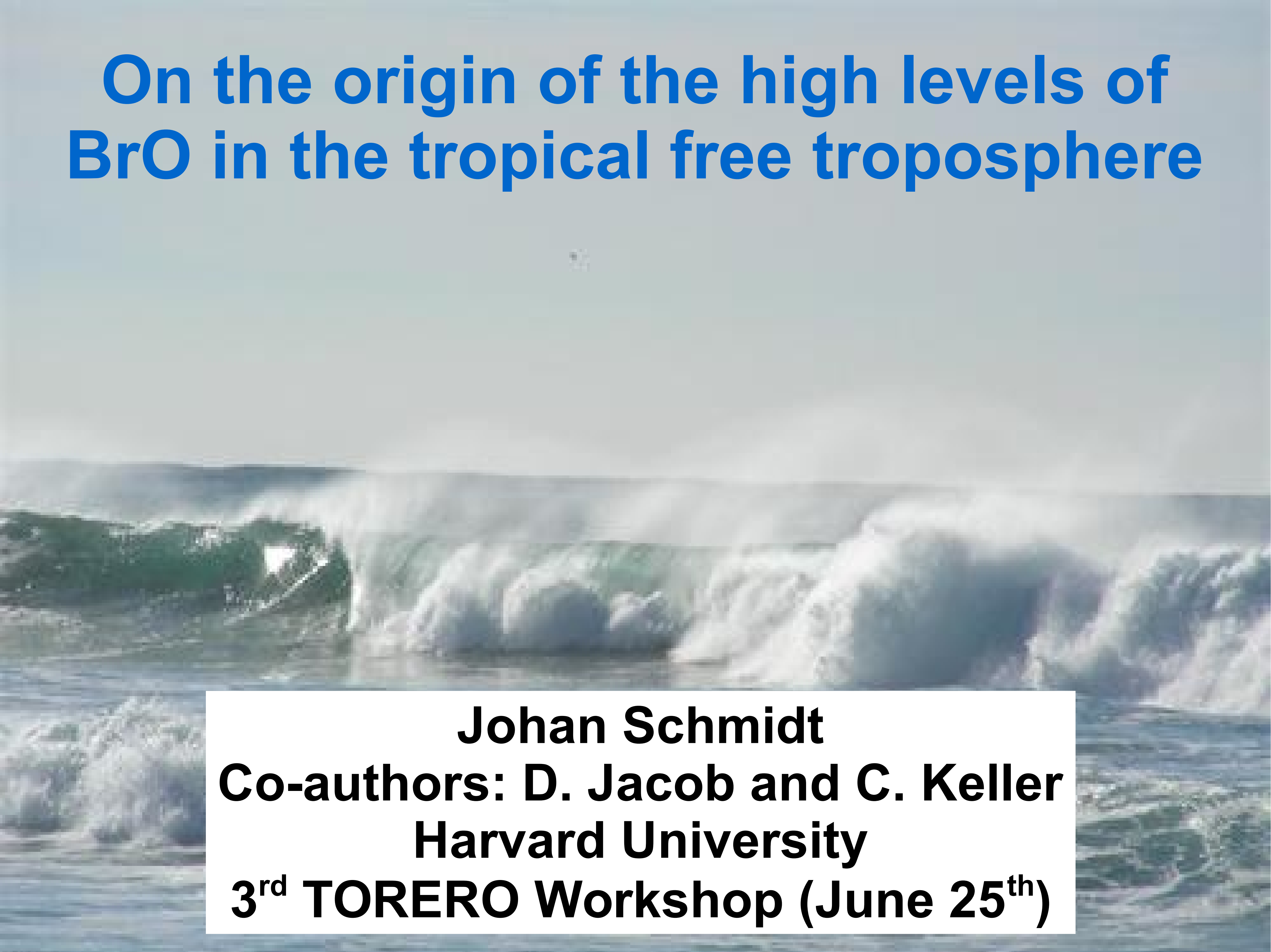
On the origin of the high levels of BrO in the tropical free troposphere



Johan Schmidt
Co-authors: D. Jacob and C. Keller
Harvard University
3rd TORERO Workshop (June 25th)

Why study tropospheric halogens?

Cl / Br / I

Ozone destruction

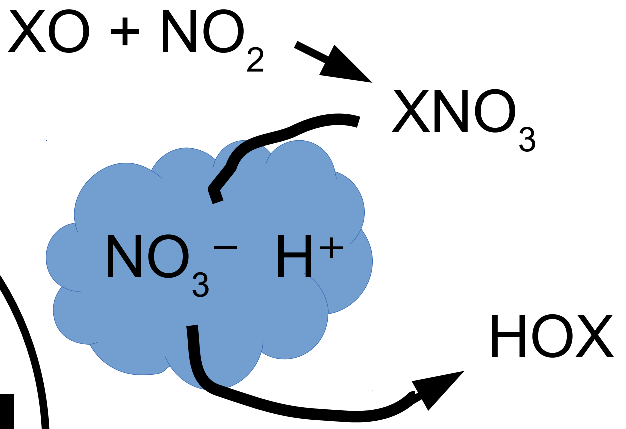
$X + O_3 \rightarrow XO$

$XO + HO_2 \rightarrow HOX$

$HOX \rightarrow OH + X$

$O_3 + HO_2 \rightarrow OH$

NO_x oxidation and deposition



$XO + NO_2 \rightarrow XNO_3$

Hg removal

$Br + Hg(0) \rightarrow HgBr$

$HgBr + X \rightarrow Hg(II)XBr$

$\downarrow$

Gas phase oxidation

$Br + CH_2O \rightarrow HBr + CHO$

$Cl + CH_4 \rightarrow HCl + CH_3$

$BrO + DMS \rightarrow Br + DMSO$

Why care about tropospheric ozone?

- **Green house gas**
- **OH precursor**
- **Oxidant**
- **Air pollutant**

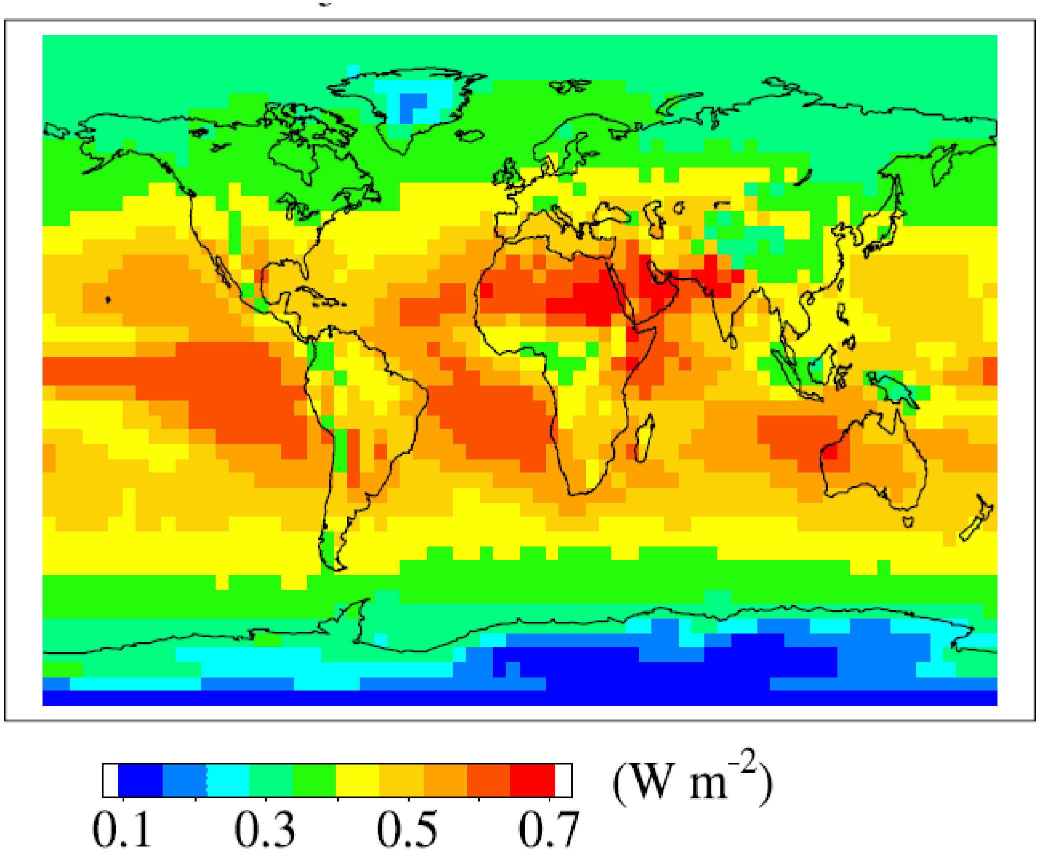


Fig. 3 of Mickley et al. (2004): Change in forcing due to uniform 18 ppb increase to pre-industrial tropospheric ozone.

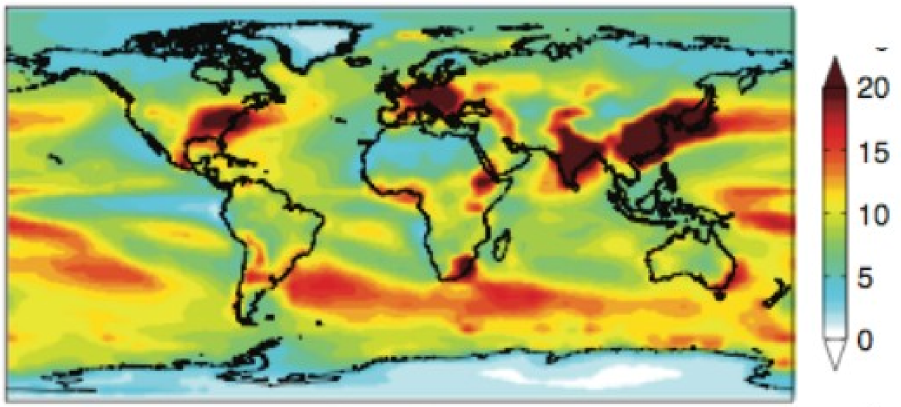
Br plays a major role in the Hg cycle

- Atomic Br is thought to be the major oxidant of Hg(0) to Hg(II) in the atmosphere (*Goodsite et al., 2004, 2012; Dibble et al., 2012*)

- Hg(II) is more water soluble than Hg(0) and therefore more readily deposited to land and ocean: a better understanding of [BrOx] will improve our ability to predict the spatial distribution of Hg deposition

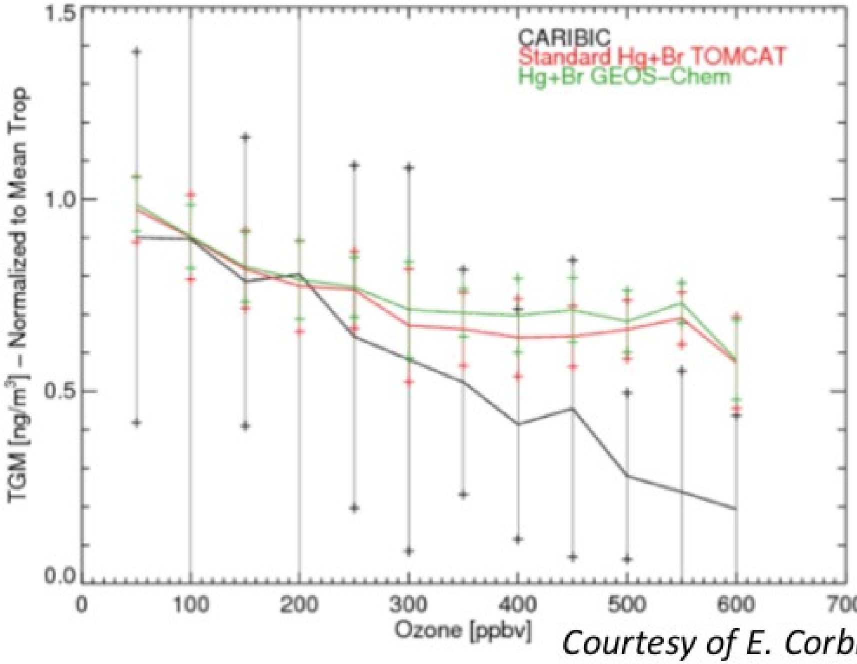
- Observations suggest greater Hg oxidation and higher [Hg(II)] in UTLS *(Lyman and Jaffe, 2011; Horowitz et al., in prep.)* than the current GEOS-Chem model estimate: higher [BrOx] than is currently in the model UTLS could reconcile this

- Greater Hg oxidation from higher [BrOx] aloft could also improve the model's low Hg deposition bias in deep convection areas (*Soerensen et al., in prep.*)



GEOS-Chem modeled Hg(II) deposition: oxidation by Br & TOMCAT BrOx fields

Holmes et al., 2010 µg m^{-2} a^{-1}

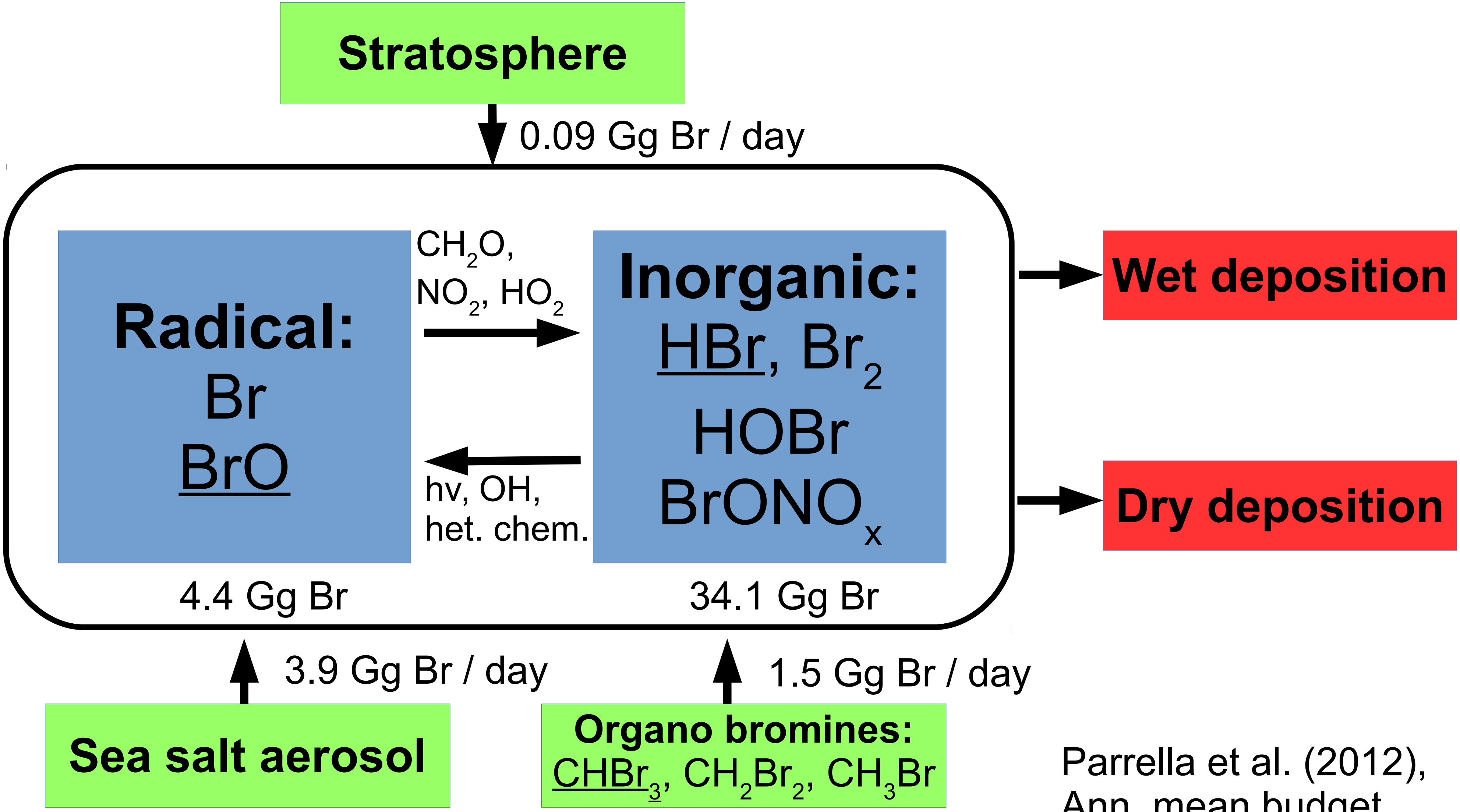


Lower stratosphere Hg – CARIBIC (2005 – 2011) vs. GEOS-Chem

Courtesy of E. Corbitt

Slide prepared by Hannah Horowitz (2014)

The GEOS-Chem bromine scheme: Sources, Sinks and Partitioning



Stratosphere

0.09 Gg Br / day

Radical:
Br
BrO

CH_2O,
NO_2, HO_2

hv, OH,
het. chem.

