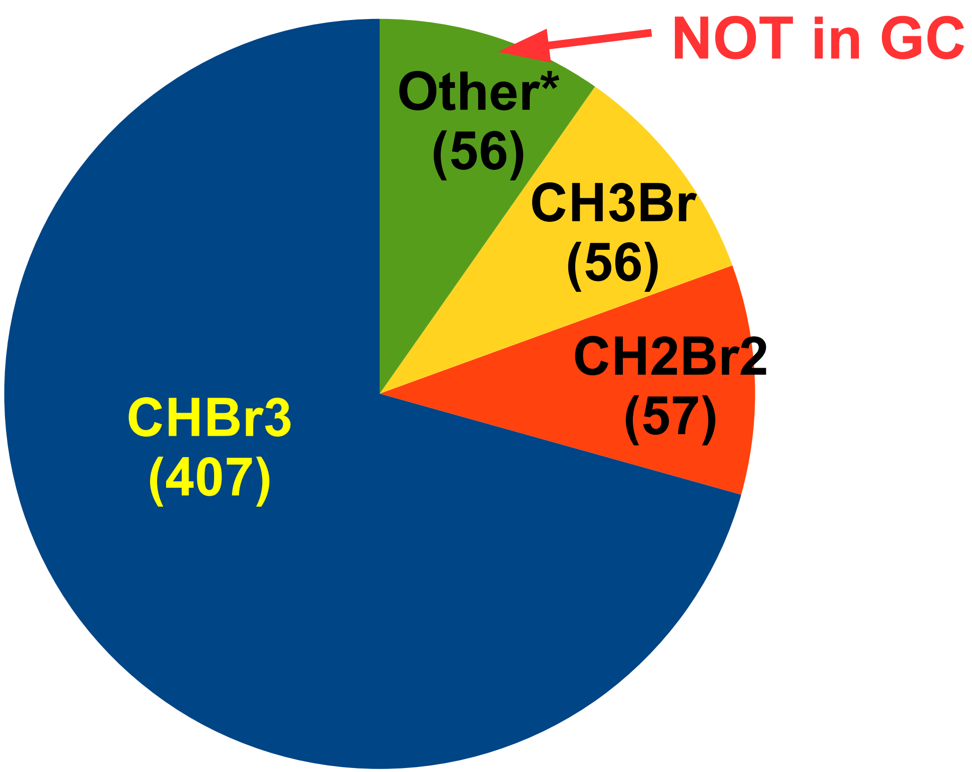
CHBr3 emission field



(Q. Liang et al (2010))

