Enhanced ozone loss by active inorganic bromine chemistry in the tropical troposphere

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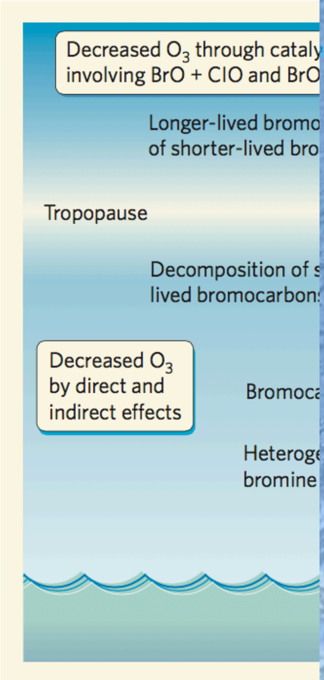
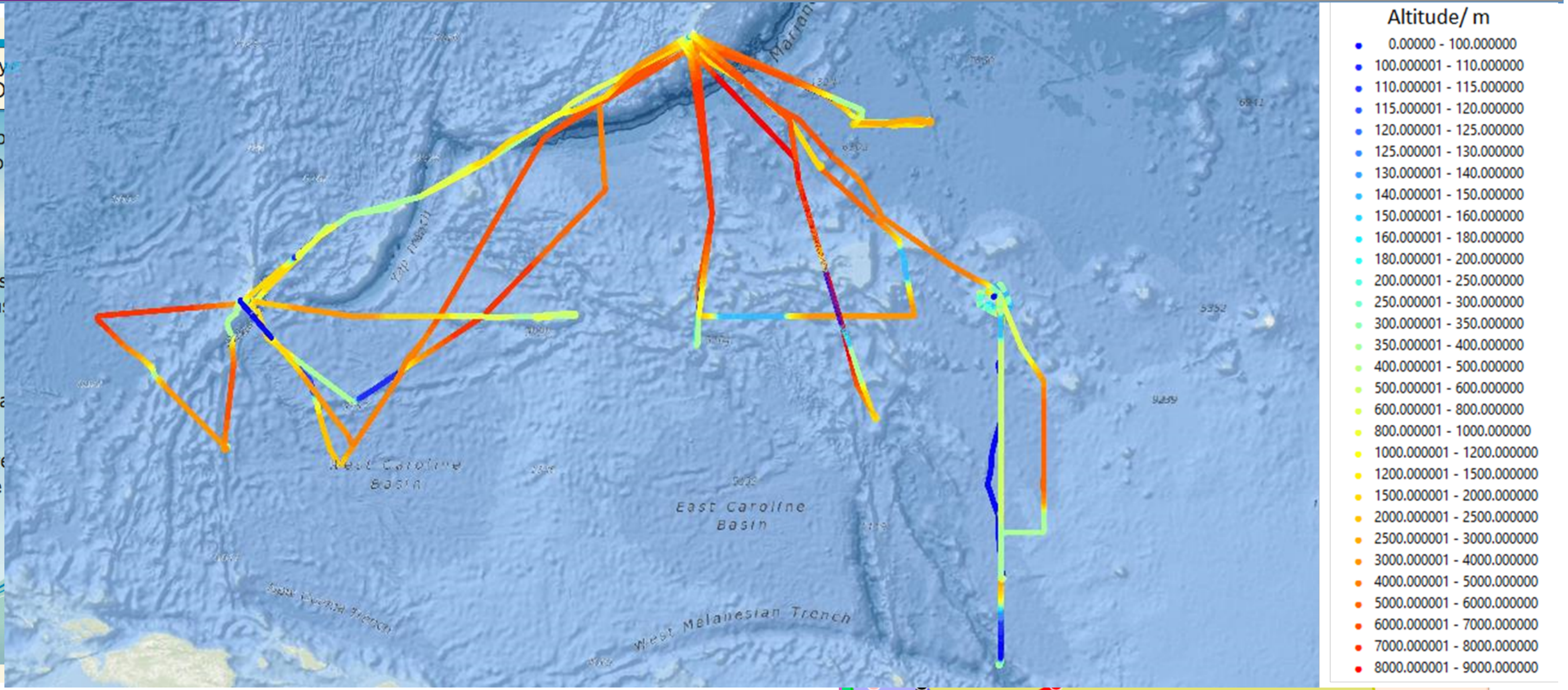
Outline

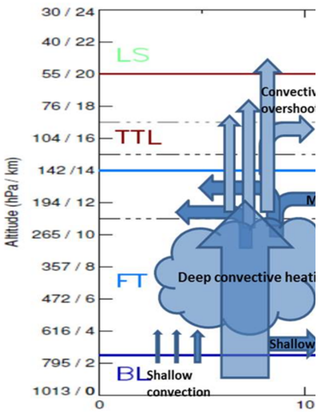
- Motivation
- Instrumental setup -CIMS
- Data coverage
- Measurement results
- Modelling vs measured
- Conclusions

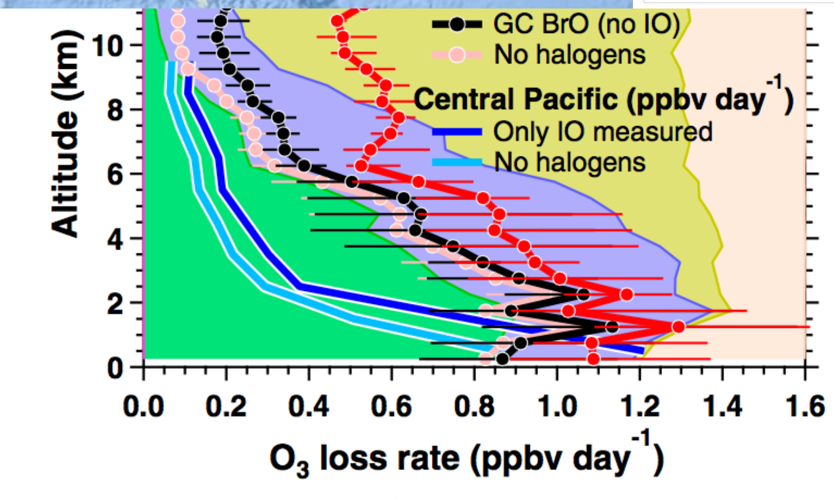
Motivation





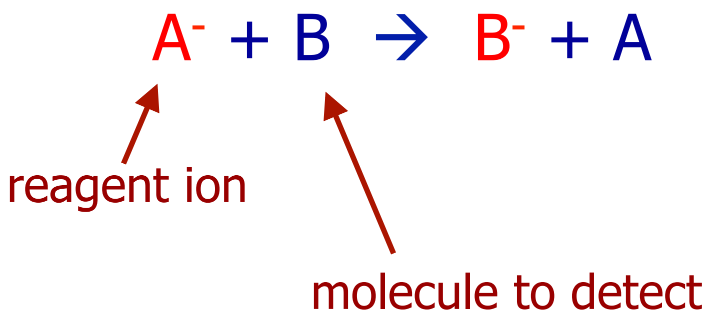
Salawitch, Nature (2006)