Inorganic:
HBr, Br_2
HOBr
$BrONO_x$

4.4 Gg Br

34.1 Gg Br

Wet deposition

Dry deposition

3.9 Gg Br / day

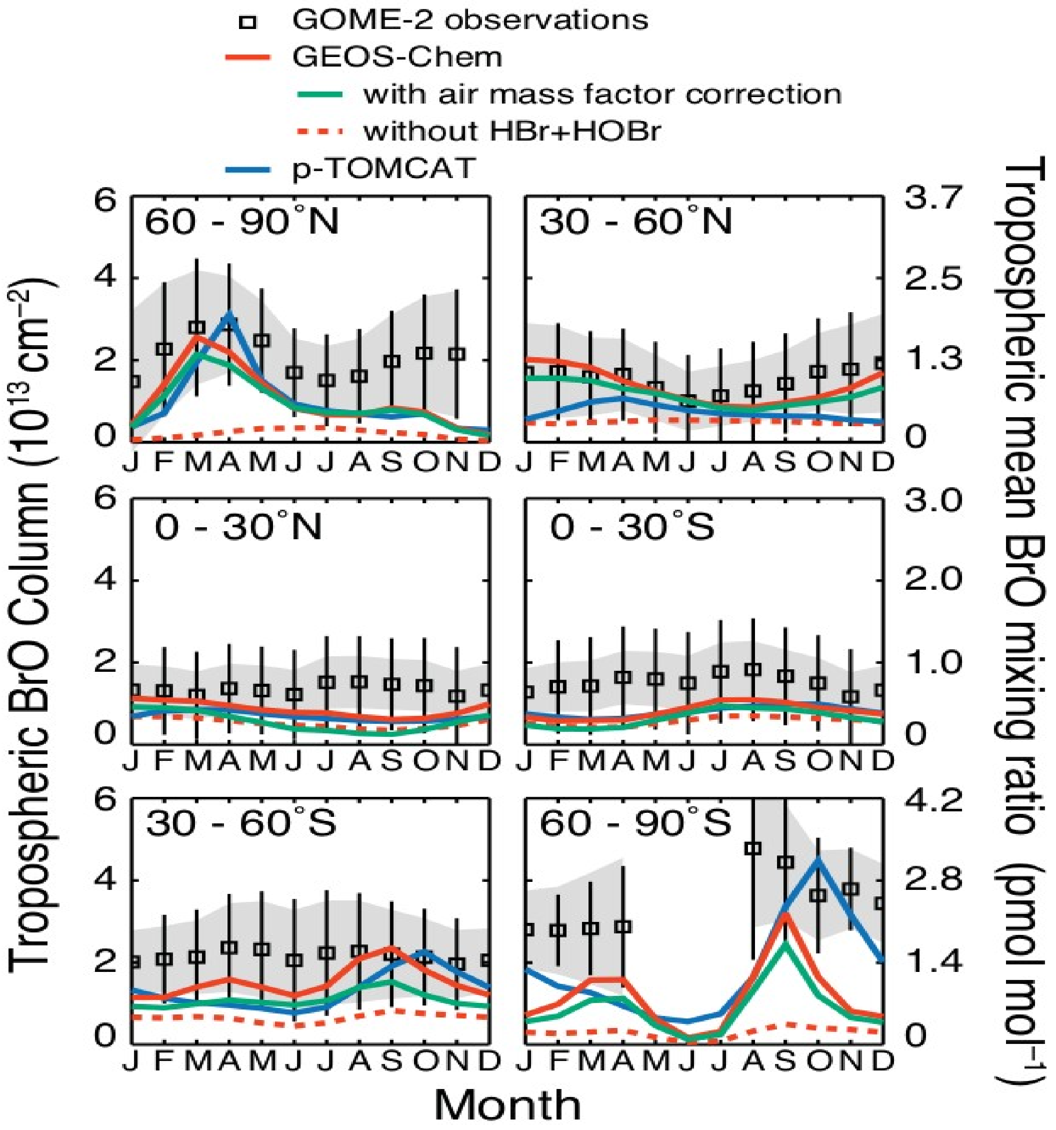
1.5 Gg Br / day

Sea salt aerosol

Organo bromines:
$CHBr_3$, CH_2Br_2, CH_3Br

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

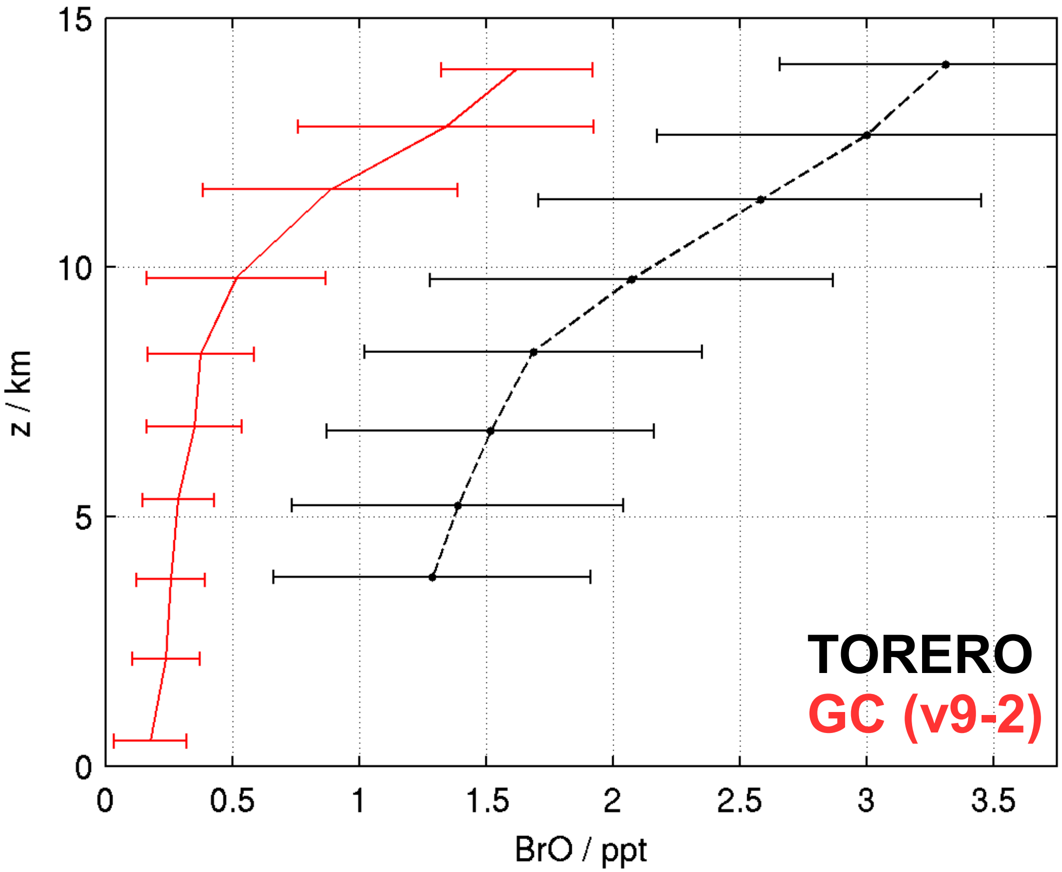
GEOS-Chem underestimates the tropospheric BrO column



Parrella et al. (2012), 9-11 LT for 2007

Large Uncertainties on the observations. But general LOW-BIAS in the GC

GEOS-Chem underestimates BrO in the free troposphere



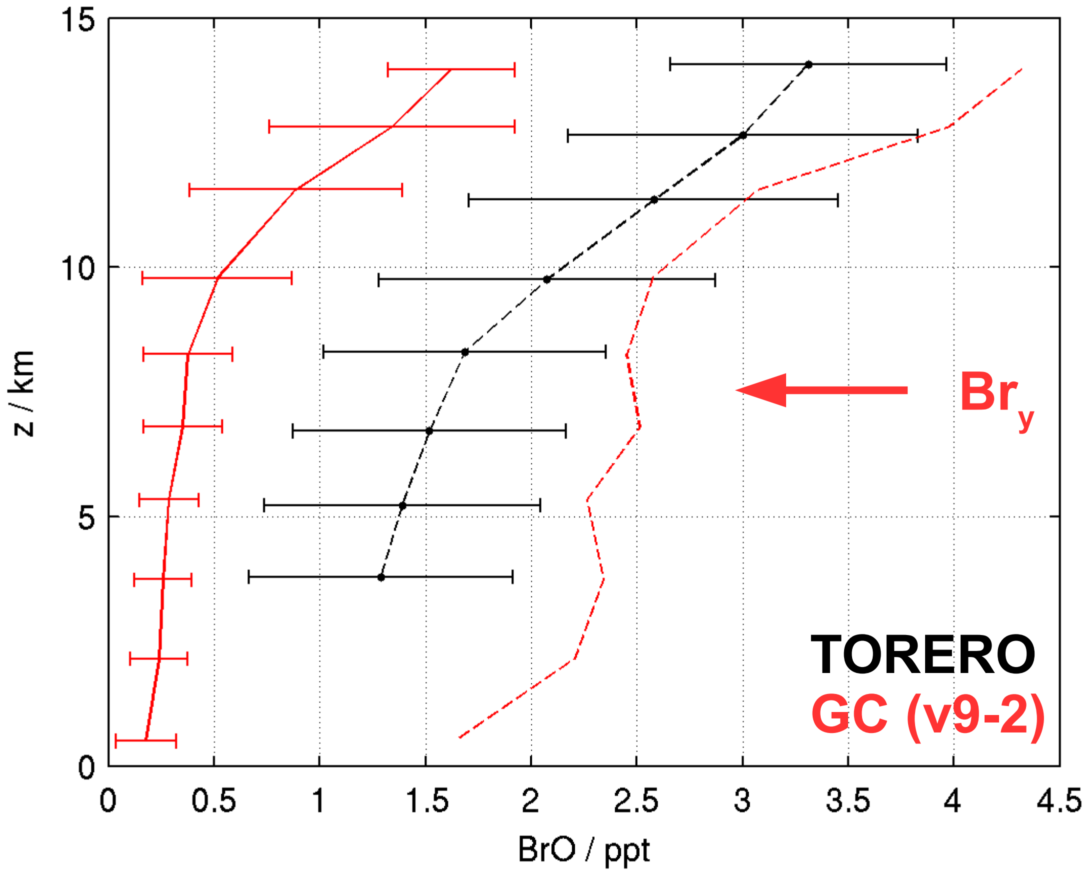
← **obs/GC = 2**

← **obs/GC = 4.5**

We are getting the shape right.

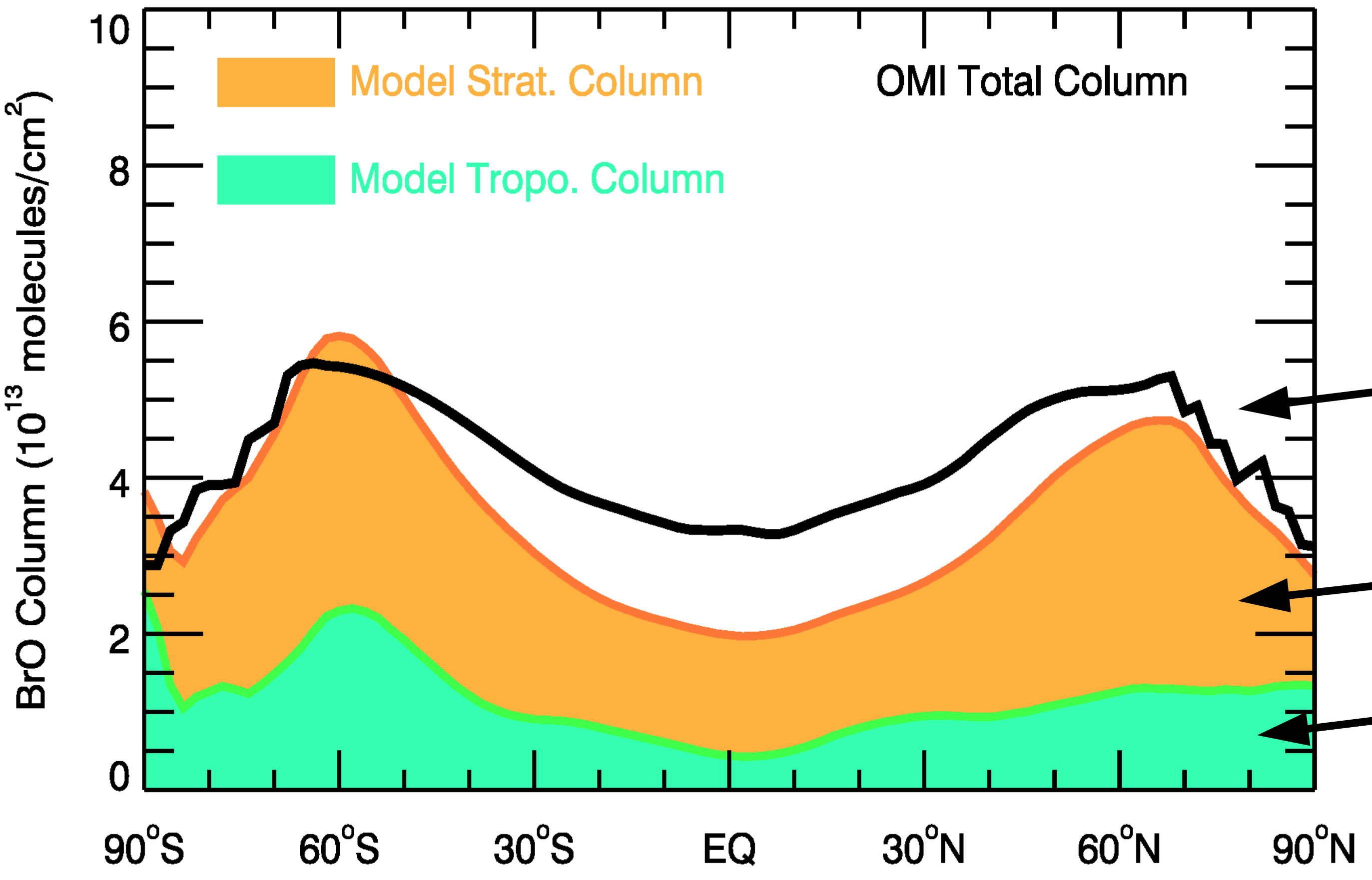
TORERO AMAX-DOAS observations vs. GC v9-02

GEOS-Chem underestimates BrO in the free troposphere



TORERO AMAX-DOAS observations vs. GC v9-02

GC underestimates the OMI BrO column of the tropics ...



OMI Satellite BrO measurements

GEOSCCM(v2) stratospheric model

GEOS-Chem(v9-1-3) tropospheric model

Figure by Qing Liang (2013)

... and there is no seasonality in the deviation in the tropics

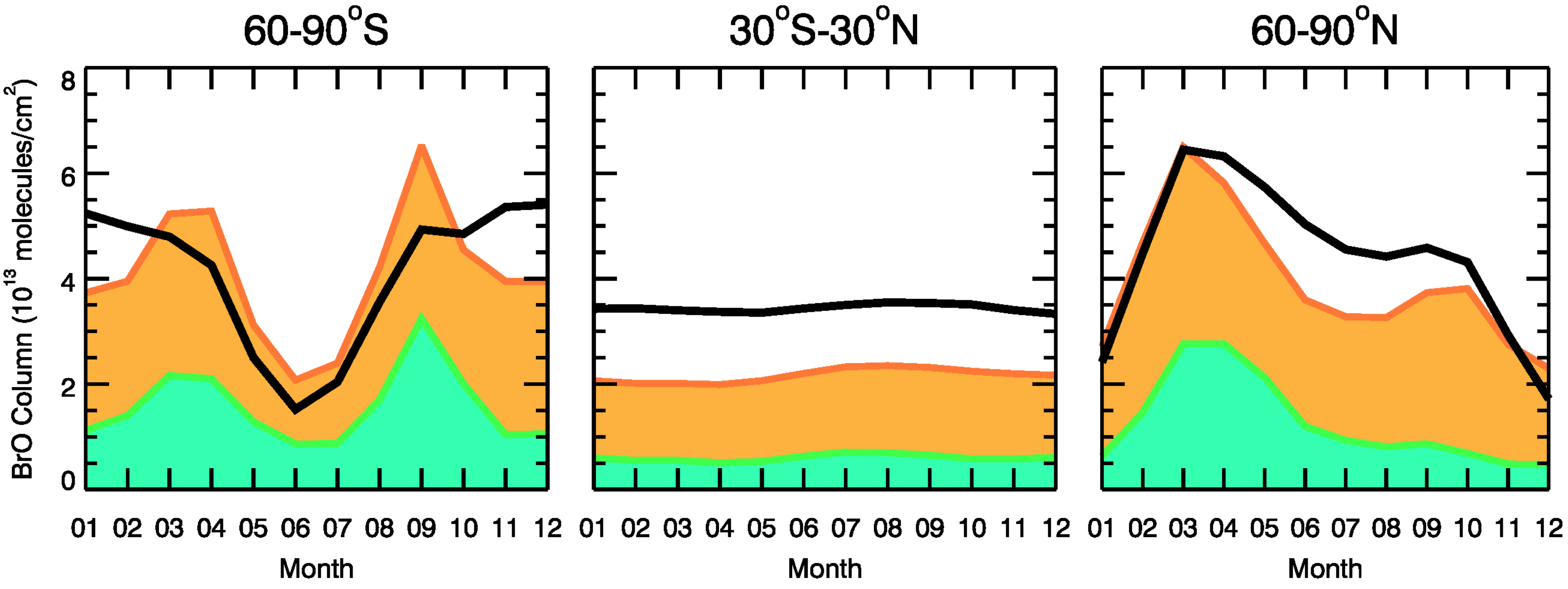
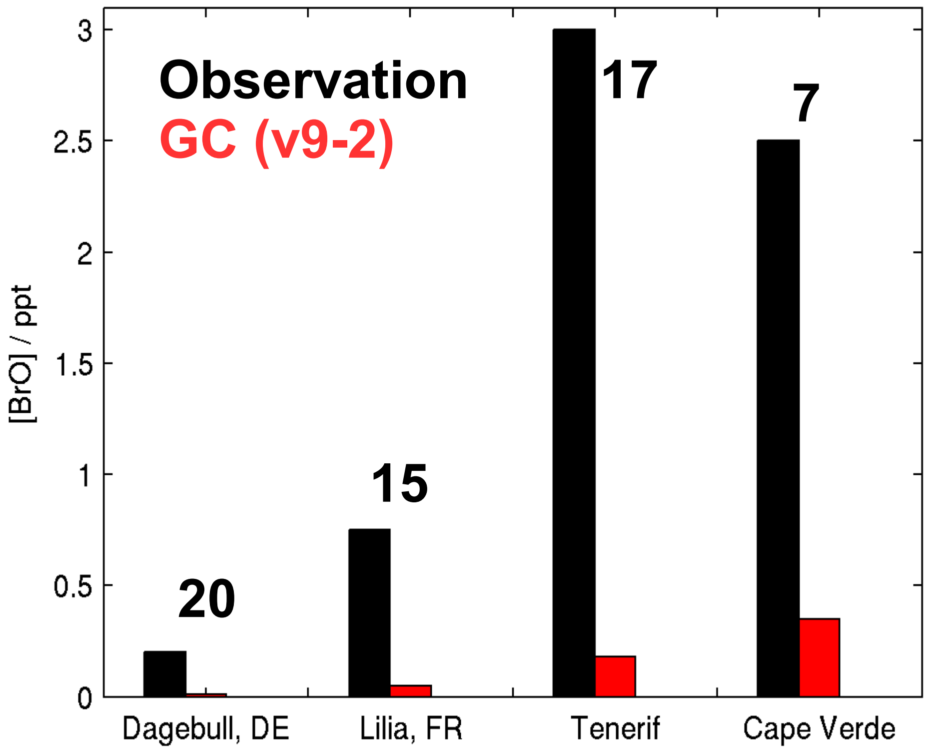
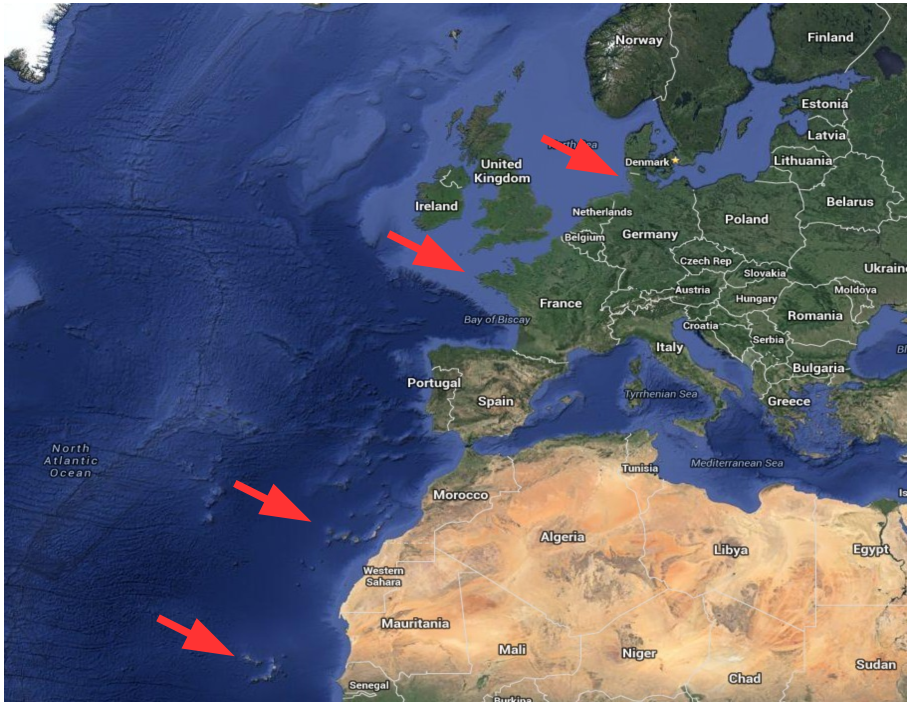