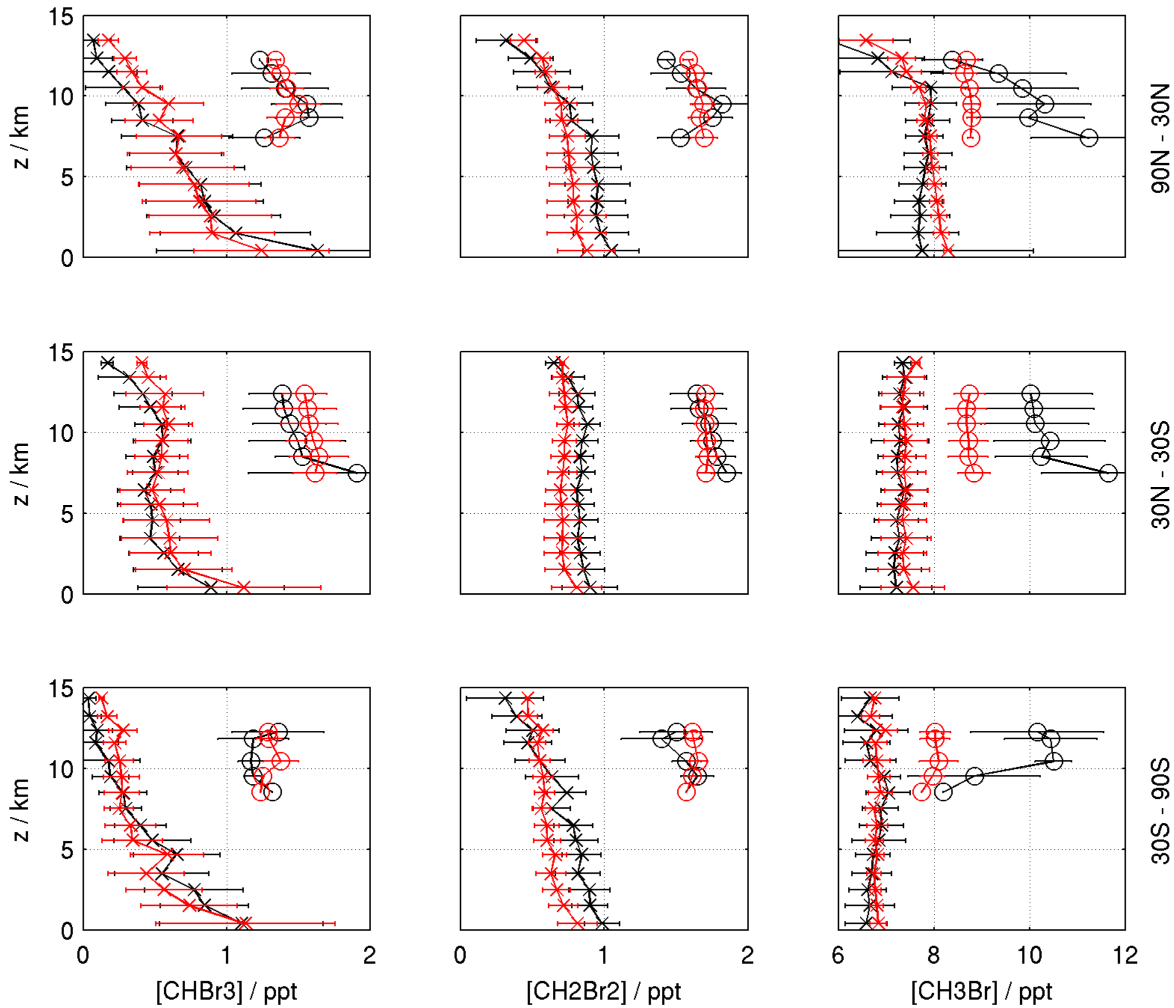
Seasonality added to CHBr3 emissions

Global source strength in Gg Br/yr



Other = CHBrCl2, CHBr2Cl, CH2BrCl
(Est. from WMO Ozone report)

GC bromocarbon consistent with HIPPO and CARIBIC observations



CHBr3:
Good agreement

CH2Br2:
Small low bias (~10%)