Wang et al., 2015

Chemical Ionisation

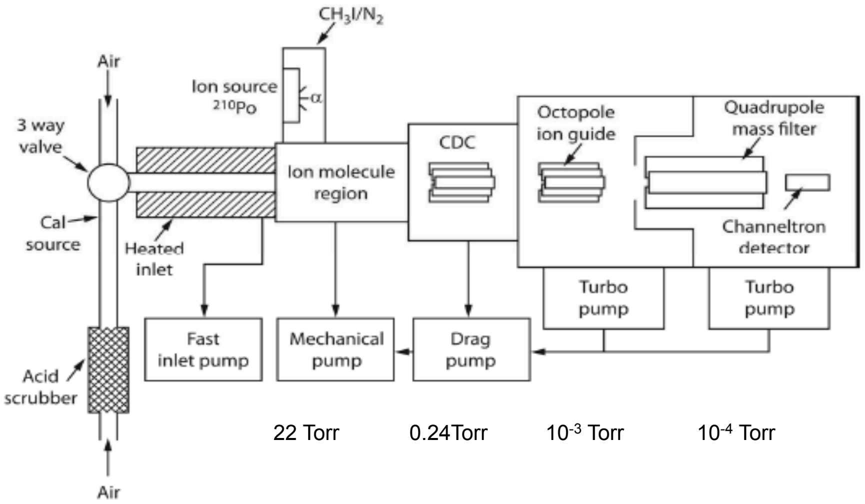


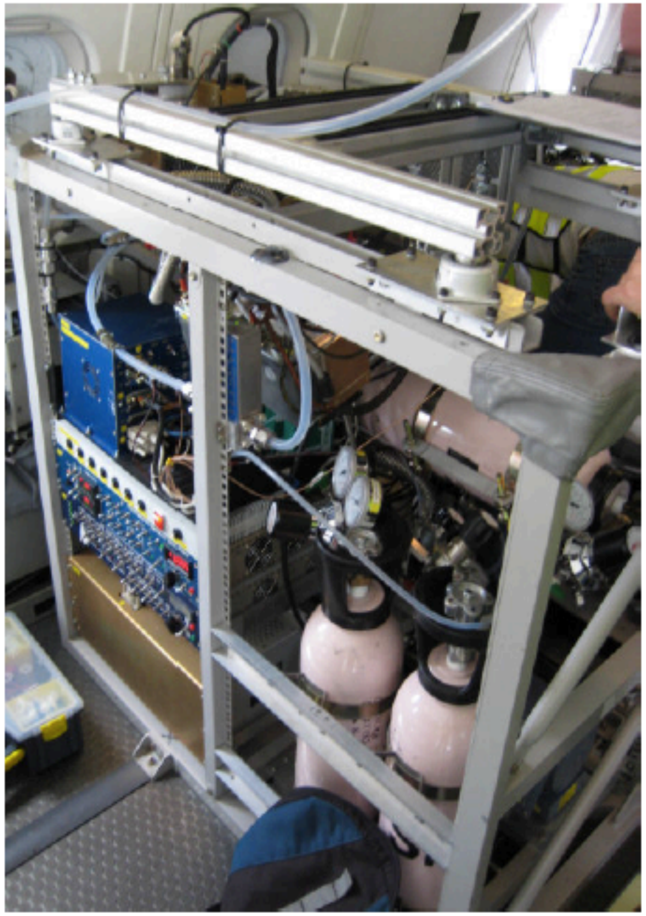
$A^{-} + B \rightarrow B^{-} + A$

- Soft ionisation
- High sensitivity
- Flexible ionization
- Detect both + and – ions
- ppt, LODs