Figure by Qing Liang (2013)

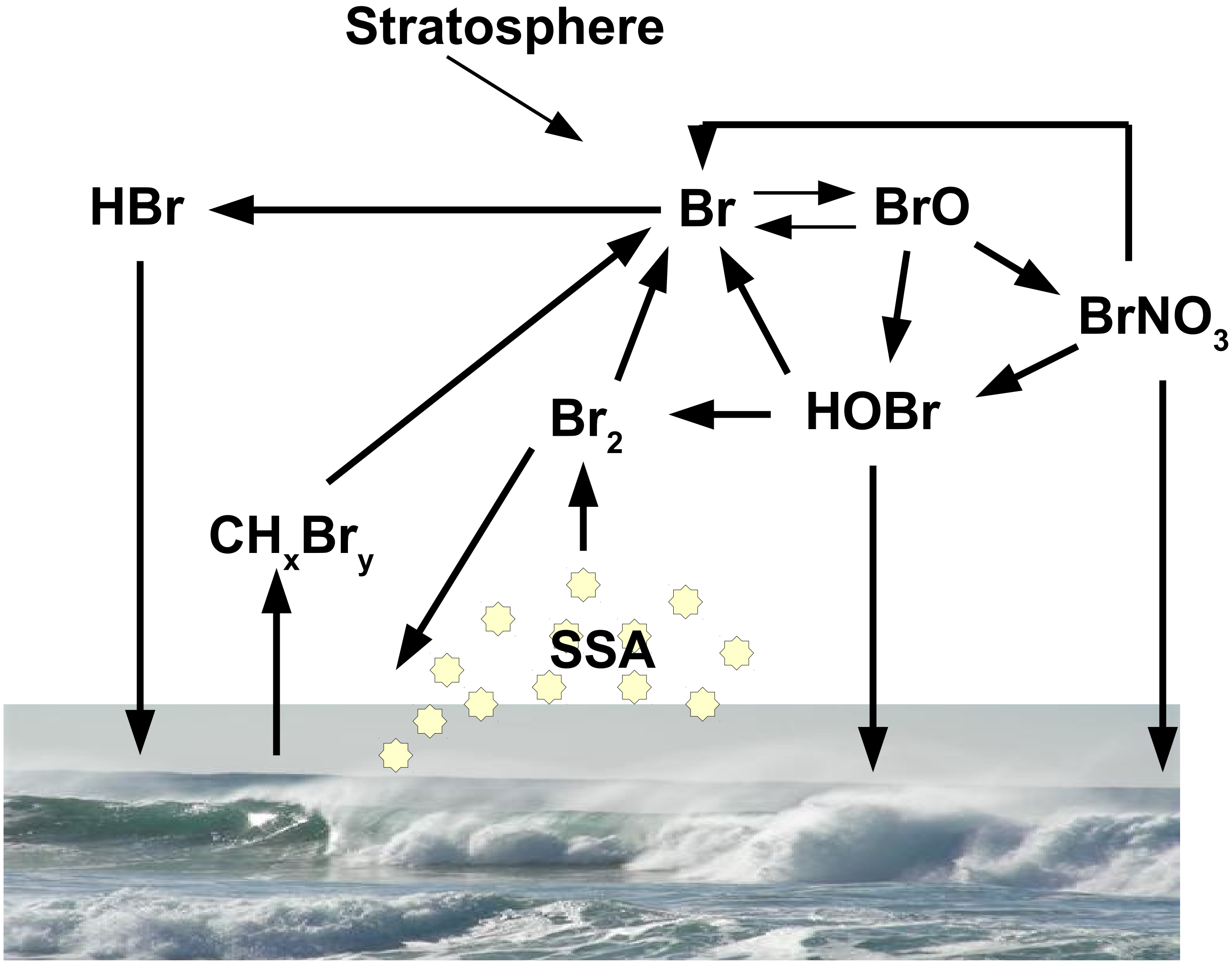
GC underestimates BrO in the MBL





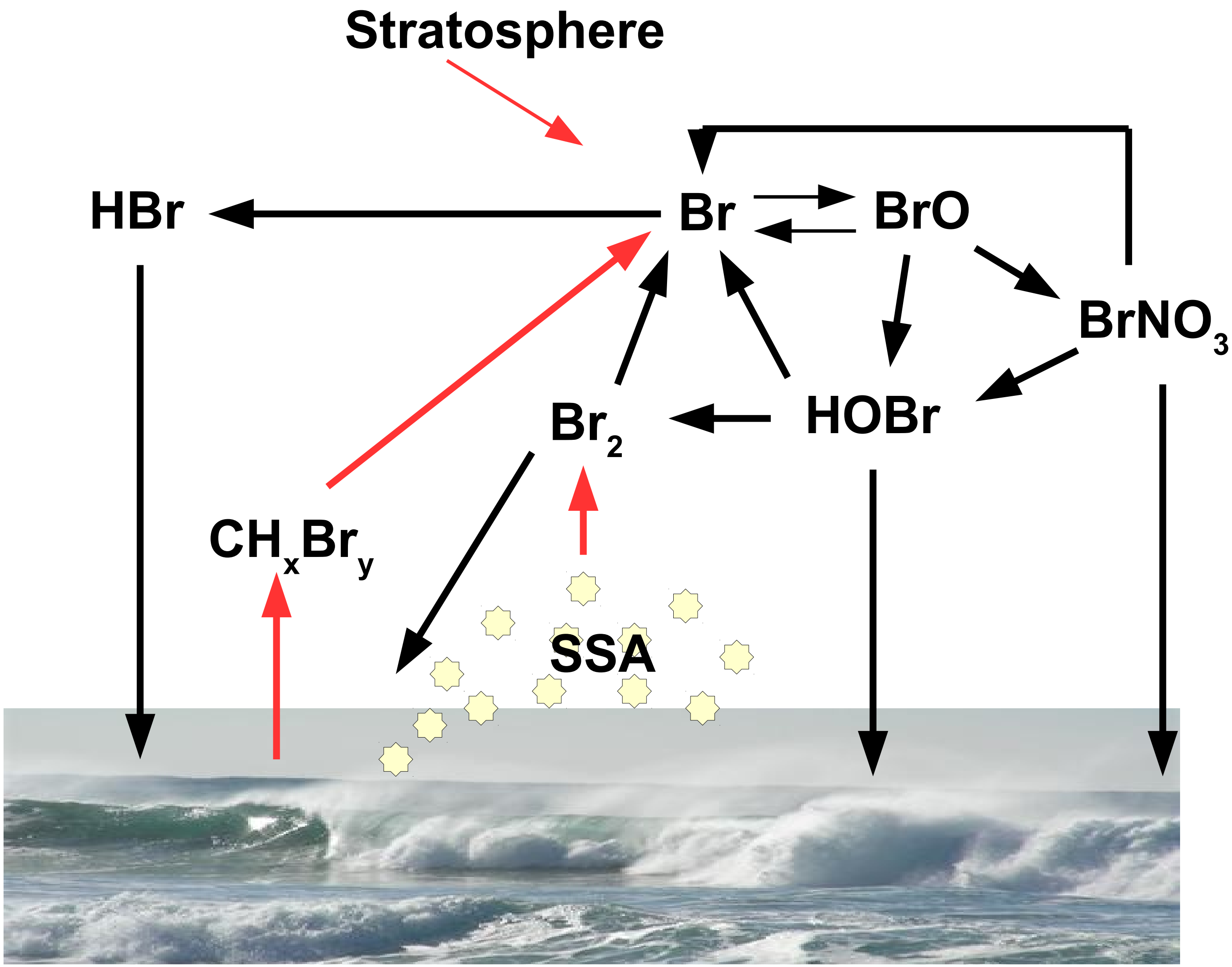
DOAS observations vs. Model output from GC v9-02

Why is GC underestimating BrO?



- **Sources**
- **Sinks**
- **Partitioning**

Why is GC underestimating BrO?



Stratosphere

HBr

Br

BrO

$BrNO_3$

Br_2

HOBr

CH_xBr_y

SSA

- **Sources**
- **Sinks**
- **Partitioning**

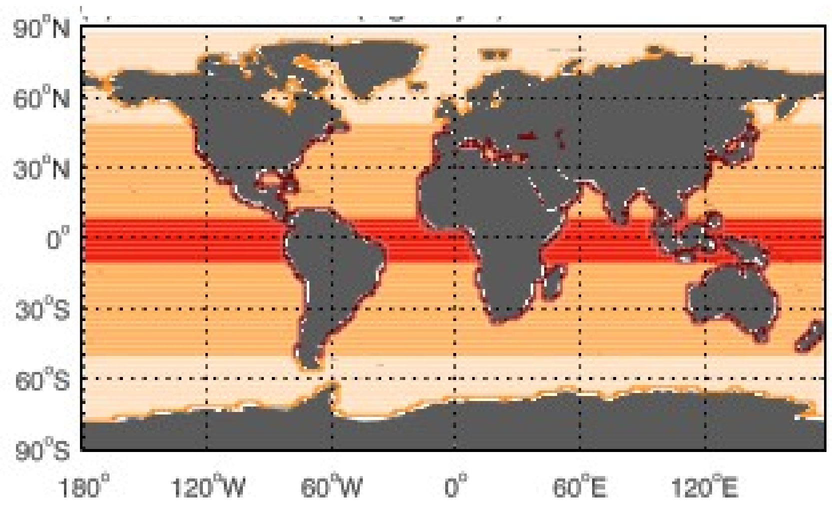
Organobromine
1.5 Gg Br / day

Sea Salt Aeros.
3.9 Gg Br / day

Stratosphere
0.09 Gg Br / day

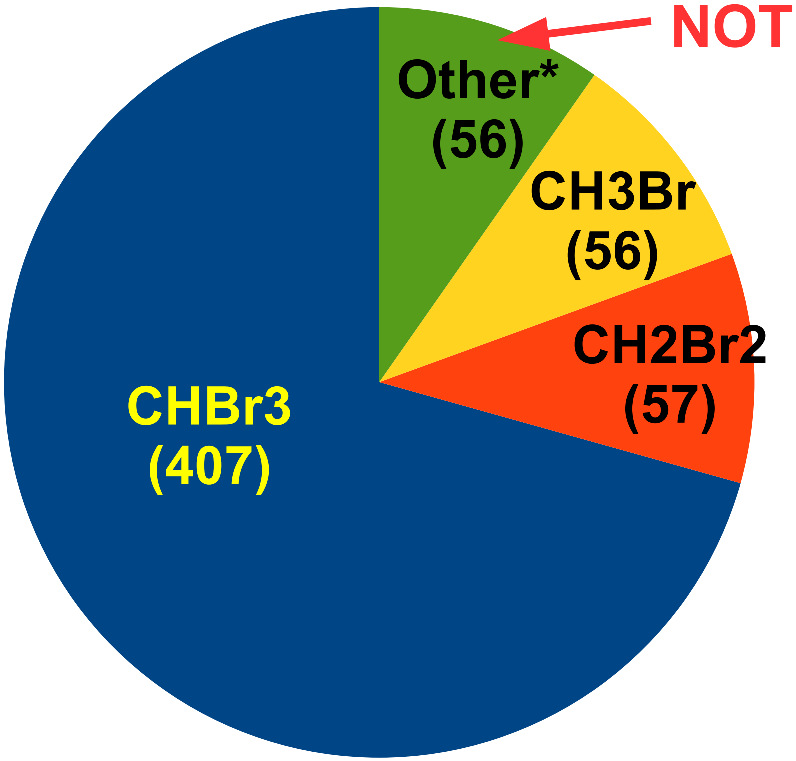
Organobromines in GEOS-Chem

CHBr3 emission field



(Q. Liang et al (2010))

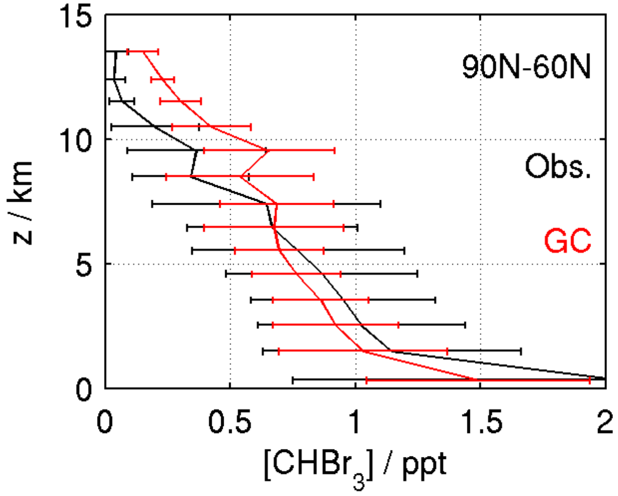
Global source strength in Gg Br/yr

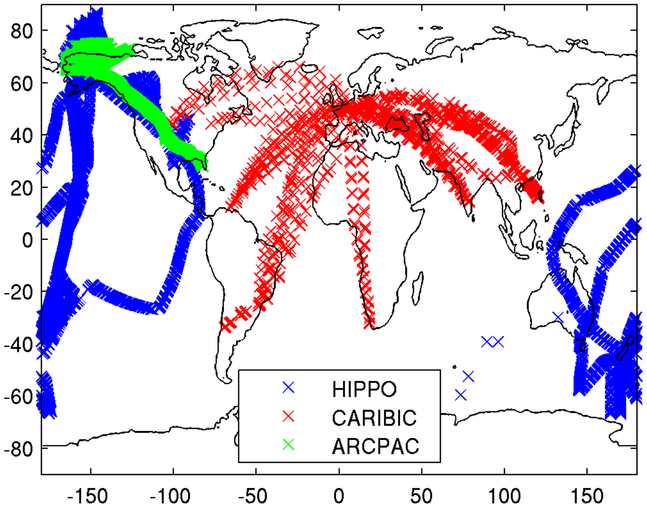


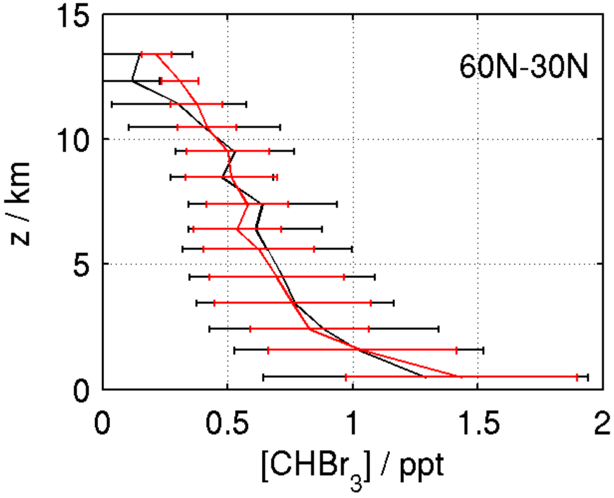
NOT in GC

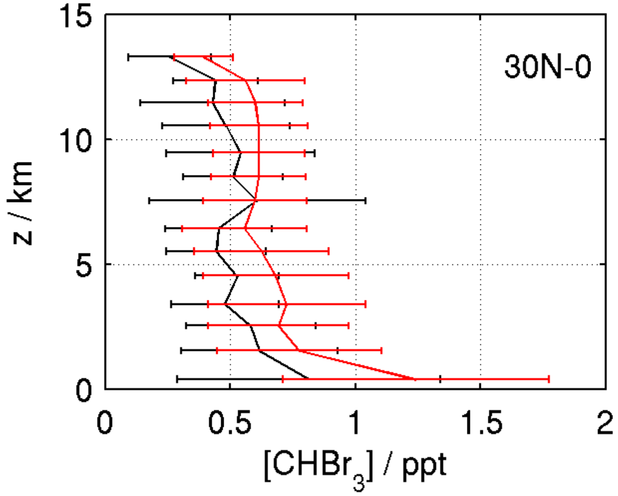
Other = CHBrCl2, CHBr2Cl, CH2BrCl
(Est. from WMO Ozone report)

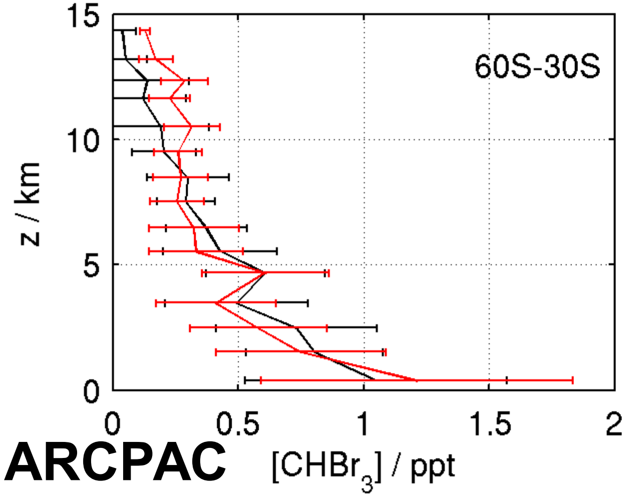
model $CHBr_3$ mixing ratios agree well with observations on a global scale