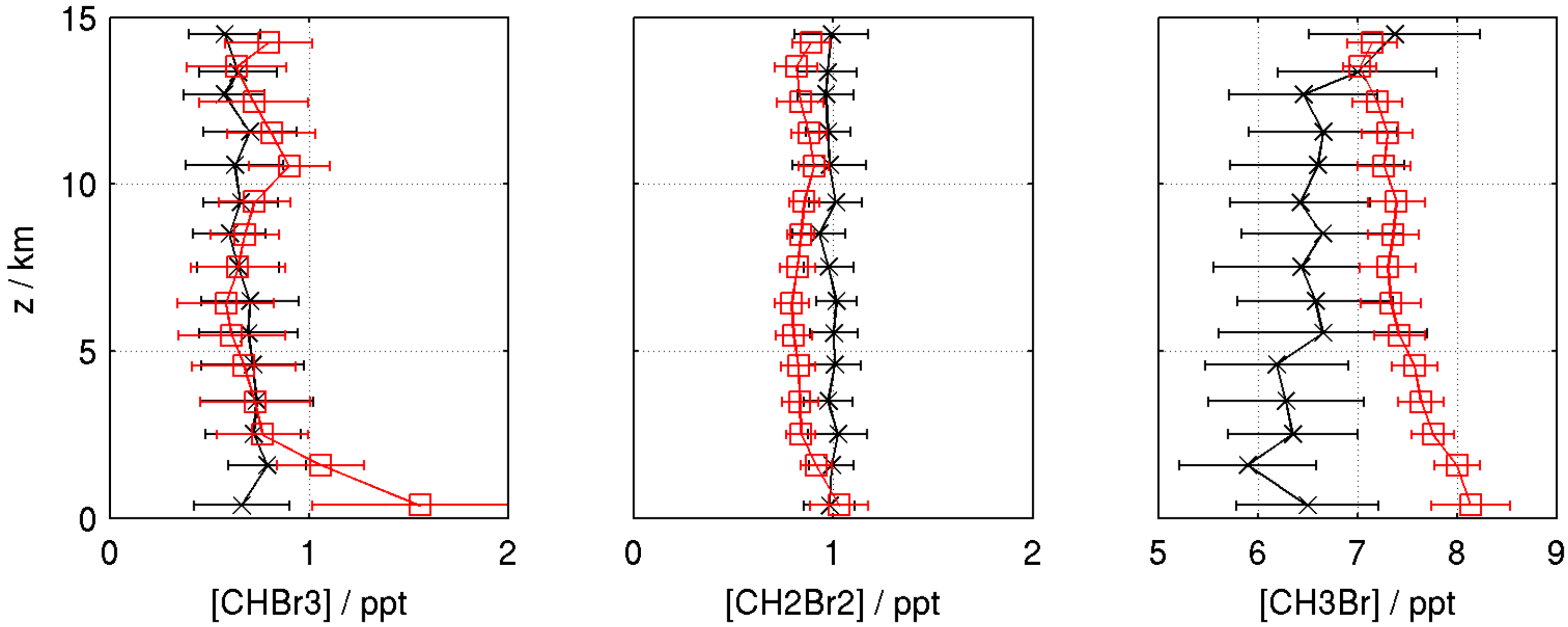
CH3Br:
Low bias against CARIBIC. Model lacks inter annual variability (decreasing trend)