$I^{-} + HCOOH \rightarrow [HCOOH].I^{-}$

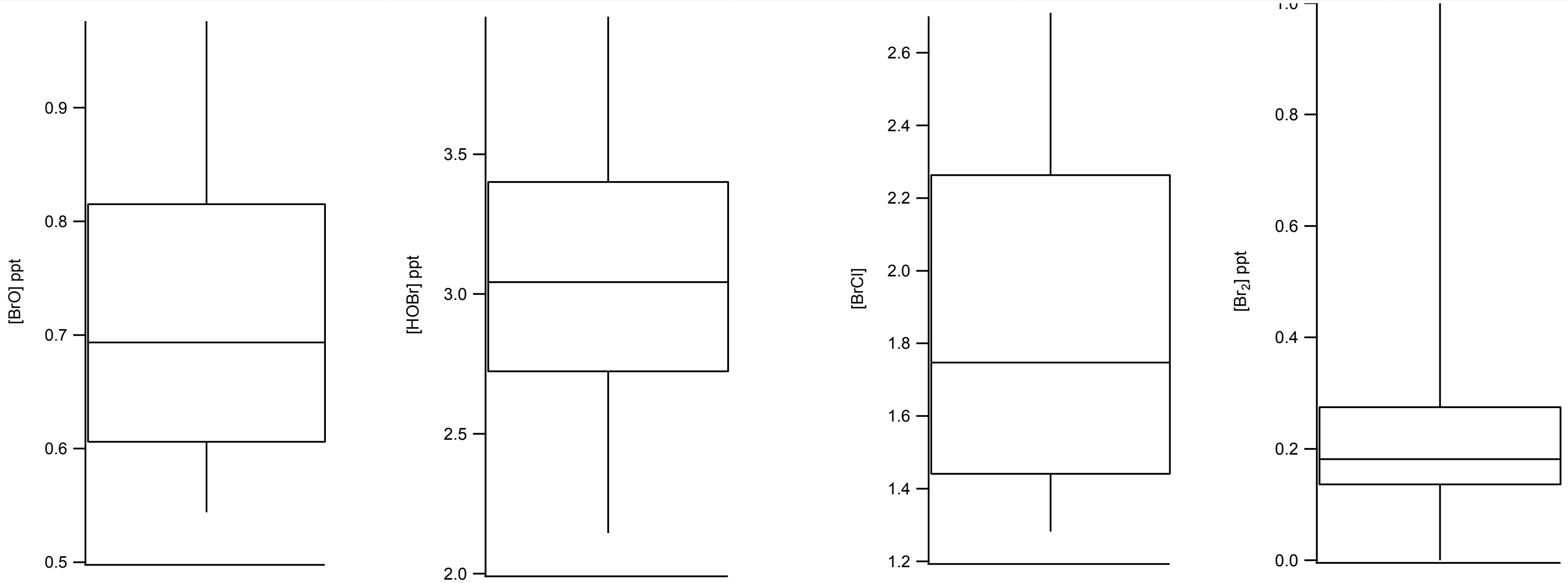
Manchester CIMS





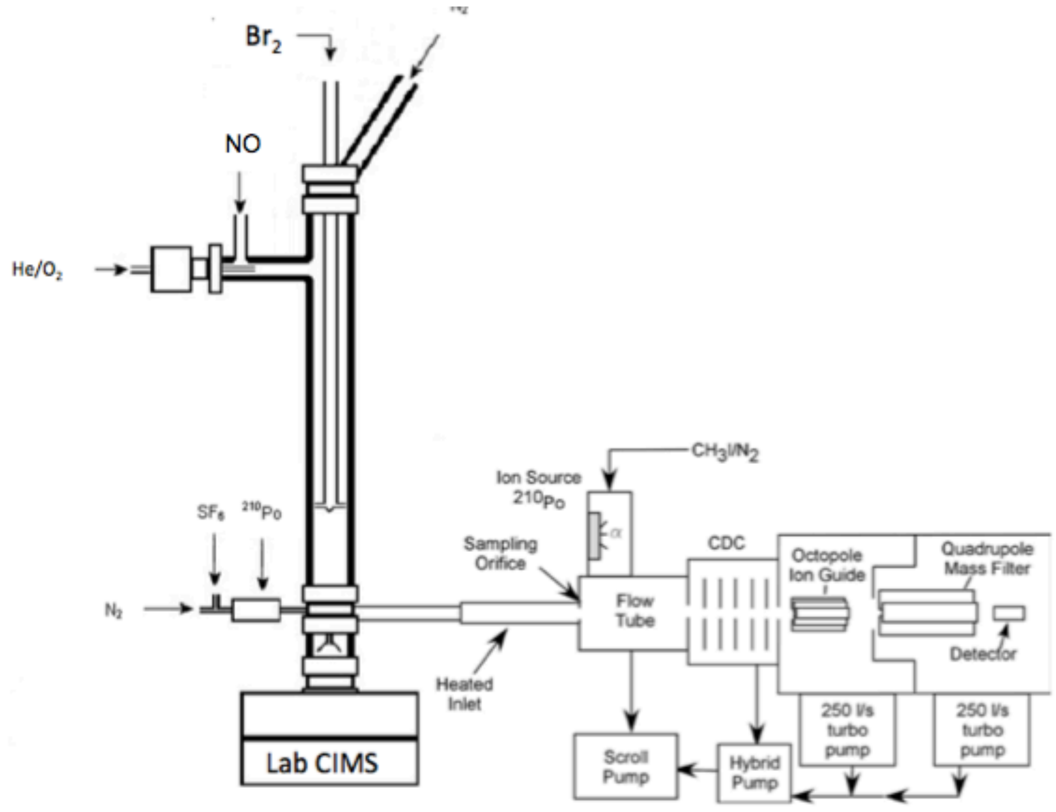
Data

species	seen as	mass	sensitivity (ion counts per ppt)	LOD (ppt)
Formic acid	I.HCOOH	173	35	25
Nitric acid	I.HNO3	190	25	36
Hydrogen chloride	I.HCl	162	1.8	4
Butanoic acid	I.C3H7COOH	215	15	25
Nitrogen pentoxide	NO3	62	27	1.9
Nitryl chloride	I.ClNO2	208	34	33
Hydrogen cyanide	I.HCN	154	33	0.4
Bromine monoxide	I.BrO	222/224	16	0.1
Hypobromous acid	I.HOBr.H2O	241	50	0.1
Bromine monochloride	I.BrCl	243	50	0.1
Bromine	I.Br2	287	100	0.1