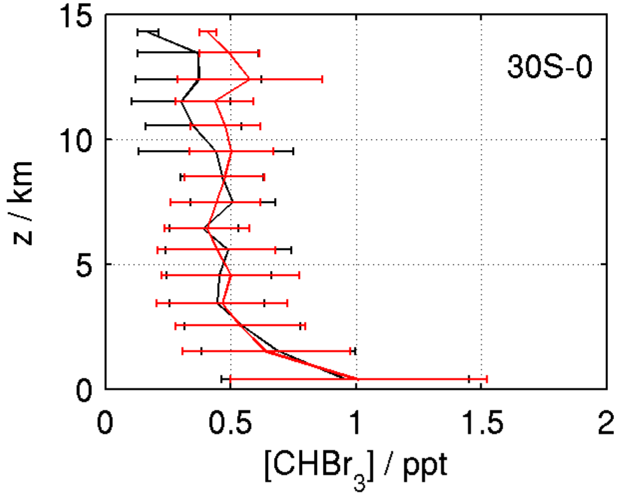






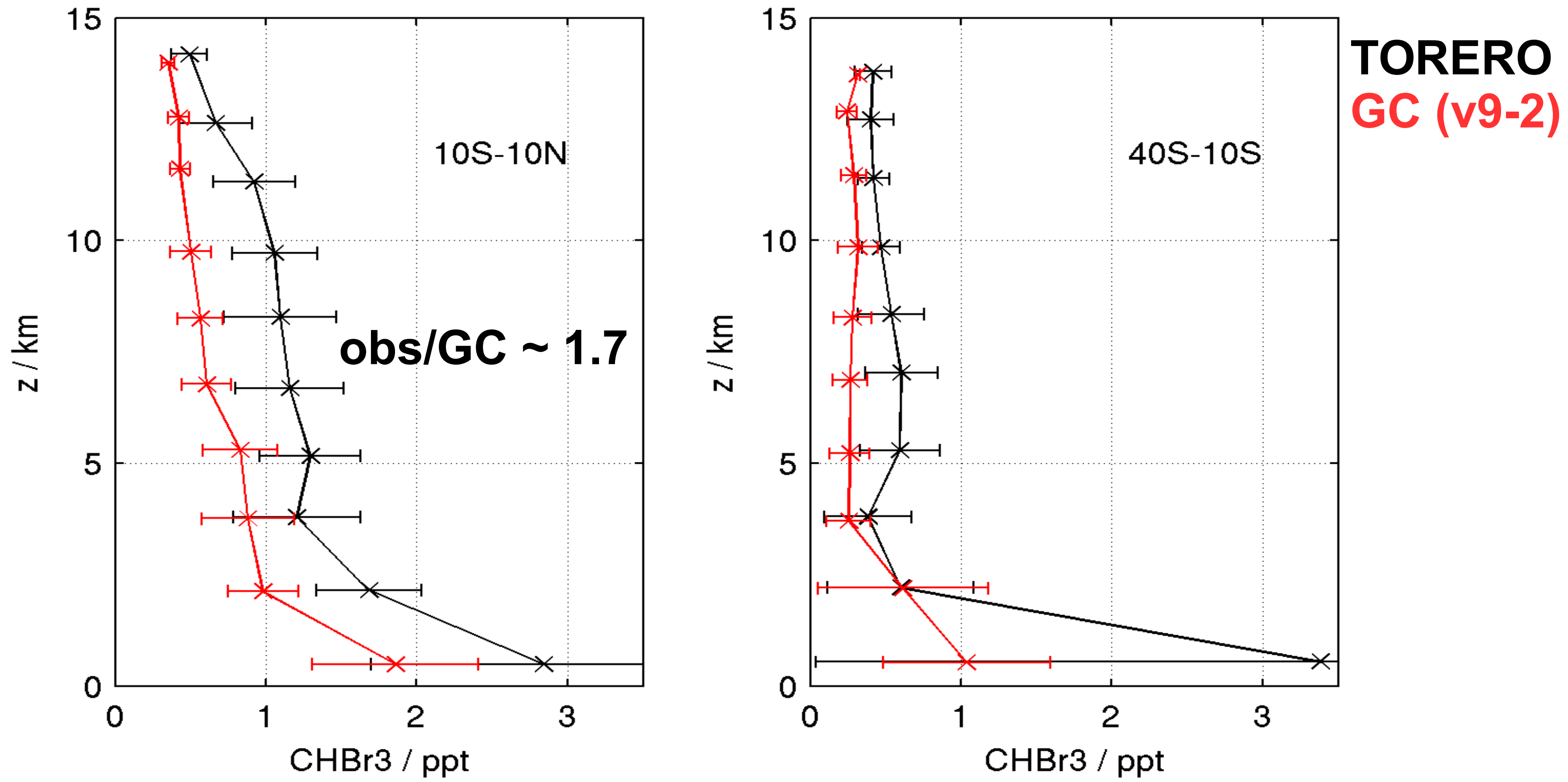






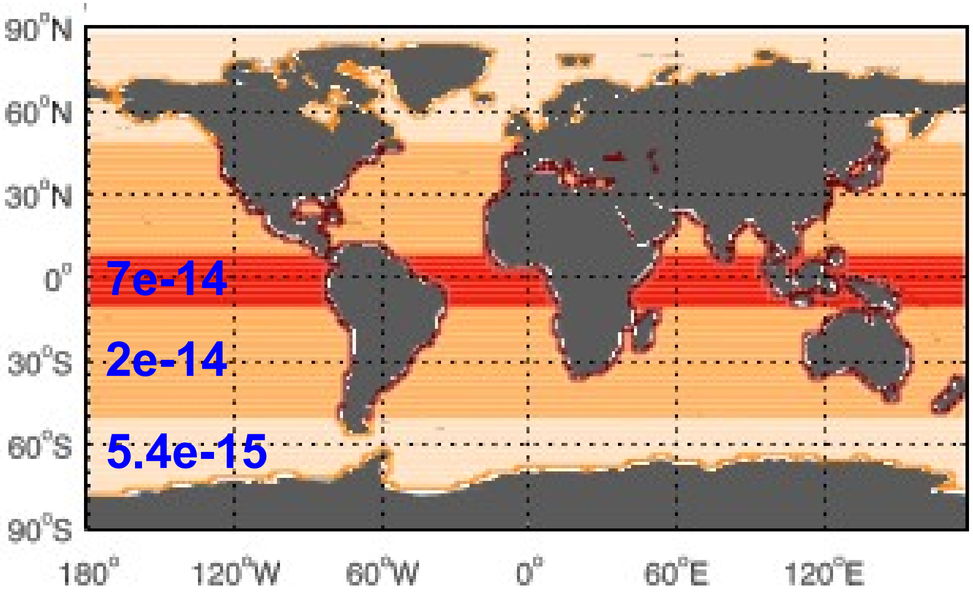
Model: GC (v9-02)
Obs.: HIPPO (1-5), CARIBIC, ARCPAC

TORERO TOGA $CHBr_3$ observations compared to GEOS-Chem

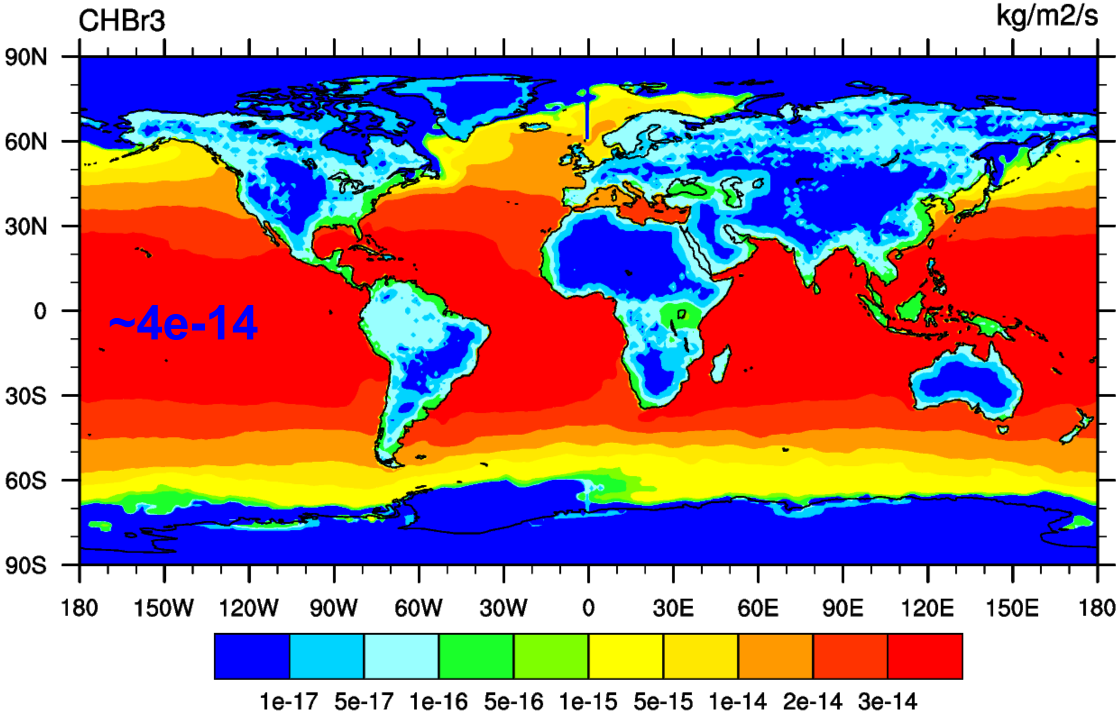


TORERO TOGA observations vs. Model output from GC v9-02

CHBr$_3$ emission fields



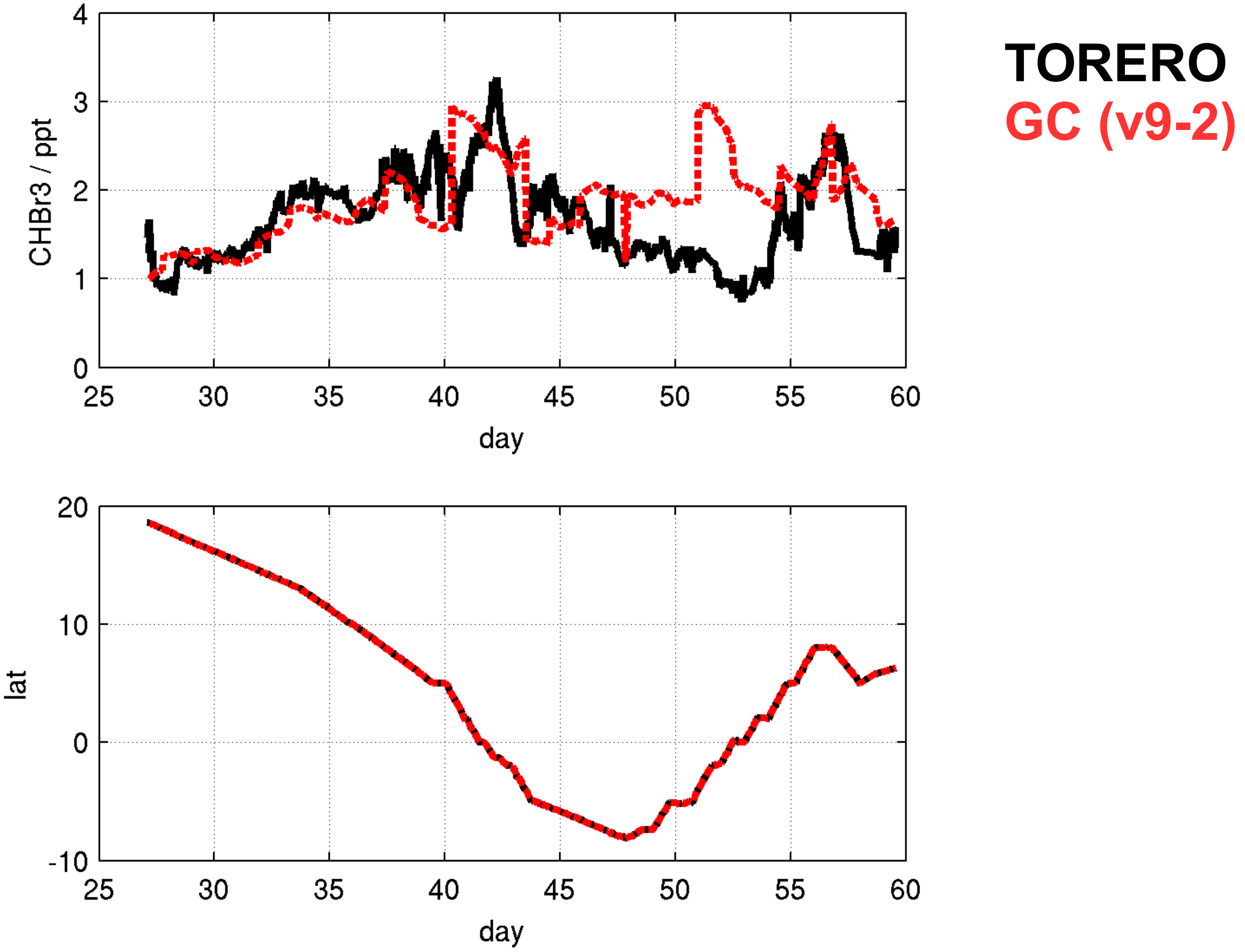
Q. Liang et al (2010)



C. Keller (2014)

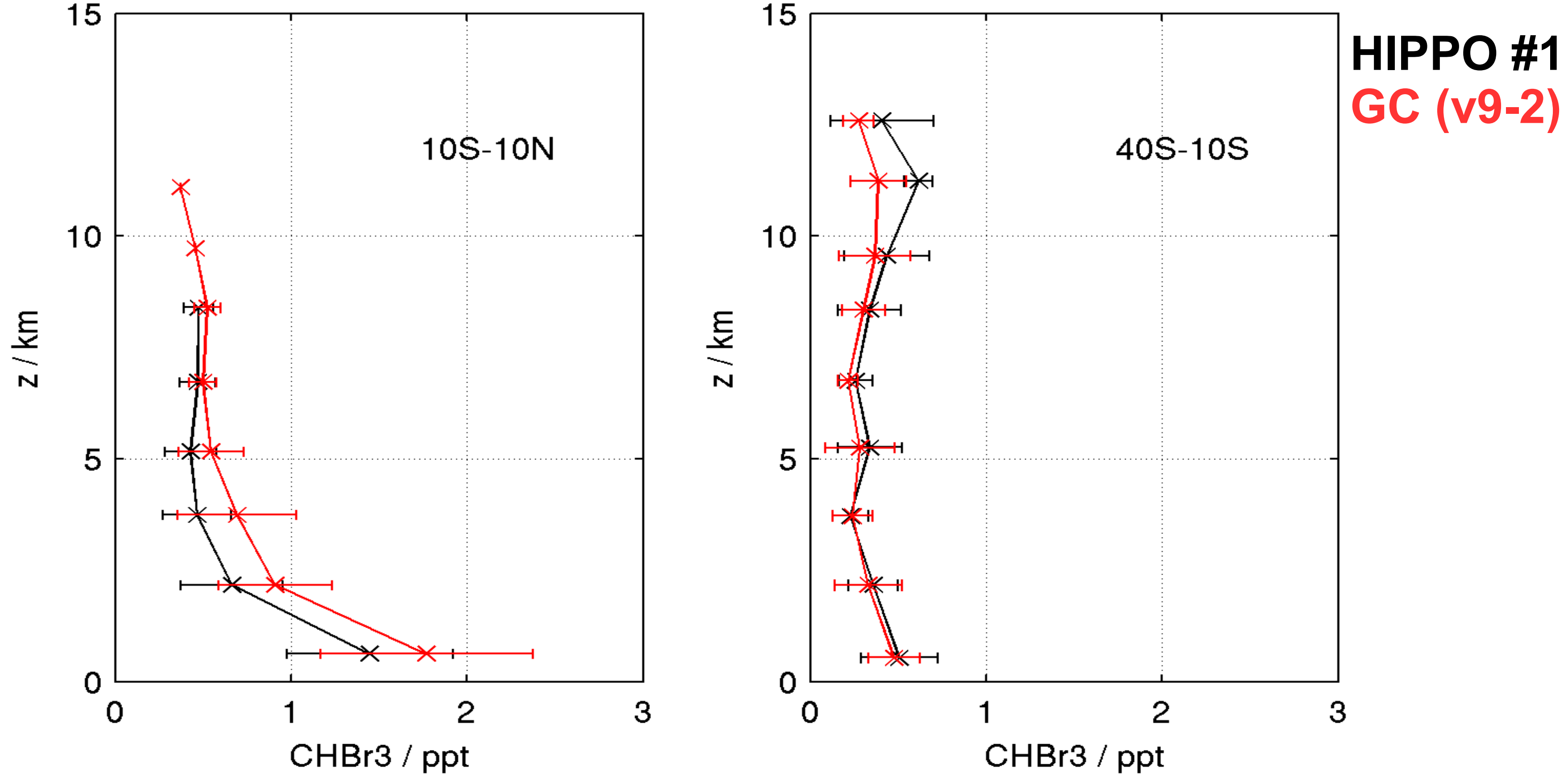
- **Emission for Jan. 2012**
- **Inversion**
- **SST, Chl-a, forest, coast**
- **HalOcAt dataset**

TORERO VSLH $CHBr_3$ observations compared to GEOS-Chem



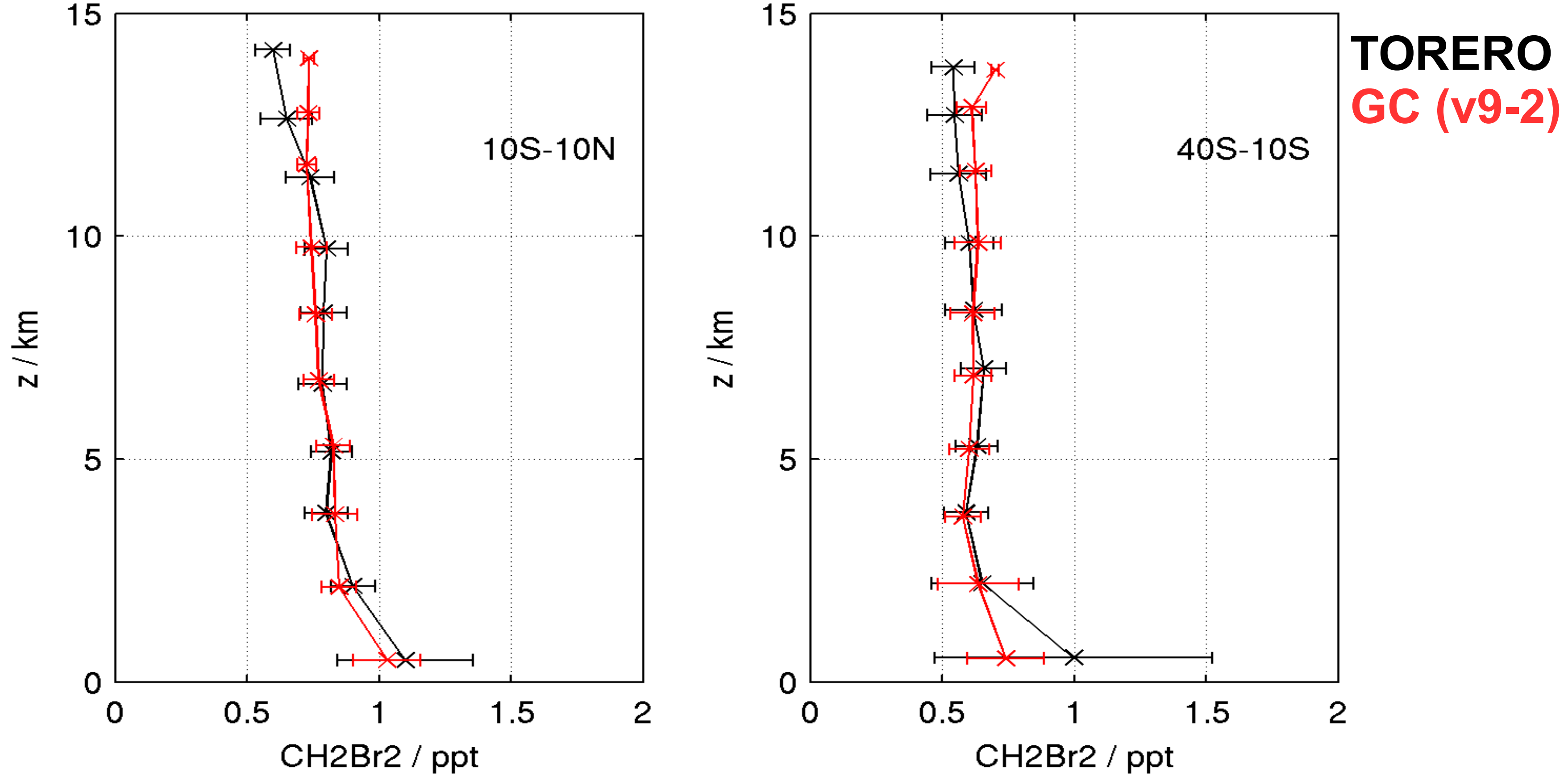
TORERO VSLH (ship) observations vs. Model output from GC v9-02