HIPPO: 2009 – 2011
CARIBIC: 2005 – 2009

Observation
GC/GEOS-5

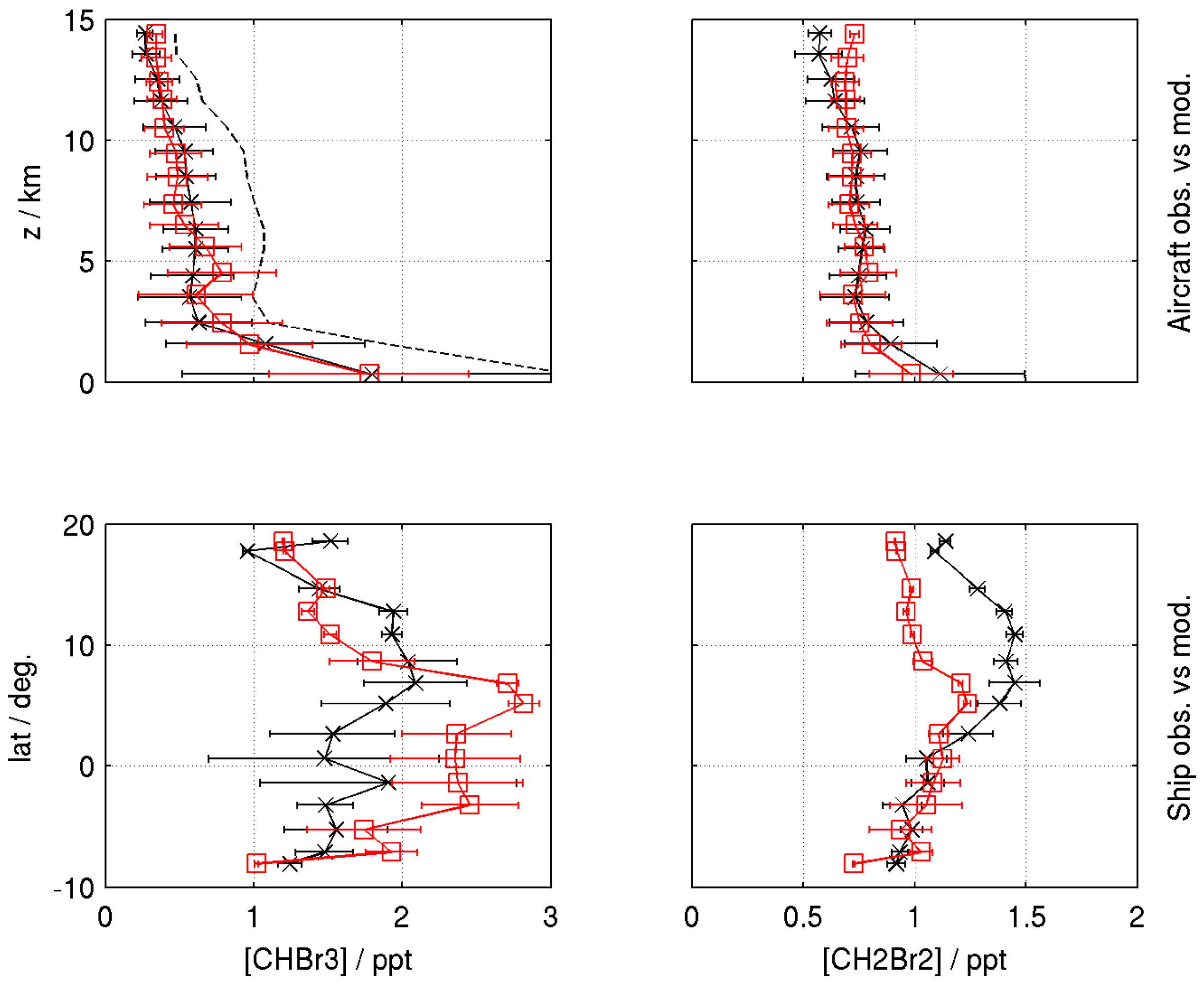
CARIBIC shifted by 1 ppt

GC bromocarbon consistent with CONTRAST TOGA observations



- Over all good agreement
- Observed VSLH profiles more “straight” than model.
- Could indicate insufficient vertical transport in model (GC/GEOS-5)
- Model CH3Br high bias reflect missing inter annual trend.

GC bromocarbon consistent with TORERO TOGA and VSLH ship obs.



Observation
GC/GEOS-5

TOGA CHBr3 calibration
Broken line: Local std.
Full line: NIST std.

Model agrees well with observations based NIST CHBr3 standard

Summary and outlook:

- Current GC(std) underestimate recent observation of high levels of BrO in the tropics.
- Inaccuracies in model bromocarbon source gas emission is unlikely to contribute significantly to model BrO low bias.
- GC BrO UT low bias is likely linked to insufficient input of stratospheric Bry.
- GC(std) BrO low bias in MBL and FT is likely linked to an incomplete description of multi-phase bromine chemistry in SSA, other hydrophilic aerosols and clouds.
- Updated halogen multi phase chemistry mechanism help close gap between BrO observations and model in tropics below the UT.
- CONTRAST/CAST BrO and HOBr observations will provide crucial constraints on multi-phase Br_y recycling.
- CONTRAST/CAST/ATTREX data will help constrain GC halocarbon emissions and vertical transport in the tropics.

Acknowledgments

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- Observations: R. Volkamer et al. (AMAX-DOAS BrO), L. Carpenter et al. (VSLH obs.), E. Apel et al. (TOGA), C. Brenninkmeijer et al. (CARIBIC), HIPPO
- Discussions: Q. Liang, T. Sherwen, M. Evans, R. Salawitch, R. Volkamer and many others
- GC Support: M. Sulprizio and C. Keller.