3.6 to 8 ppt inorganic halogens

Calibration



$$Br_2 + O \rightarrow BrO + Br$$

$$BrO + NO \rightarrow NO_2 + Br$$

$$OH + Br_2 \rightarrow HOBr + Br$$

Br_2 – perm tube and gas mix

Calibration

$$Br_2 \quad + \quad H_2O \quad \leftrightharpoons \quad HOBr + H^+ + Br^-$$

$$Br^- \quad + \quad Ag^+ \quad \rightarrow \quad AgBr \downarrow$$

$$HOBr \quad + \quad NaBr \quad \rightarrow \quad Br_2 + NaOH$$

$$Br_2 \quad + \quad Cl_2 \quad \rightarrow \quad 2BrCl$$

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Data coverage

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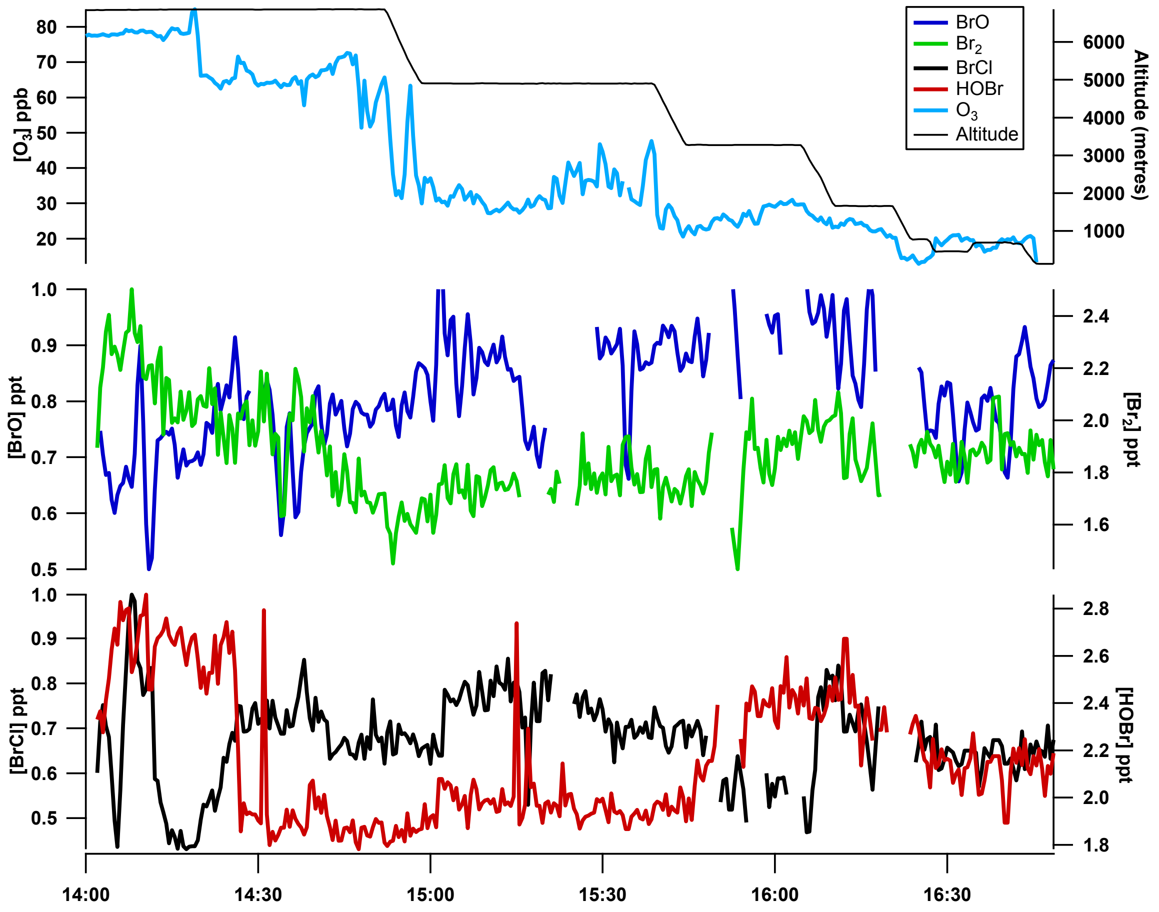
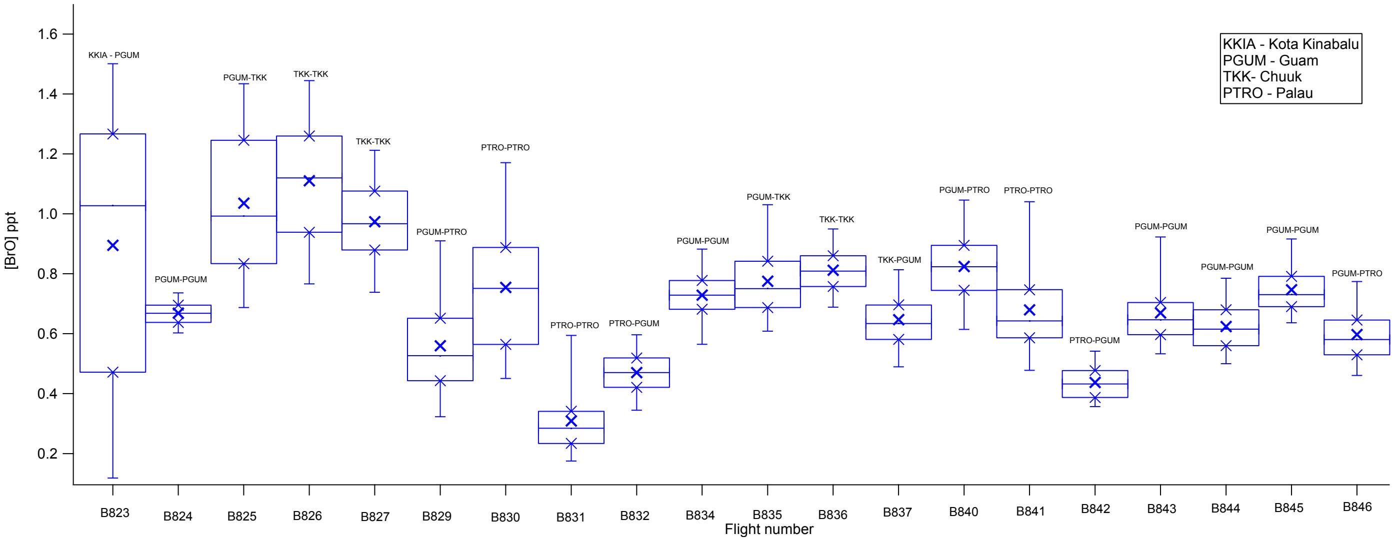
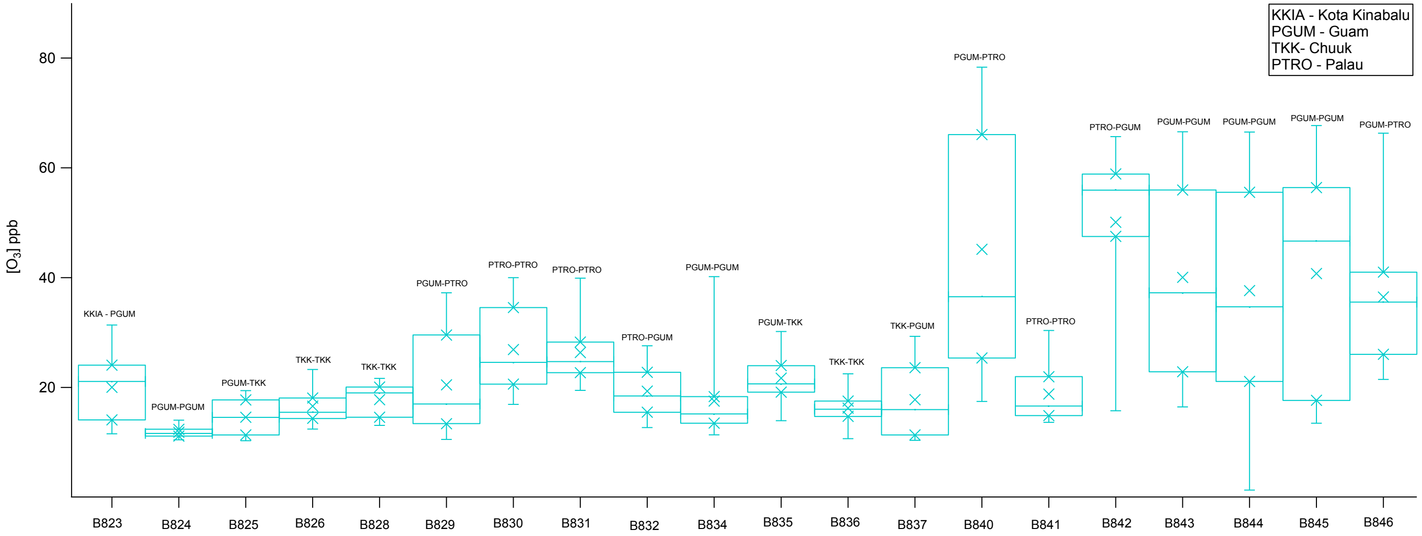
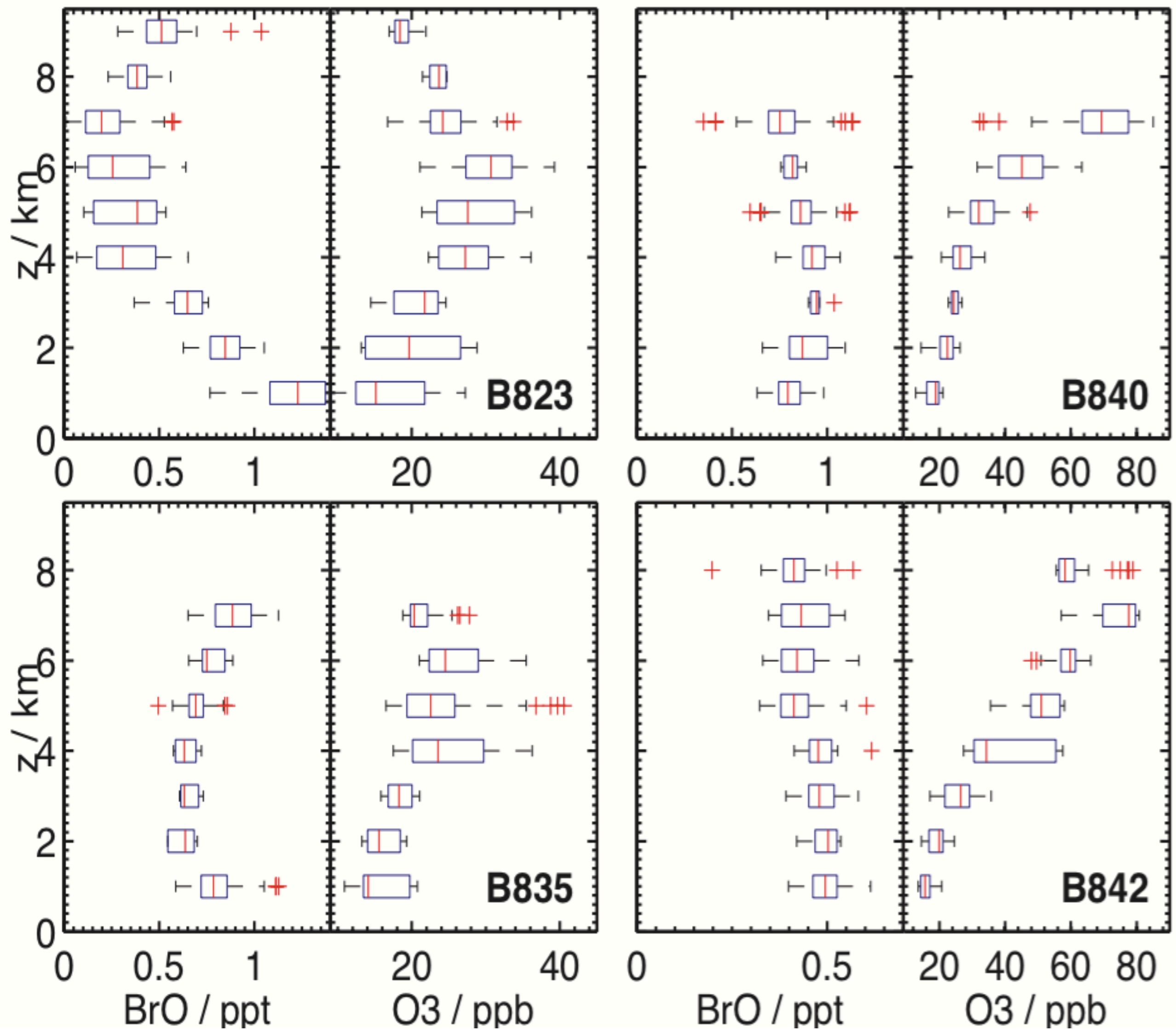