GC $CHBr_3$ mixing ratios in E. Pacific agree well with observations



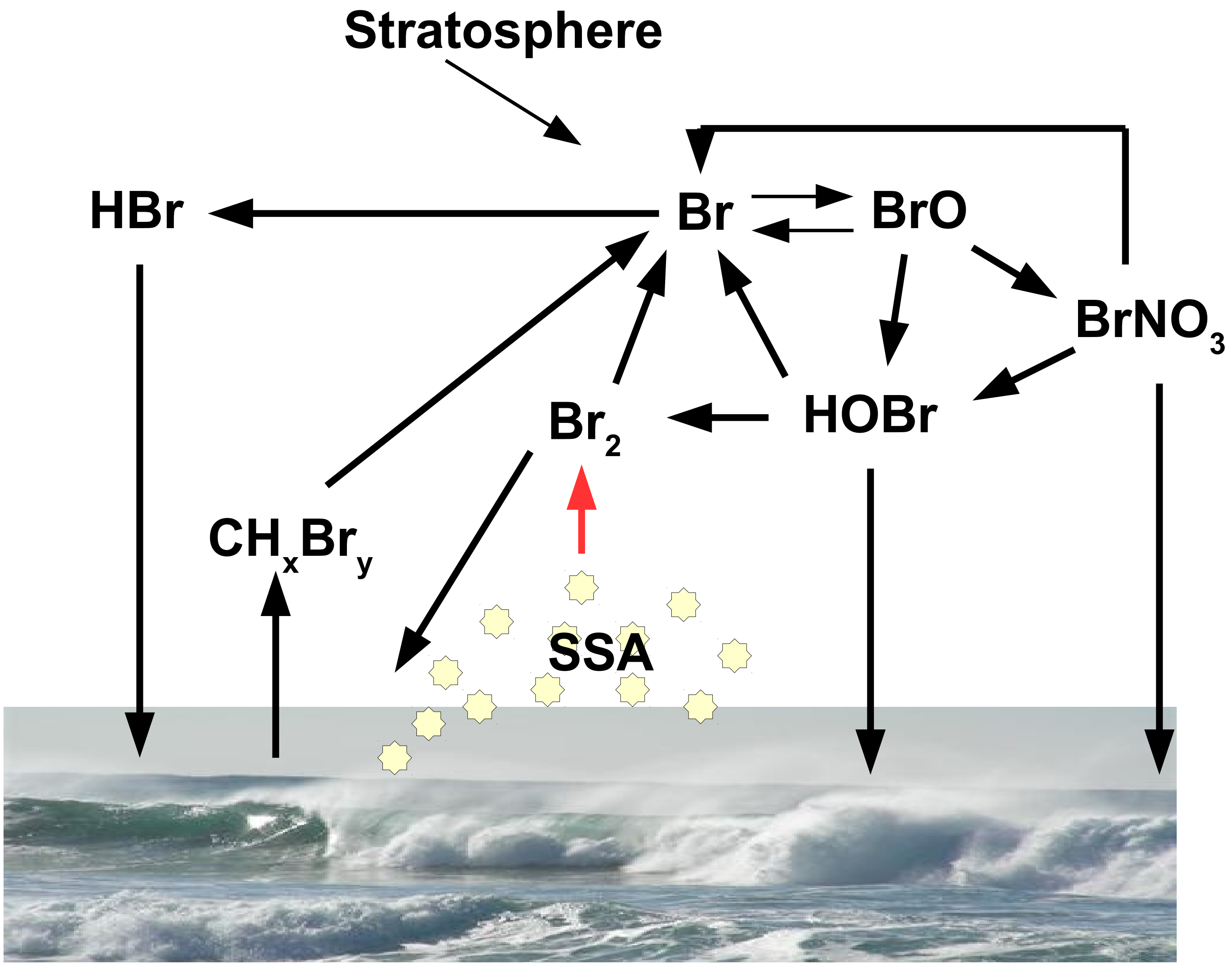
HIPPO #1 aircraft observations vs. Model output from GC v9-02

Comparison of TORERO TOGA CH_2Br_2 observations to GEOS-Chem



TORERO TOGA observations vs. Model output from GC v9-02

The SSA bromine source



Stratosphere

HBr

Br

BrO

$BrNO_3$

Br_2

HOBr

CH_xBr_y

SSA

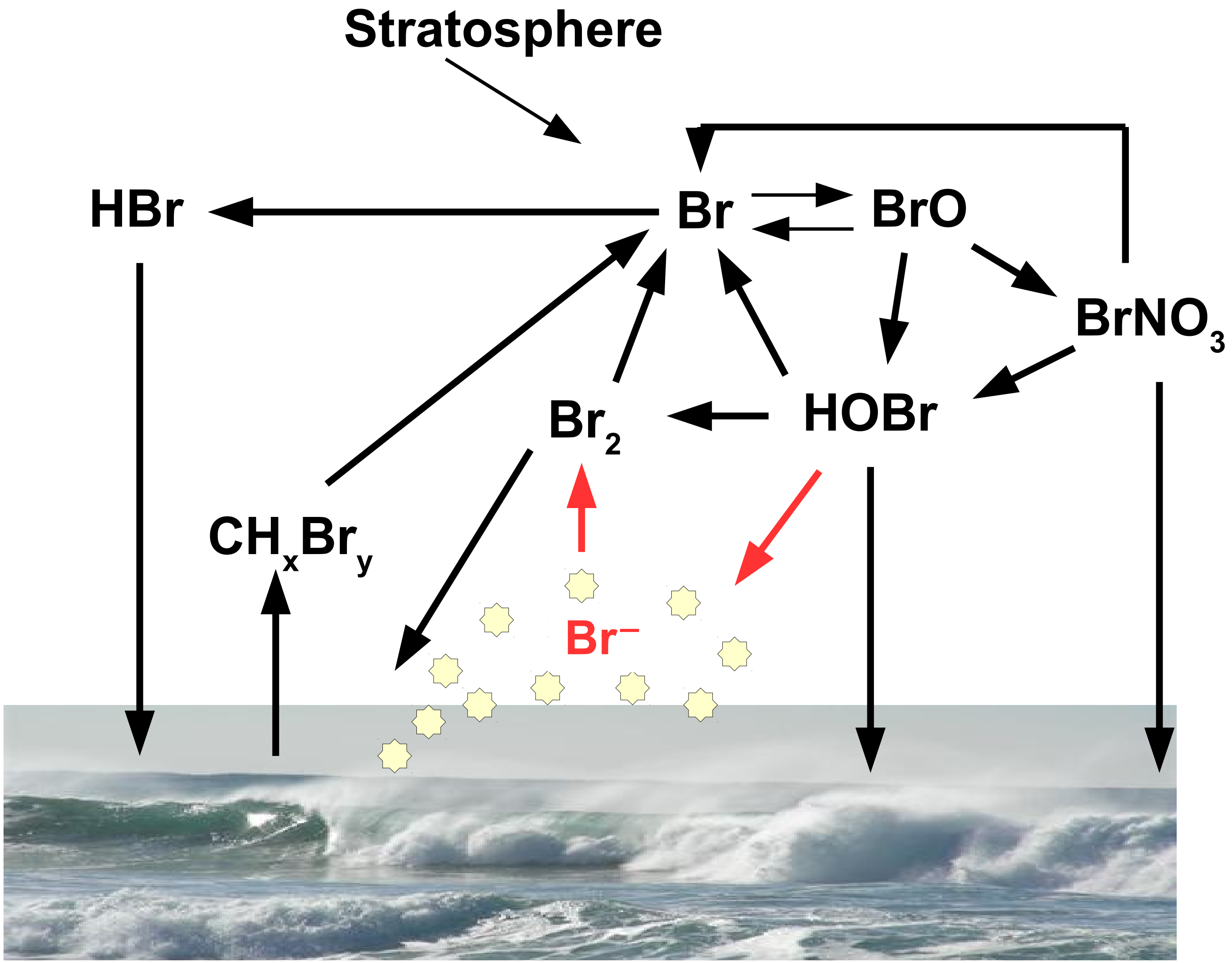
- **Sources**
- **Sinks**
- **Partitioning**

Organobromine
1.5 Gg Br / day

Sea Salt Aeros.
3.9 Gg Br / day

Stratosphere
0.09 Gg Br / day

SSA bromine activation



Stratosphere

HBr

Br

BrO

$BrNO_3$

Br_2

HOBr

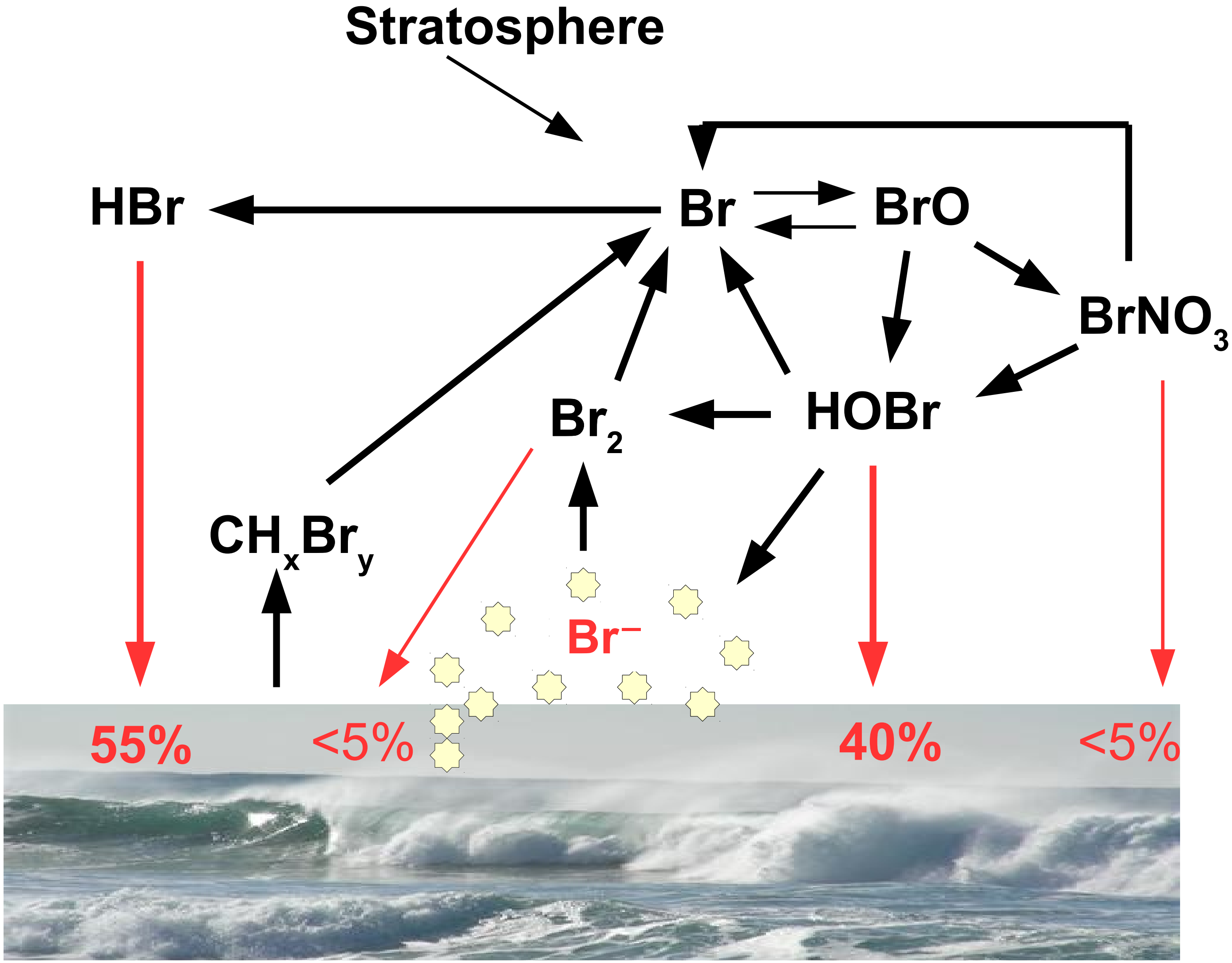
CH_xBr_y

Br^-

- **Sources**
- **Sinks**
- **Partitioning**

Sea Salt Aeros.
Br^- activation

Why is GC underestimating BrO?



Stratosphere

HBr

Br

BrO

$BrNO_3$

Br_2

HOBr

CH_xBr_y

Br^-

55%

<5%

40%

<5%

- **Sources**
- **Sinks**
- **Partitioning**

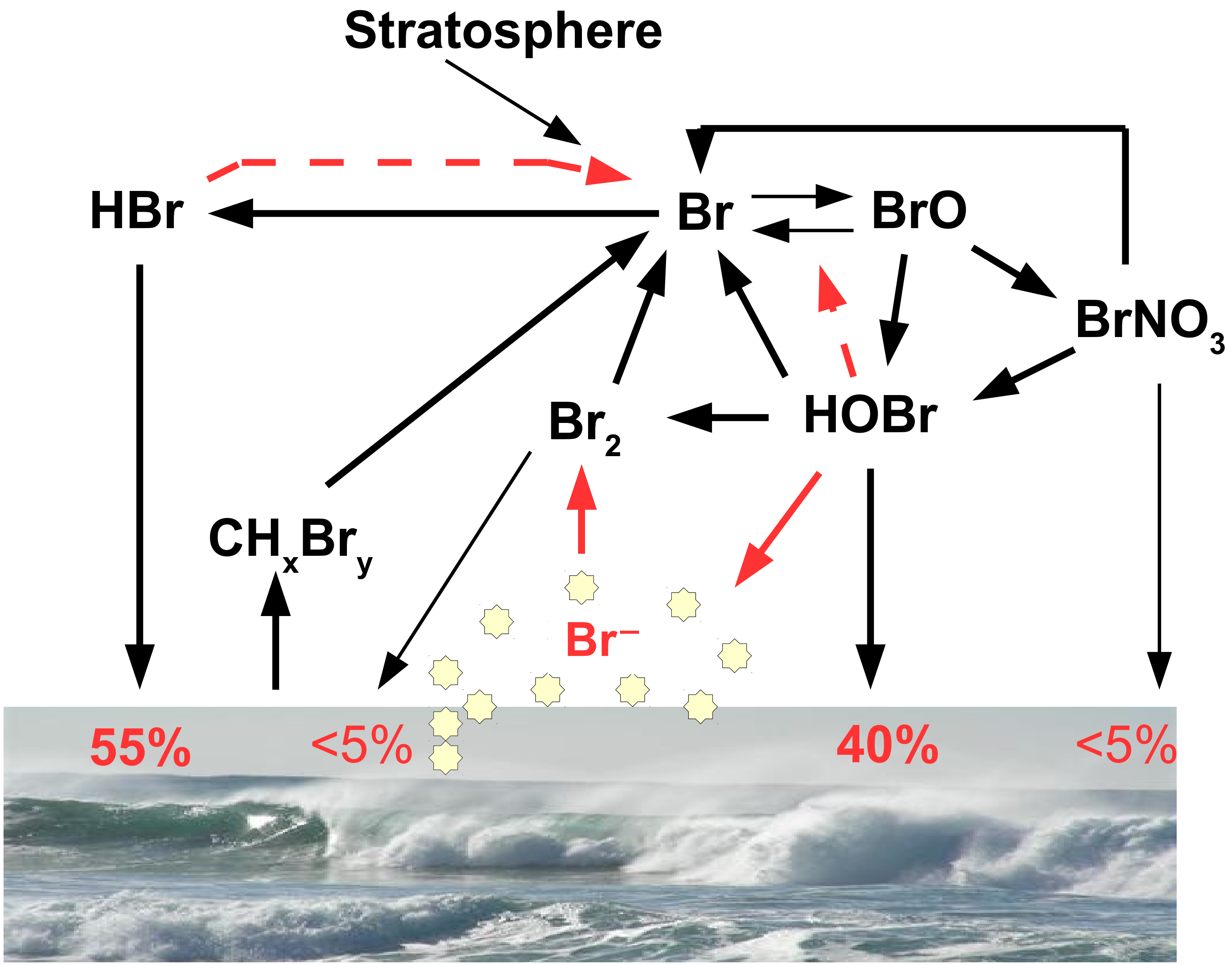
Dry deposition
(at surface)

Wet deposition
(in particular HBr)

- Rain out
- Wash out
- Conv. scavenging

Sink strength from Parrella et al (2012)

Why is GC underestimating BrO?



Stratosphere

HBr

Br

BrO

$BrNO_3$

Br_2

HOBr

CH_xBr_y

Br^-

55%

<5%

40%

<5%

- **Sources**
- **Sinks**
- **Partitioning**

Is GC underestimating the recyling of HBr or HOBr?

Yes, key heterogeneous processes are missing

Sink strength from Parrella et al (2012)

The kinetics of heterogeneous reactions is parametrized by the reac. uptake coef. (γ)

$X(g) \xrightarrow{\text{het}} X(s)$ $\quad$ $X(g) \xrightarrow{\text{het}} X(aq)$

$X(g) \xrightarrow{\text{het}} \text{products}$ $\quad$ $X(g) + Y \xrightarrow{\text{het}} \text{products}$

$\text{rate} = d[X(g)]/dt = - \gamma\ (c_{avg}/4)\ [\text{Surf area}]\ [X(g)]$

- Prob. to reactive uptake coefficient (γ)
- Prob. to surface area concentration
- Prob. to concentration of X(g)
- No explicit dependence on Y!

Amman et al. (2013)

The reac. uptake coef. is determined by the “bottleneck” of the heterogeneous reaction

Reaction involves several steps, e.g,
1) Diffusive to surface
2) Uptake on/into particle
3) Reaction in condensed phase

rate = $- \gamma (c_{avg}/4)$ [Surf area] [X(g)]

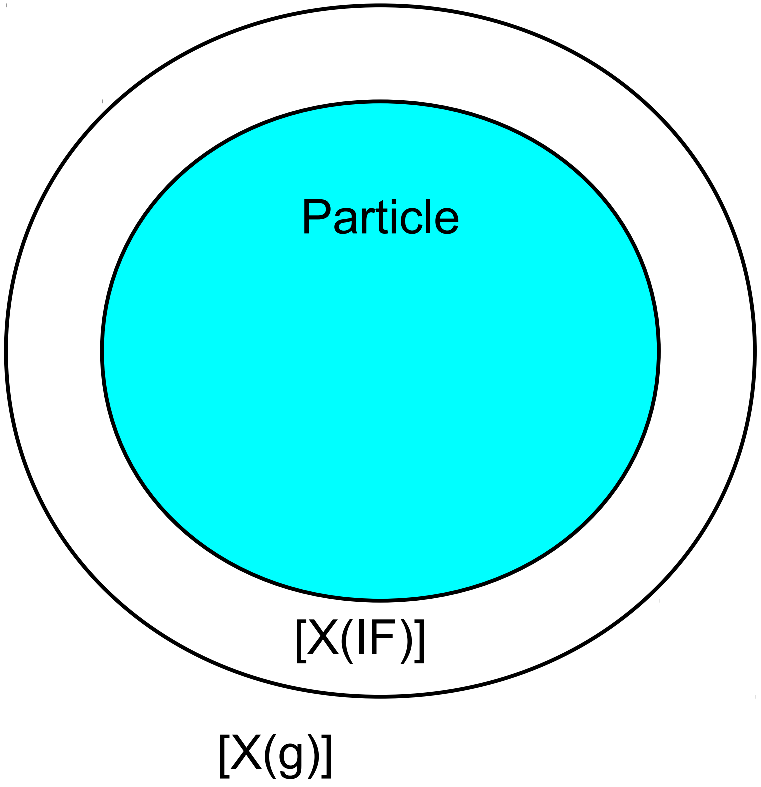
$1/\gamma = 1/\Gamma_{diff} + 1/\gamma'$

$\Gamma_{diff} = 4\ D_g\ /\ (c_{avg}\ r)$

$D_g \approx 3\ (\ k_B T\ /\ (2\pi\mu_{X\text{-}air})\ )^{½}\ /\ (8\ n_{air}\ \sigma_{X\text{-}air}{}^2)$

1st approximation of Chapman-Enskog

Γ_{diff} ~ 0.2 @ 1bar but sensitive to **n_{air}** and **r**



[X(g)] ≥ [X(IF)]

The reac. uptake coef. for reactions in the bulk liquid phase

$X(g) + Y(aq) \longrightarrow$ products

rate = $- \gamma\, (c_{avg}/4)$ [Surf area] $[X(g)]$

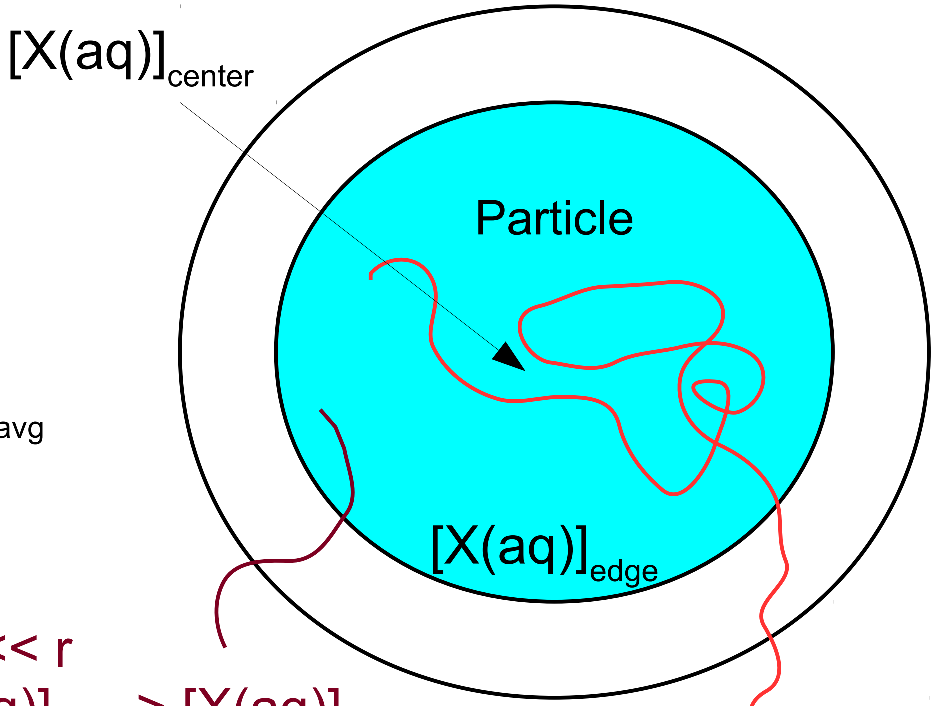
Two possible bottlenecks:
1) Uptake into bulk
2) Reaction in bulk

$$1/\gamma' = 1/\alpha_b + 1/\Gamma_b$$

$$\Gamma_b = 4\, H_X\, R\, T\, (D_l\, k_b\, [Y(aq)]\,)^{1/2}\ \beta / c_{avg}$$

$$\beta = \coth(r/l) - (l/r)$$

$$l = D_l / (k_b\, [Y(aq)])$$



$[X(aq)]_{center}$

Particle

$[X(aq)]_{edge}$

If $l \ll r$
$[X(aq)]_{edge} > [X(aq)]_{center}$
$\Gamma_b = W\, (k_b[Y(aq)])^{1/2}$

If $l \gg r$
$[X(aq)]_{edge} = [X(aq)]_{center}$
$\Gamma_b = W\, k_b[Y(aq)]$

The uptake coef. for reactions on surfaces: Two mechanisms

rate = $- \gamma (c_{avg}/4)$ [Surf area] [X(g)]

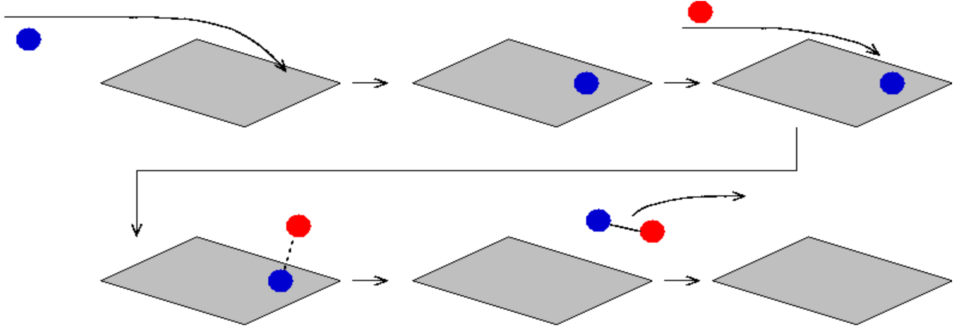
$X(g) + Y(s) \longrightarrow$ products

Eley-Rideal (ER) mechanism

$X(g) + Y(s) \longrightarrow$ products

$\gamma' = \gamma_X \theta_y$

- Prob. to some intrinsic reaction probability
- Prob. to surface coverage of Y
- Does not depend surface uptake coef. (α_s)



Langmuir-Hinshelwood (LH) mechanism

1) $X(g) \longrightarrow X(s)$

2) $X(s) + Y(s) \longrightarrow$ products

$1/\gamma' = 1/\alpha_s + 1/\Gamma_s$

$\Gamma_s = k_s[X(s)][Y(s)]\ 4/(c_{avg}[X(g)])$

- Prob. to surface concentrations
- "$4/(c_{avg}[X(g)])$" cancels out
- Does depend on α_s

The Extended Heterogeneous Chemistry (EHC) mechanism

Liquid phase reaction:

- HOBr + Br^{-}/Cl^{-}
- HOCl + Br^{-}/Cl^{-}
- $ClNO_3$ + Br^{-}
- O_3 + Br^{-}
- Cl_2 + Br^{-}
- BrCl + Br^{-}

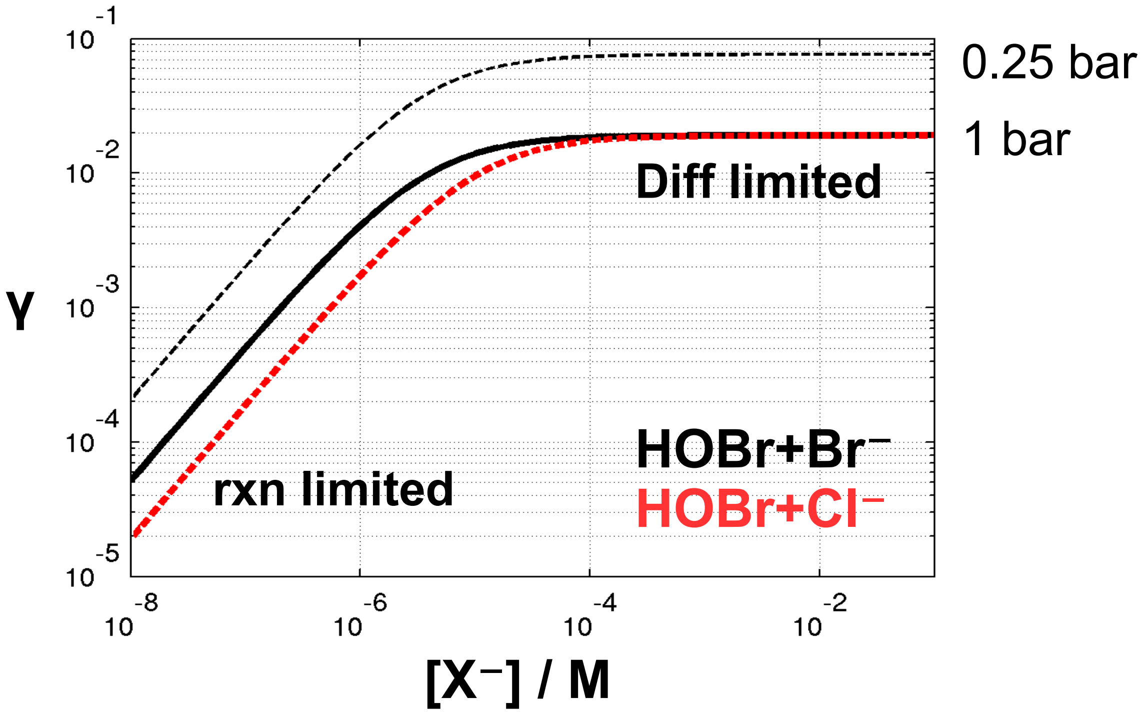
Solid phase reaction:

- HOBr + HBr/HCl
- HOCl + HBr/HCl
- $ClNO_3$ + HBr/HCl
- HONO + HBr

Chemistry driven SSA bromine emission

Uptake and rxn parameters from Ammann et al (2013) and Crowley et al. (2010) (IUPAC recommendations)

EHC computes reac. uptake coefficients for each grid box and time step

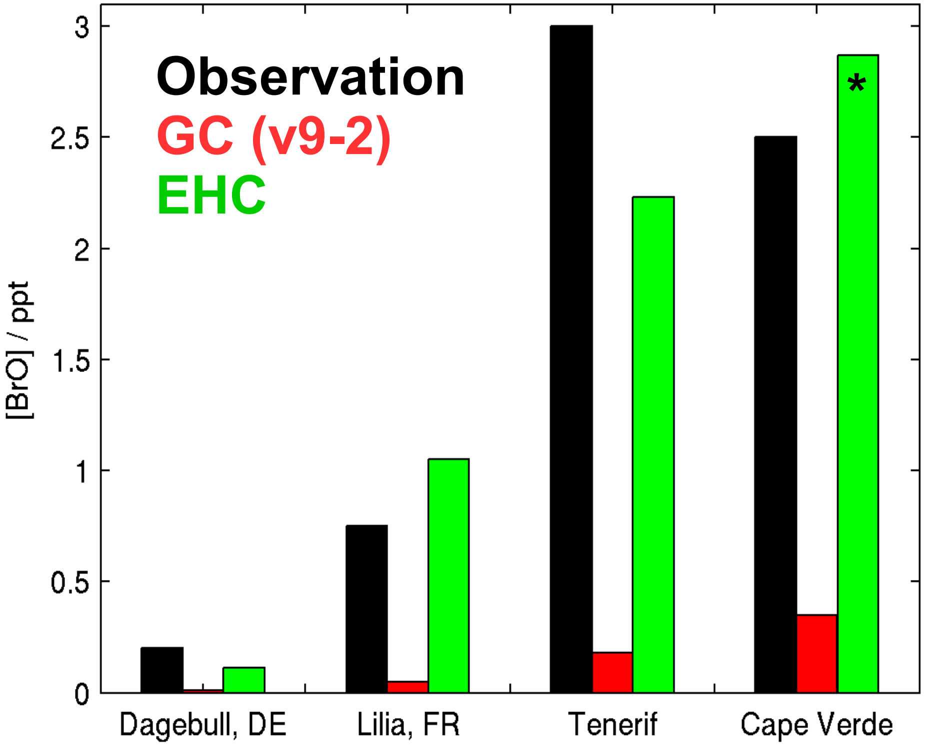


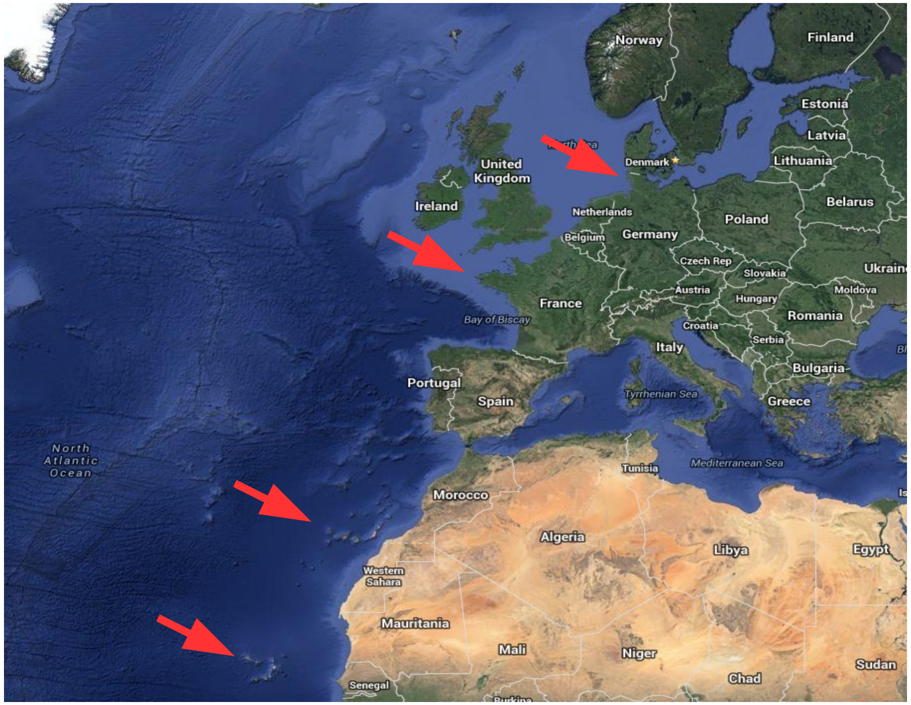
$$\text{Rate} = \gamma\, c_{avg}\, [\text{Surf}][\text{OX(g)}] / 4$$

$$\gamma = (\gamma_{diff}^{-1} + \gamma_{uptake}^{-1} + \gamma_{rxn}^{-1})^{-1}$$

Uptake and rxn parameters from Ammann et al (2013) (IUPAC recommendation)

Chemistry driven SSA bromine emission increases BrO in the MBL

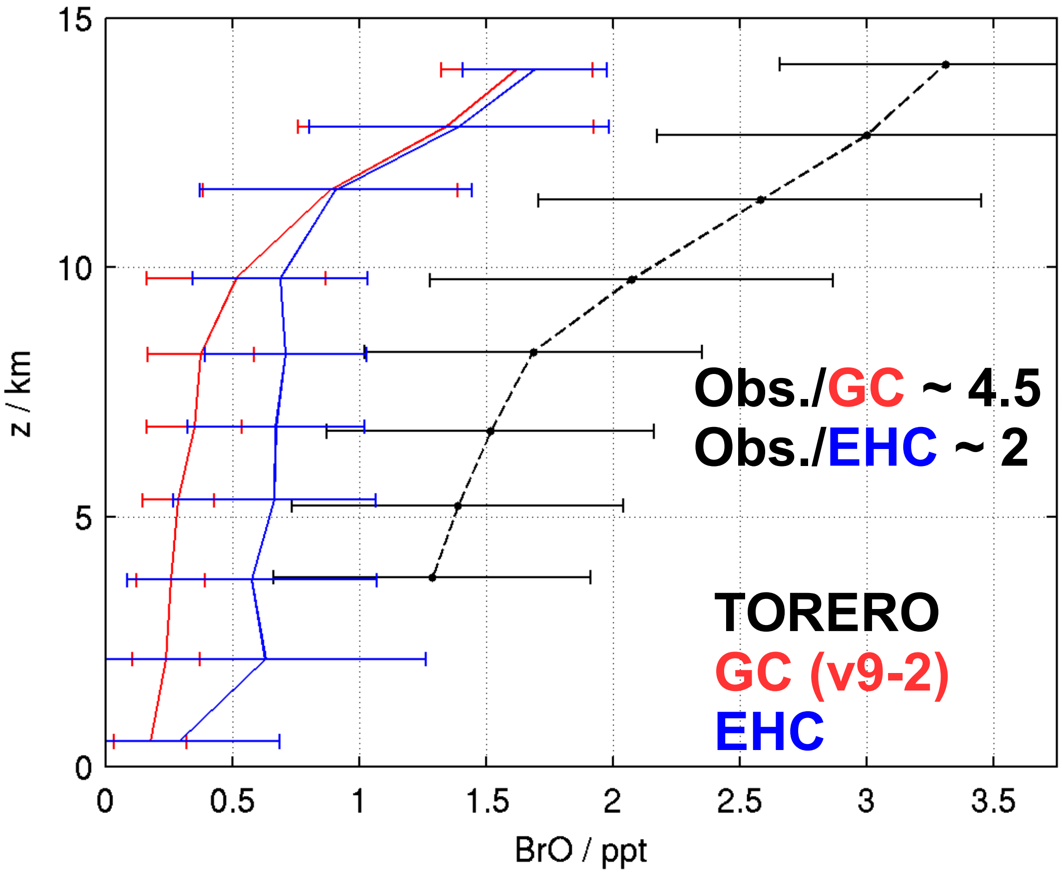




DOAS observations vs. Model output from GC v9-02 and EHC

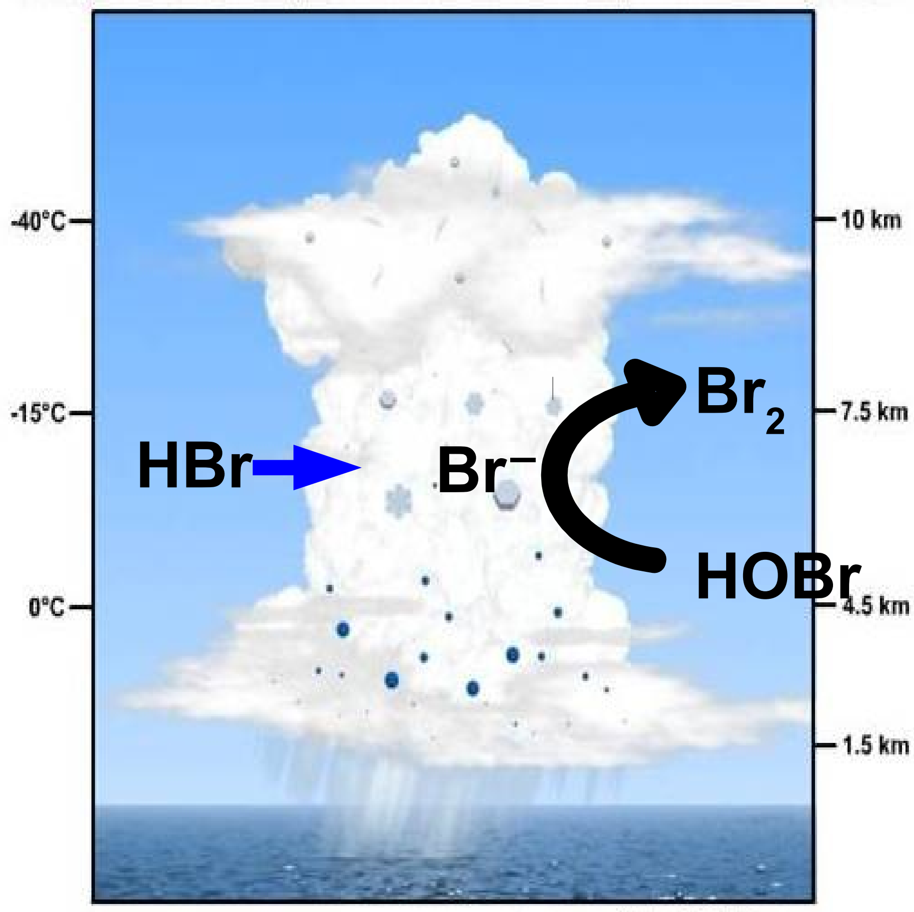
***) Summer months average**

Heterogeneous recycling of HOBr and cloud scavenged HBr enhances FT BrO



Obs./GC ~ 4.5
Obs./EHC ~ 2

b Conceptual Model of Precipitation Processes inside a Tropical Cumulonimbus Cloud