BrO and O_3 data

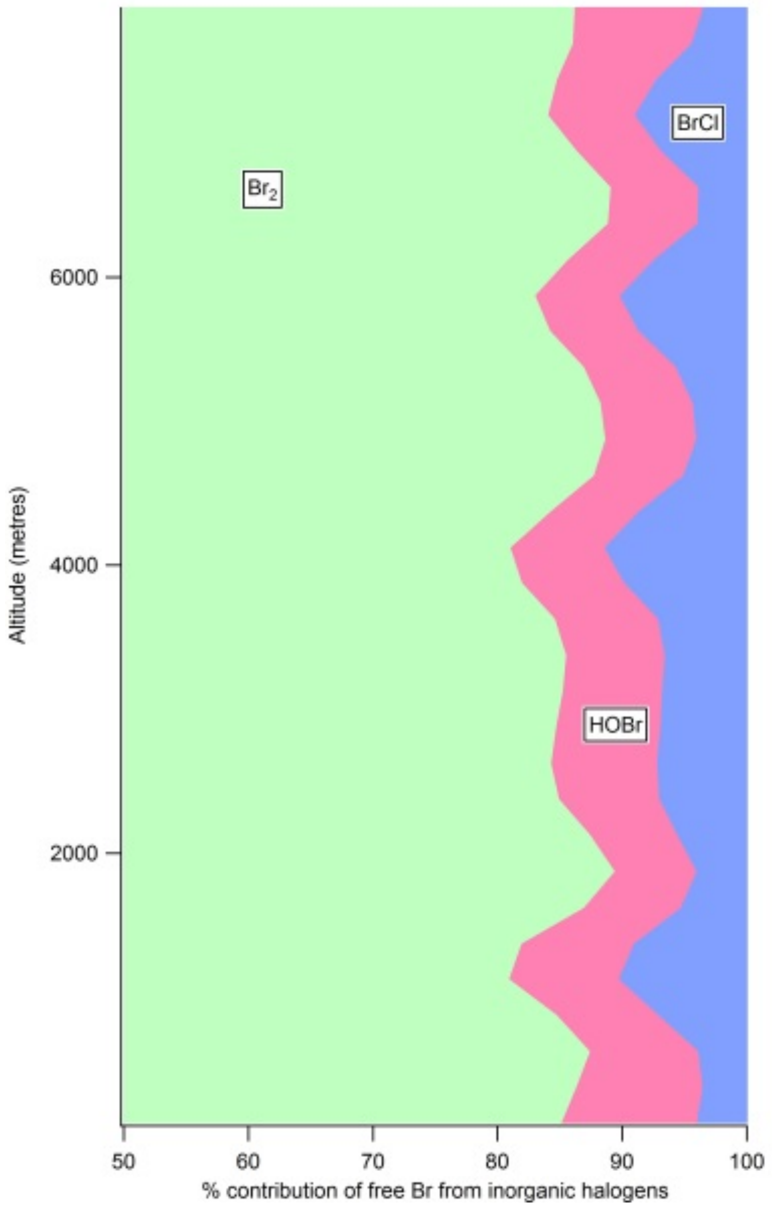


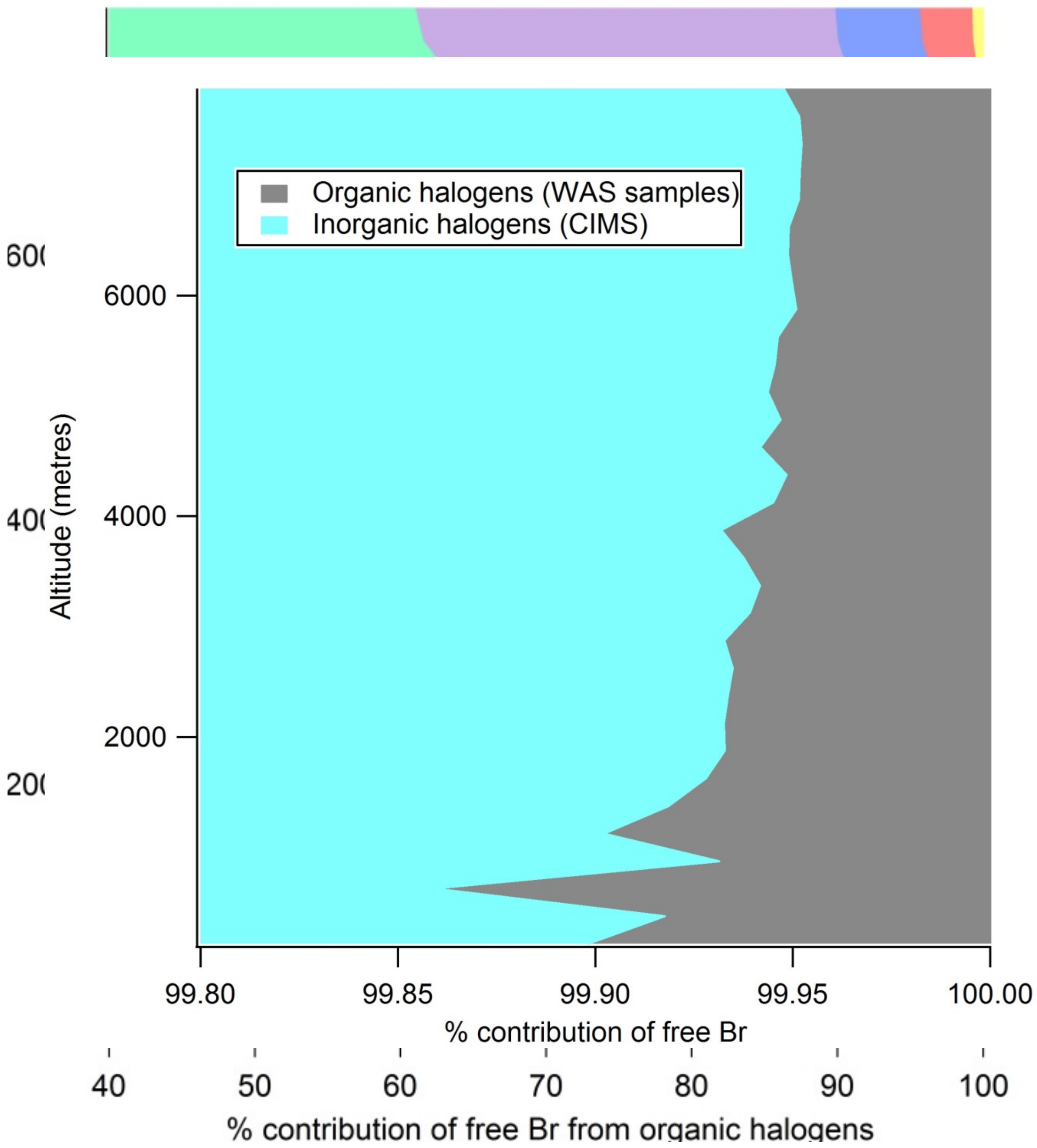


Altitude profiles



Contribution to Bromine