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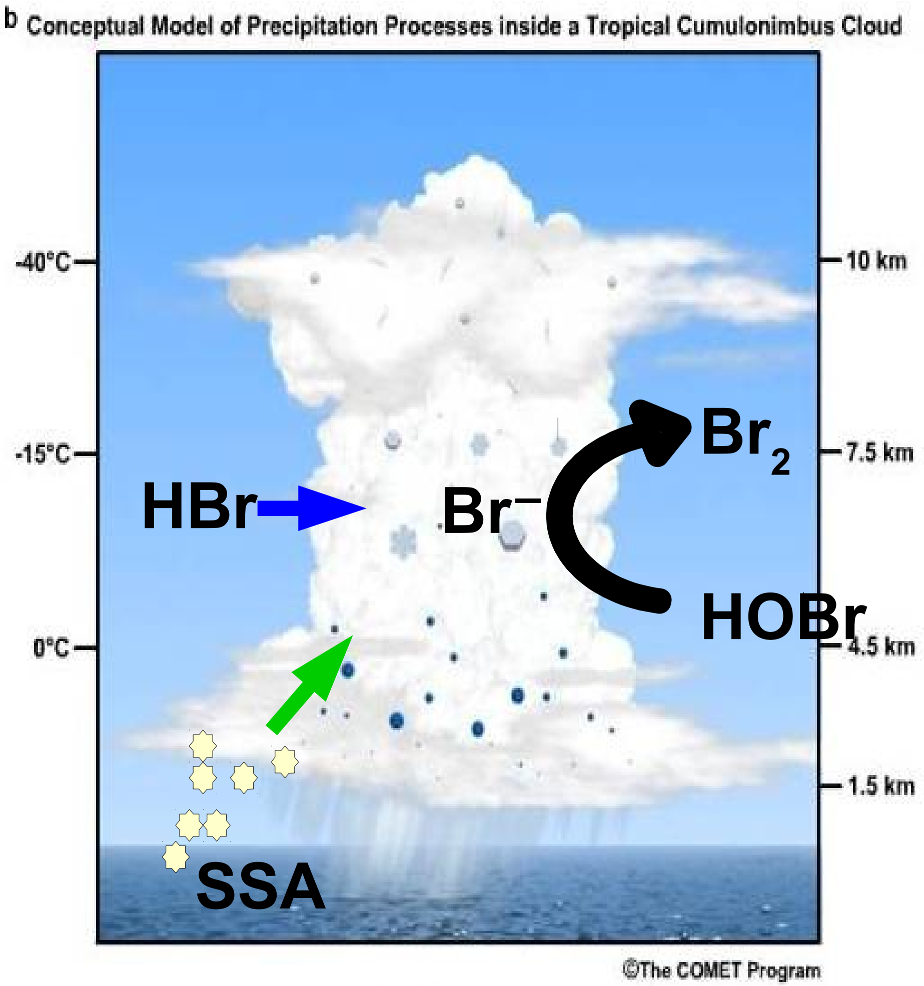
TORERO AMAX-DOAS observations vs. GC v9-02 and EHC

Sources of cloud and aerosol bromide

Location	$[Na^+]$/μM	$[Cl^-]$/μM	$[Br^-]$/nM
Netherlands *	204	251	540
Whiteface Mt, NY	11	31	(30)
HI99, Hawaii*	25	31	(60)
Porto Rico*	55	69	(140)
Taiwan	153	200	(400)

* Precipitation
(estimate from $[Cl^-]/[Br^-]=500$)



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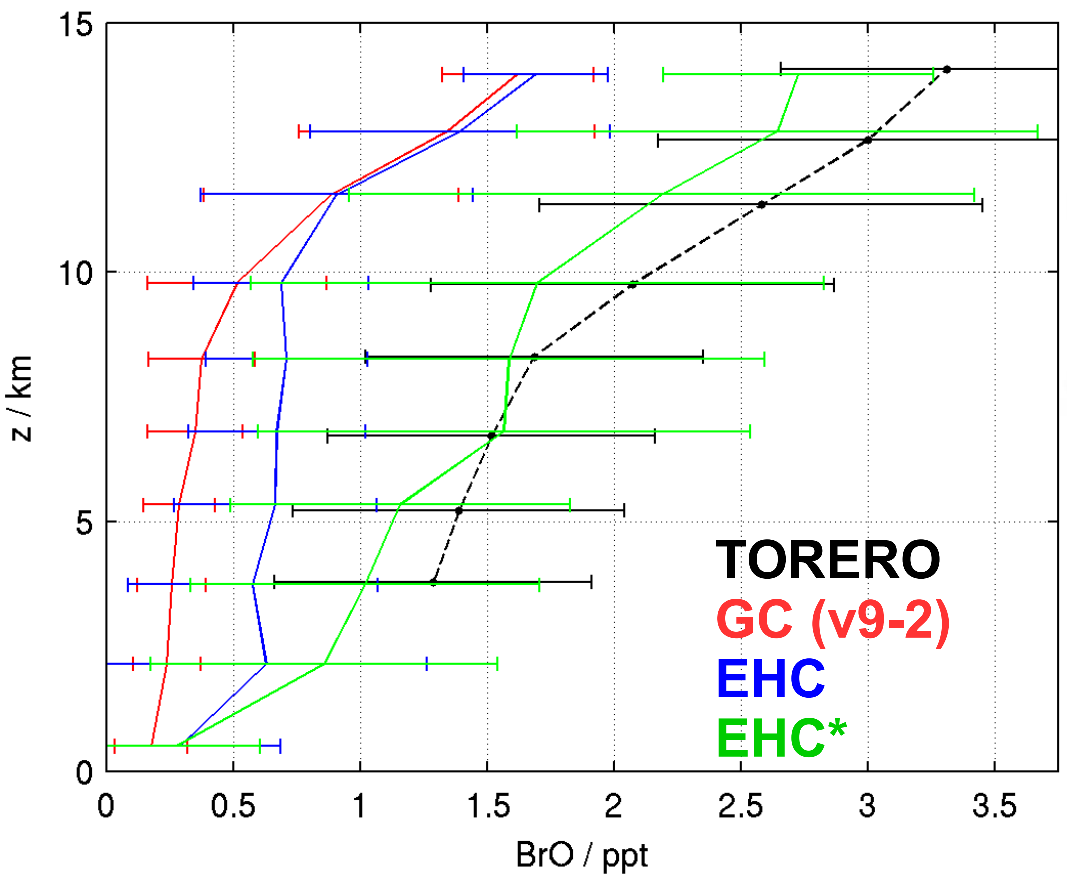
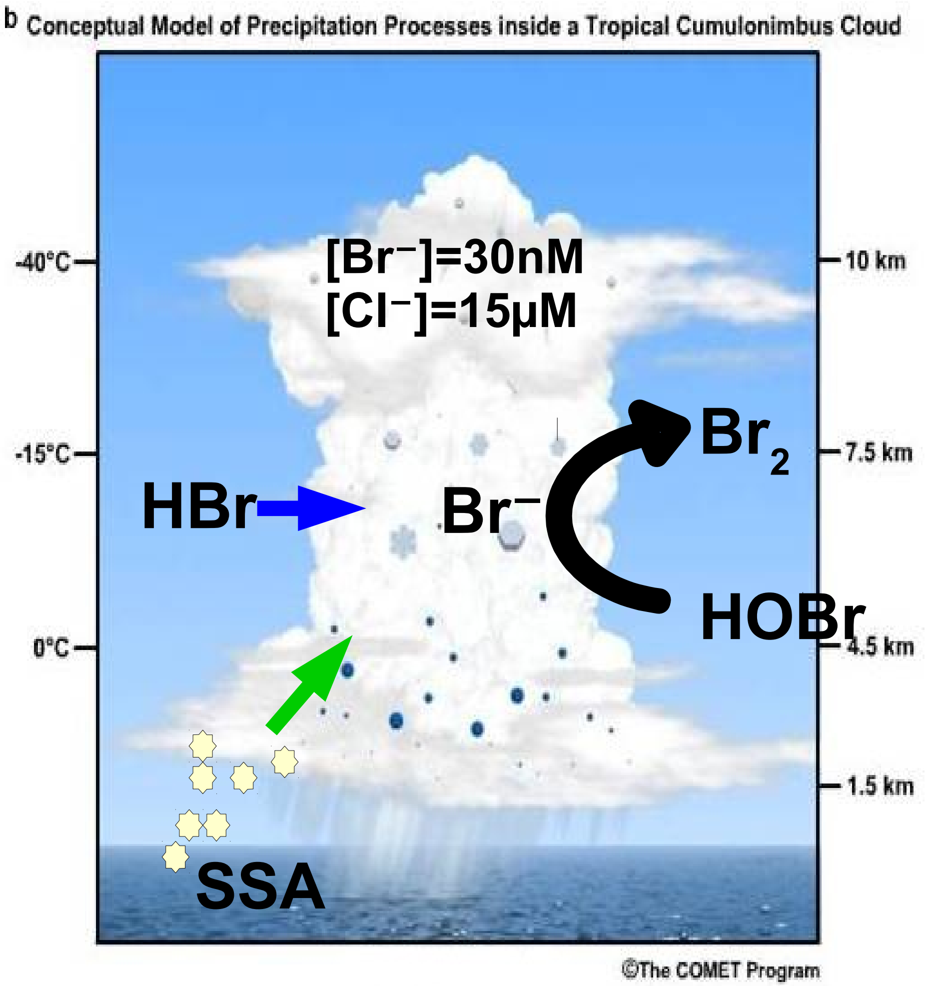
GEOS-Chem underestimates BrO in the free troposphere





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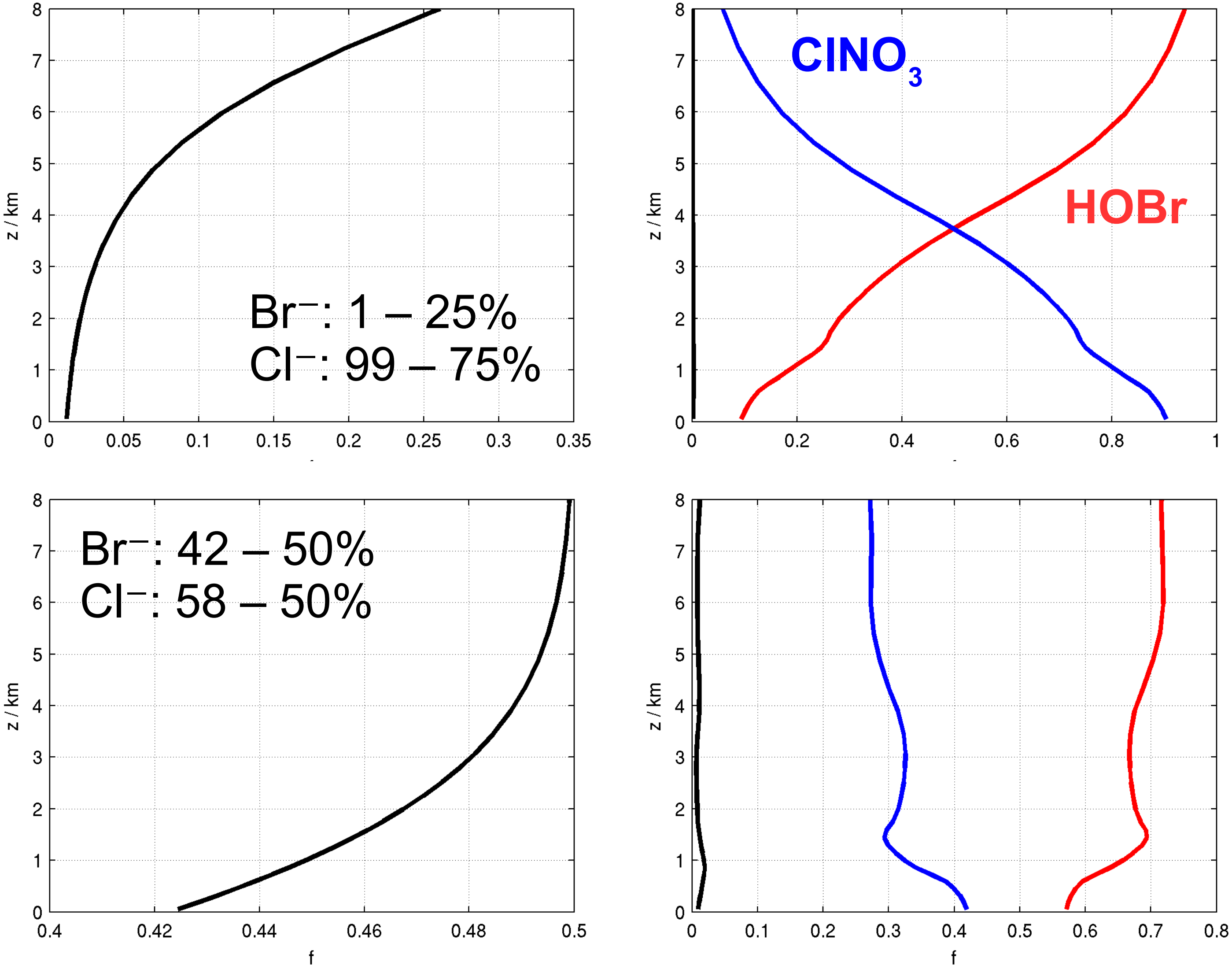
TORERO AMAX-DOAS observations vs. GC v9-02 and EHC

What (liquid phase) reactions are responsible for recycling and activation?



HOBr recycling

Br^- activation

Cloud droplet

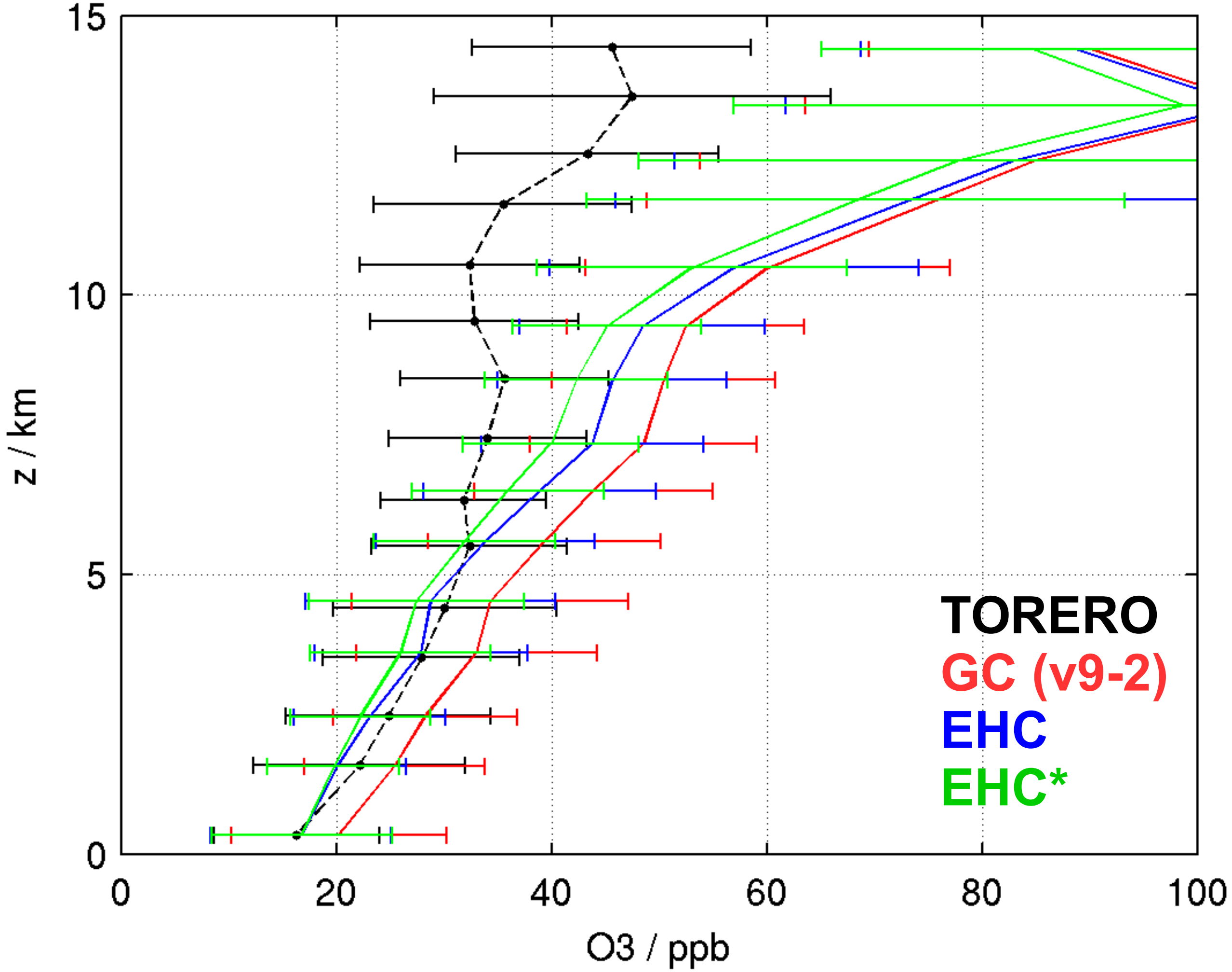
Br^-: 1 – 25%
Cl^-: 99 – 75%

Sea salt aero.

Br^-: 42 – 50%
Cl^-: 58 – 50%

Implications for tropospheric ozone

Density Weighted Mean Difference
DWMD(GC-EHC*) ≈ 6 ppb



TORERO O3 observations vs. GC v9-02 and EHC

Summary

- GEOS-Chem underestimates the levels of BrO in the troposphere compared to observations:
  - TORERO (Free Troposphere)
  - OMI and GOME-2 columns (Tropical Regions)
  - Surface stations (MBL)
- Recycling of scavenged HBr in cloud water droplets enhances BrO in the FT.
- Activation of SSA derived Br^- in cloud water droplets is potential overlooked source of tropospheric bromine.

Acknowledgments

- TORERO Team:
  - R. Volkamer (DOAS)
  - L. Carpenter (VSLH)
  - E. Apel (TOGA)
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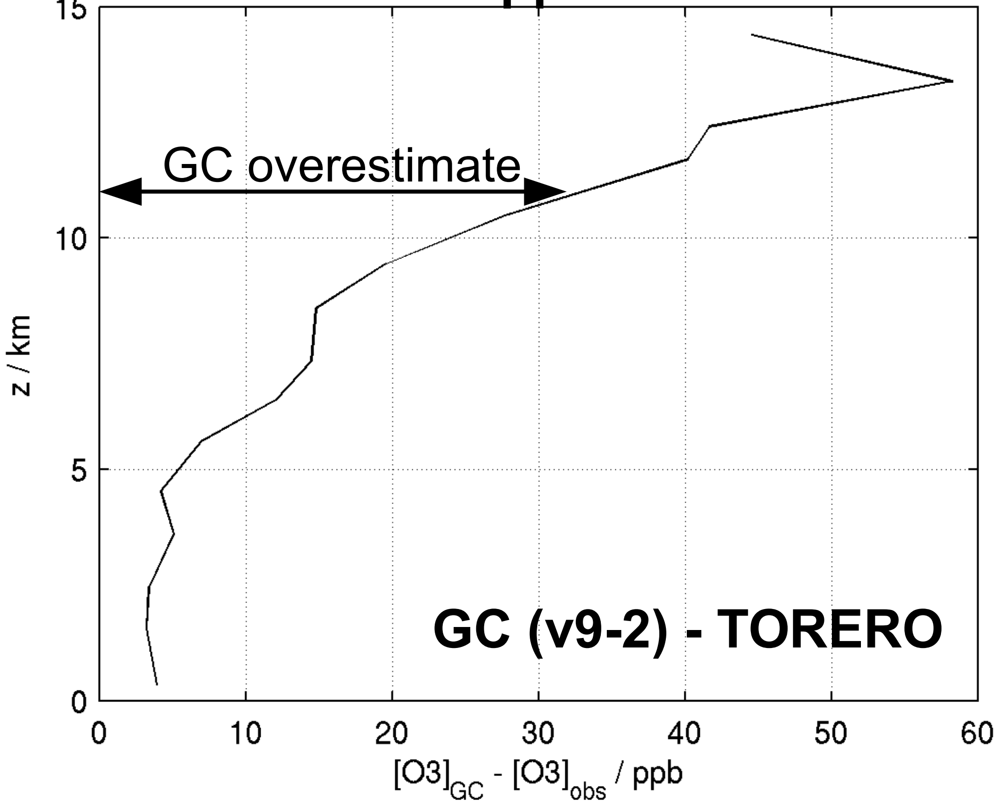
- Q. Liang
- M. Evans and T. Sherwen
- S. Choi
- G. Abad
- Danish Council for Independent Research ($$$)

Thank you for your attentions!

Additional slides

Implications for tropospheric ozone

Density Weighted Mean Dev.
DWMD ≈ 12 ppb



TORERO O3 observations vs. GC v9-02

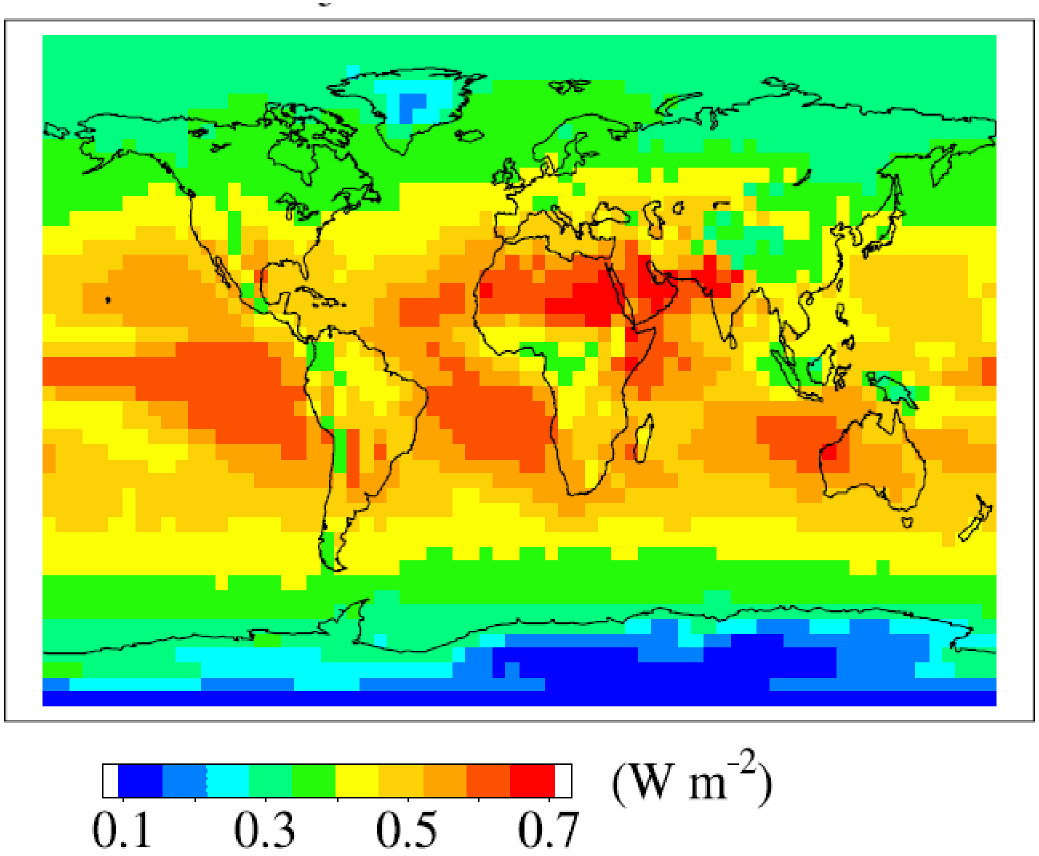
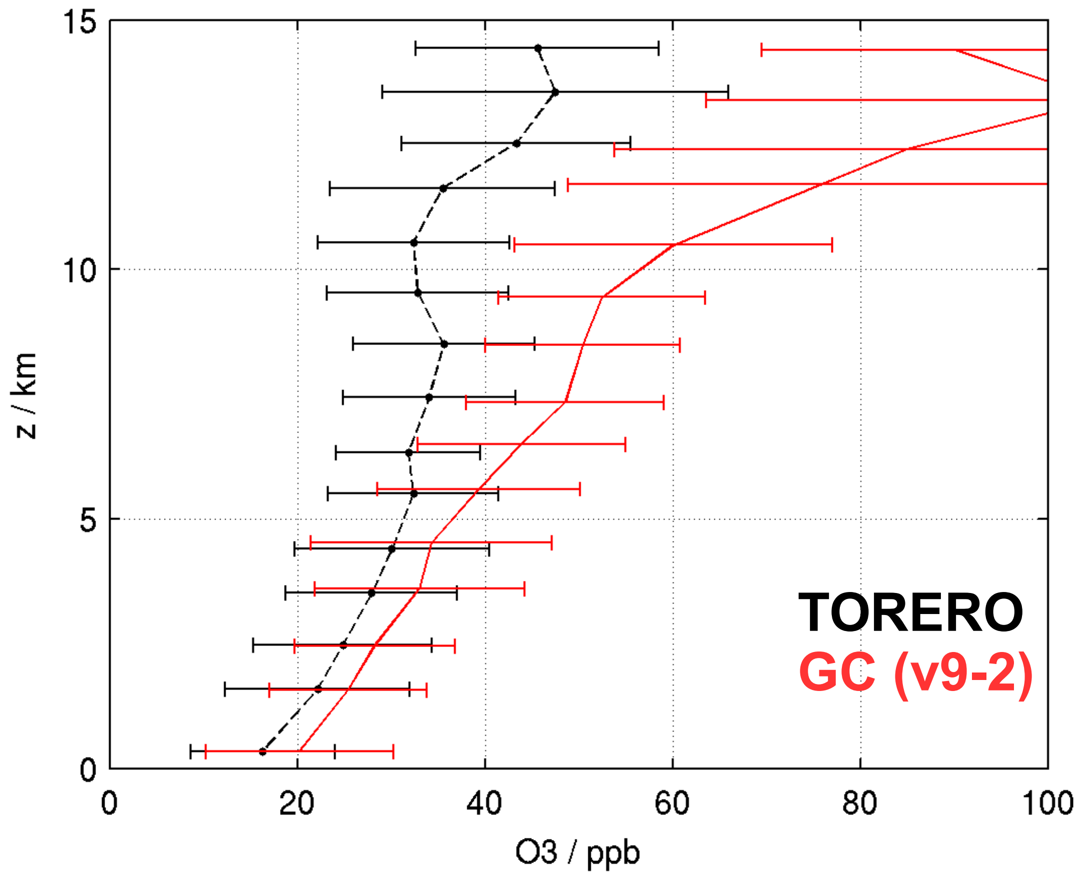


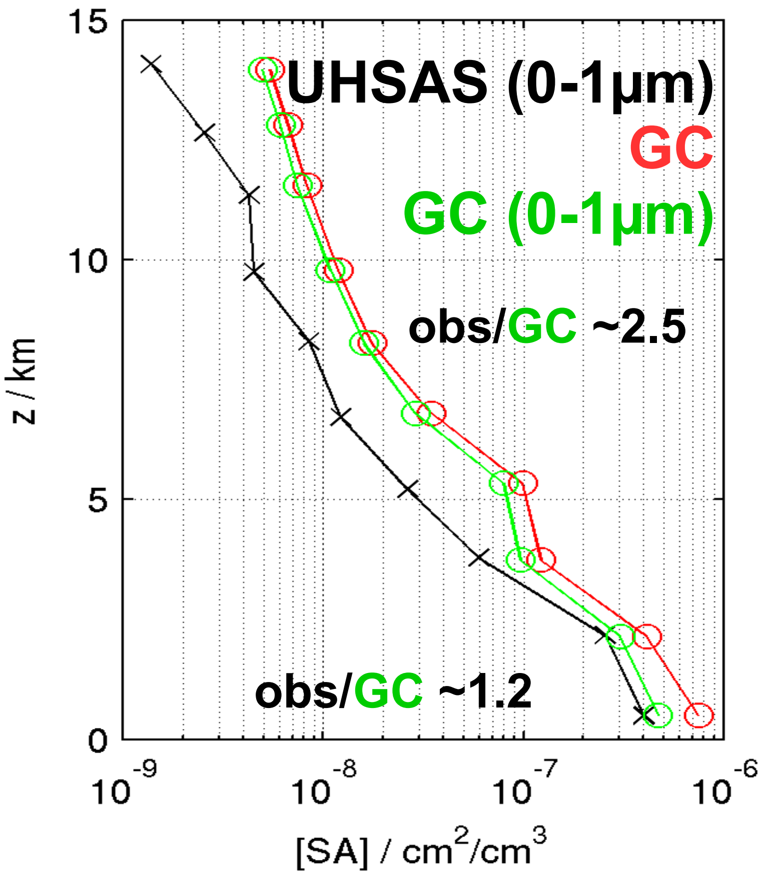
Fig. 3 of Mickley et al. (2004): Change in forcing due to uniform 18 ppb increase to pre-industrial tropospheric ozone.

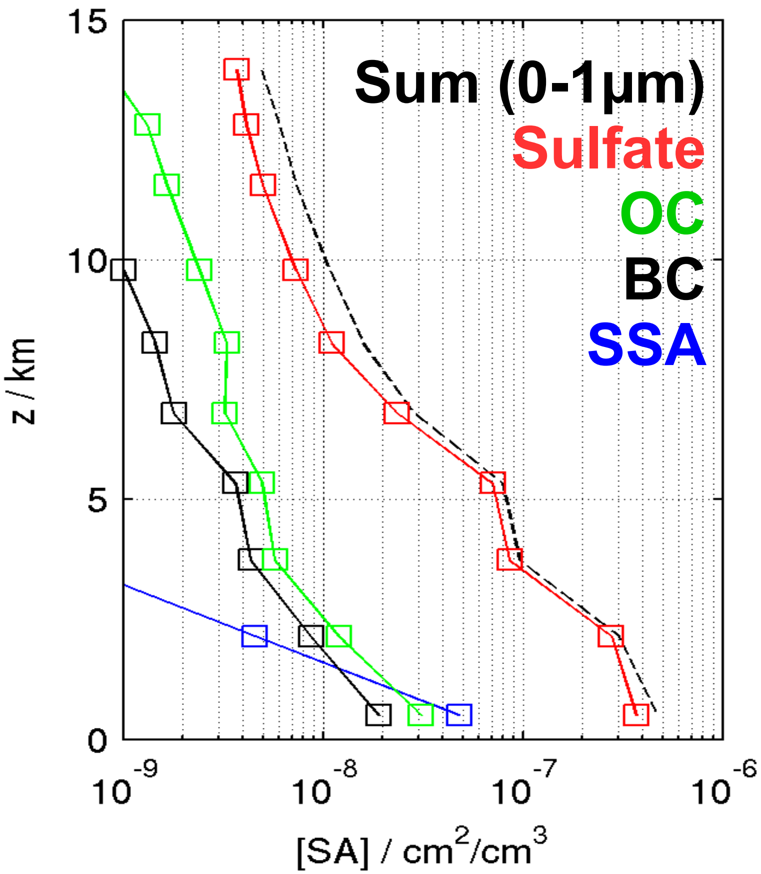
Implications for tropospheric ozone



TORERO O3 observations vs. GC v9-02

(Fine) Aerosol surface area

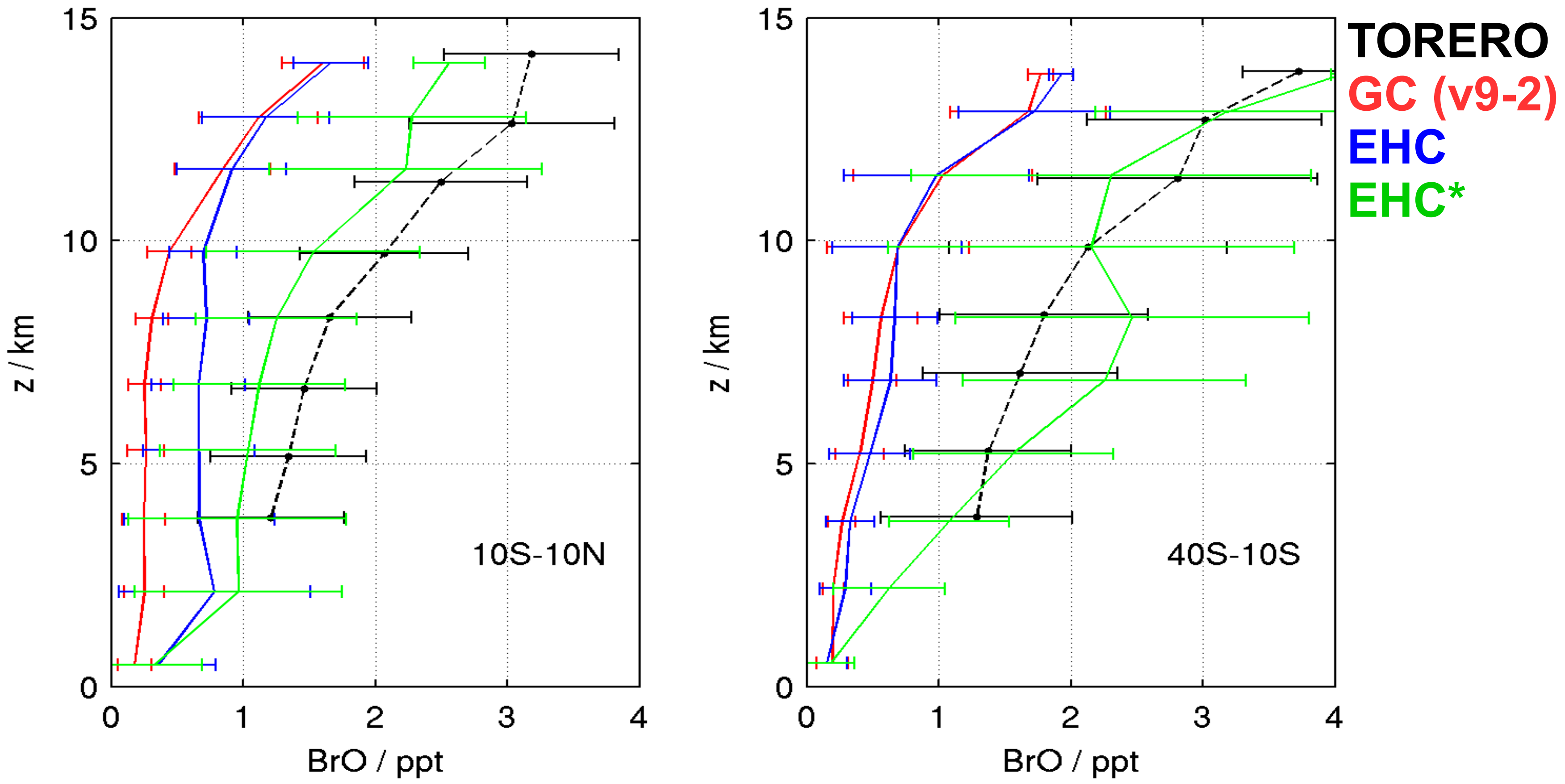




- **Model is overestimating sulfate aerosol**
- **Due to missing BrO + DMS → DMSO + Br ?**

TORERO UHSAS observations vs. GC v9-02

Deviation between GC and Obs. is largest around equator



TORERO AMAX-DOAS observations vs. GC v9-02 and EHC