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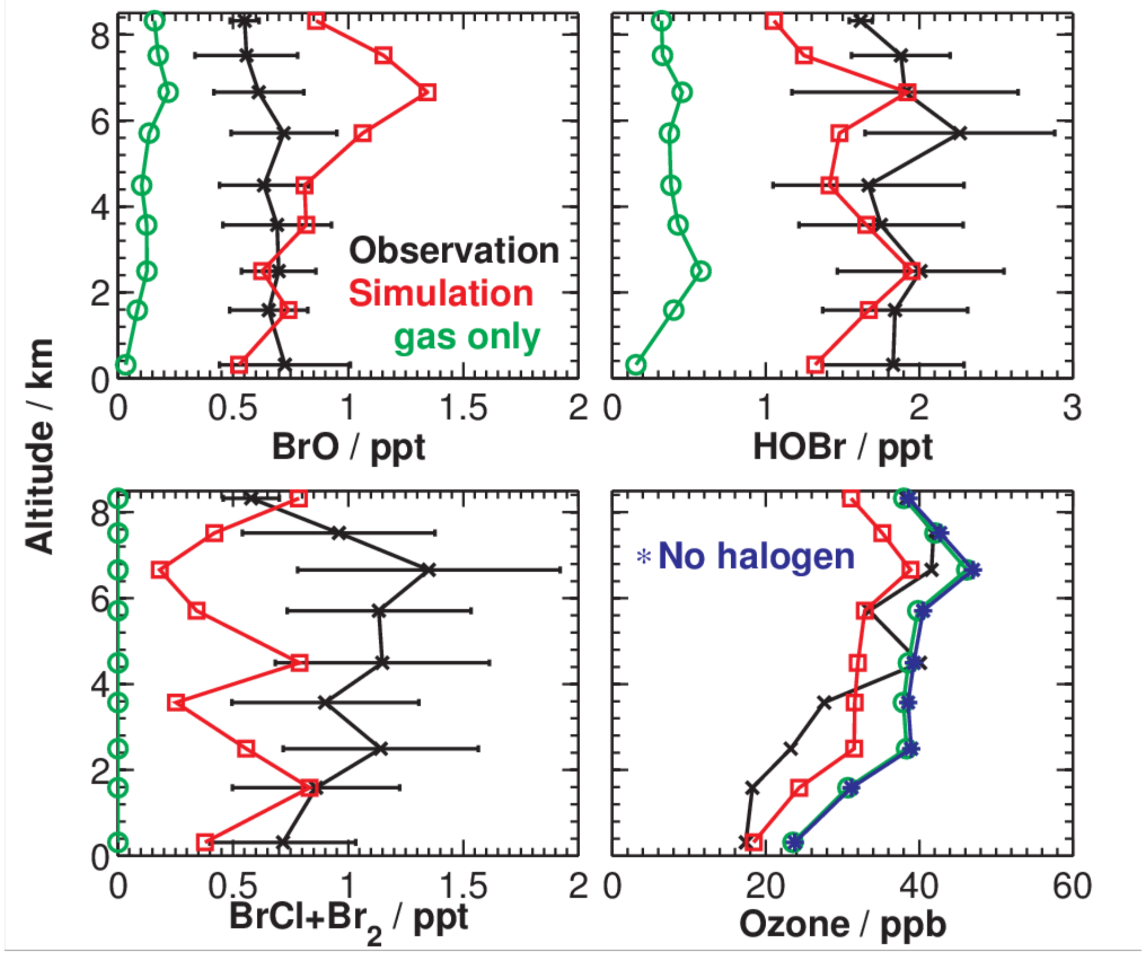
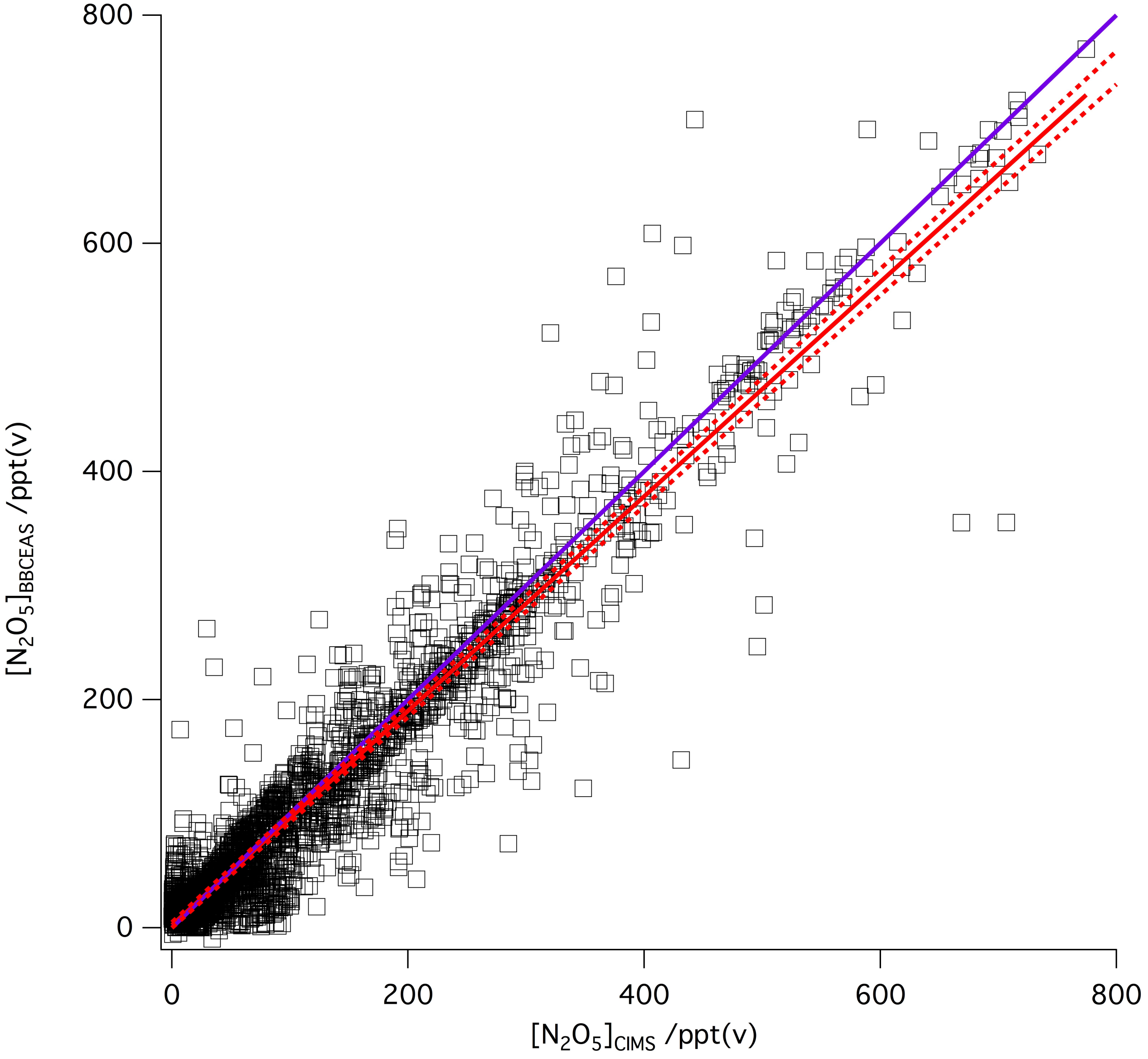
BrO and O_3 data



The red line is the output from the GEOS-Chem with the new heterogeneous chemistry mechanism and 50% debromination of sea salt.

Model vs. observations



Results and summary

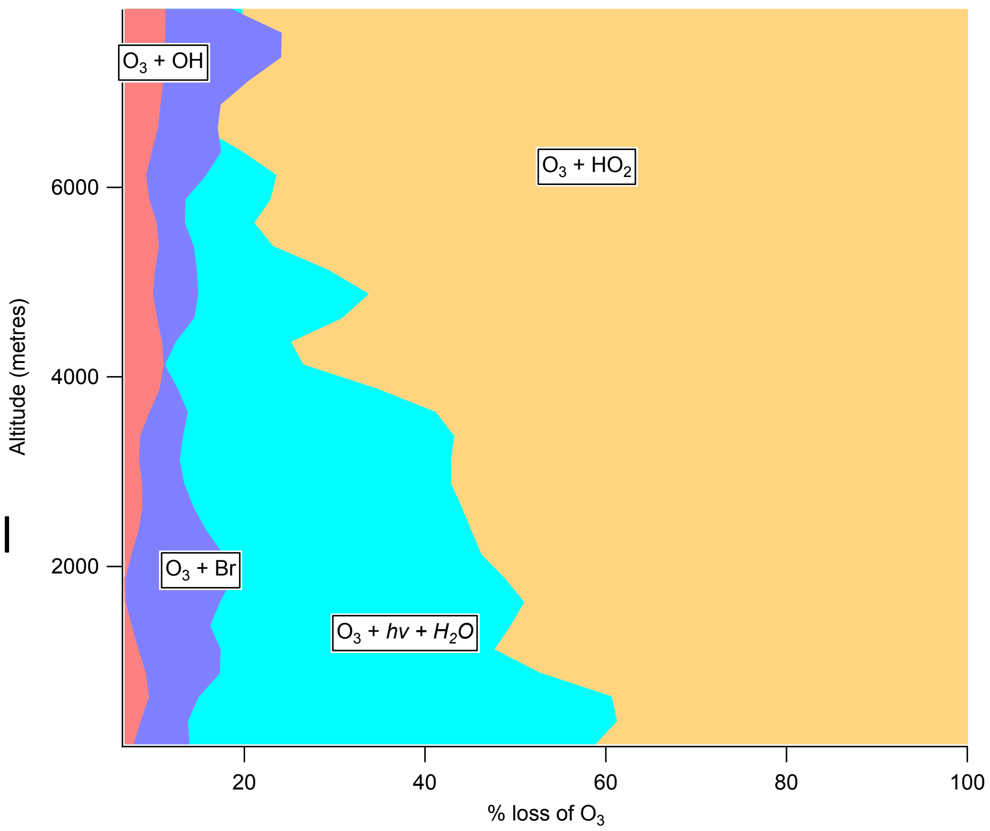
Up to 15% O_3 loss from Br

6 ppb loss O_3 loss to halogen chemistry

Model comparison to measurements
Suggest much higher Br_y than previously considered

Anti-correlation between BrO and O_3
Provides clear support for the significant bromine driven ozone loss in the tropical free troposphere

99% of the instantaneous free Br in the troposphere originates from inorganic halogen photolysis rather than from photolysis of organobromine species



- **1.** **$Br + O_3 \rightarrow BrO + O_3$**
- *2.* *Br + DMS → products*
- **3.** **$BrO + HO_2 \rightarrow HOBr$**
- **4.** **BrO + DMS → Br + DMSO**
- **5.** **HOBr + hν → OH + Br**

- **6.** **$Br_2 + h\nu \rightarrow Br + Br$**

- **7.** **BrCl + hν → Br + Cl**

- **8.** **HOBr (wet deposition) →**
- 9. *BrCl (wet deposition) →*

- *10.* *Br_2 (wet deposition) →*

$[HO_2]$ = *J5[HOBr]/k3[BrO]*

[Br] = (*k4[BrO][DMS]+ J5[HOBr]+ 2J6[Br2]+ J7[BrCl])/k1[O3]*

If one assumes that the 4 main pathways for O_3 destruction in the remote MBL are

$O_3 + HO_2 \rightarrow OH + 2O_2$
$O_3 + OH \rightarrow HO_2 + O_2$

$O_3 + h\nu \rightarrow O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow OH + OH$
$Br + O_3 \rightarrow BrO + O_3$

The four loss rates for these reactions are therefore

$O_{3O1D} = F1 * J_{12}[O_3]$
$O_{3\ HO2+O3} = k_{11}[HO_2][O_3]$
$O_{3\ OH+O3} = k_{16}[OH][O_3]$
$O_{3\ Br+O3} = k_1[Br][O_3]$