Simultaneous Airborne Measurements of BrO, HOBr, BrCl and Br_2 in the Tropics: Inorganic Halogens and Subsequent O_3 Depletion

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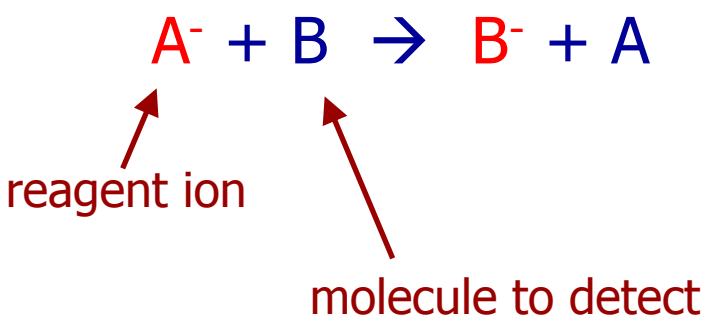
Outline

- Instrumental setup - CIMS
- Data coverage
- Data results
- Modelling vs measured
- SS O_3 depletion

Data coverage

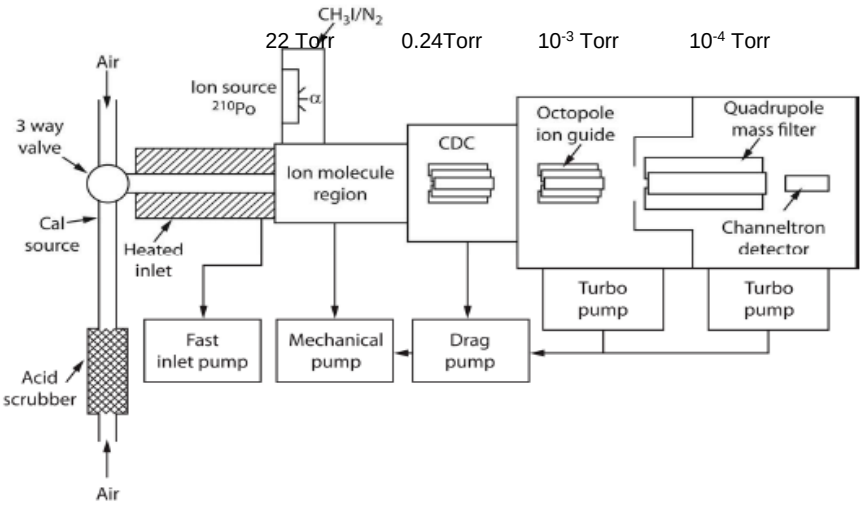
Flight	duration	CIMS data	QCL data	SP-2	Notes
B823	03:05	03:05	03:05	03:05	Data still needs to be worked up
B824	03:17	03:17	03:17	03:17	QCL Calibration needs to be worked on
B825	02:42	02:42	02:42	02:42	
B826	03:37	04:37	03:37	03:37	
B827	03:13	04:13	03:13	03:13	
B828	03:05	00:00	03:05	03:05	Power failure pre flight so no CIMS
B829	03:20	04:20	03:20	03:20	
B830	04:23	05:23	04:23	04:23	
B831	04:10	05:10	04:10	04:10	
B832	03:45	04:45	03:45	03:45	
B833	04:00	04:00	04:00	04:00	
B834	04:00	04:00	04:00	04:00	
B835	02:00	02:00	02:00	02:00	QCL Calibration needs to be worked on
B836	03:55	03:55	03:55	03:55	QCL Calibration needs to be worked on
B837	03:45	03:45	03:45	03:45	
B838	02:20	00:00	02:20	02:20	Overheating has affected CIMS data - being worked on
B839	03:49	00:00	03:49	03:49	Overheating has affected CIMS data - being worked on
B840	04:00	04:00	04:00	04:00	QCL Calibration needs to be worked on
B841	03:42	03:42	03:42	03:42	
B842	03:46	03:46	03:46	03:46	
B843	03:40	03:40	03:40	03:40	
B844	03:35	03:35	03:35	03:35	
B845	03:45	03:45	03:45	03:45	
B846	04:00	04:00	04:00	04:00	
TOTAL	84:15	73:02	83:00	84:15	10 minute segments of QCL flights lost where software crashed
%	100%	87%	96%	100%	

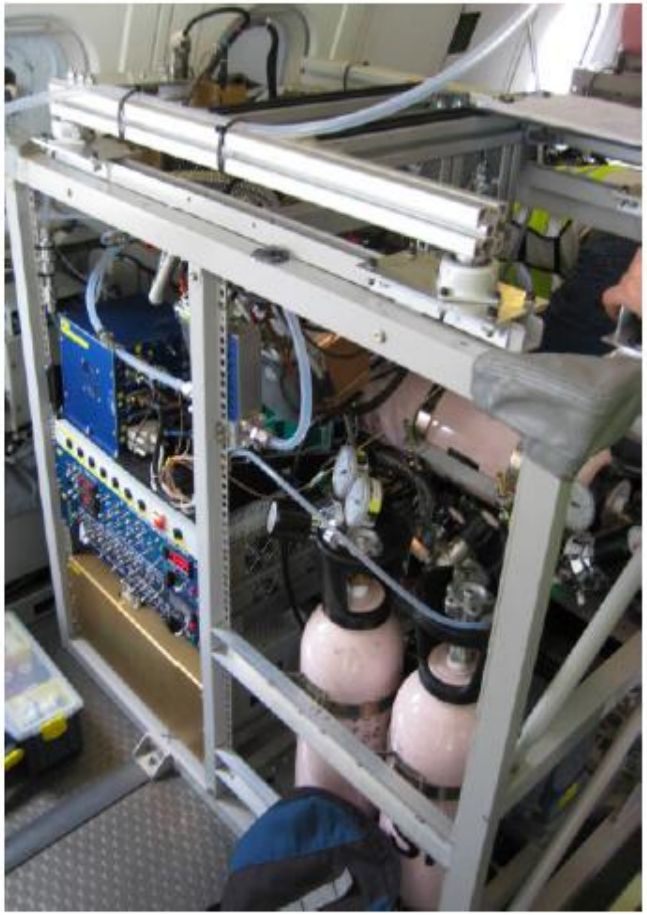


- Soft ionisation
- High sensitivity
- Flexible ionization
- Detect both + and – ions
- ppt, LODs

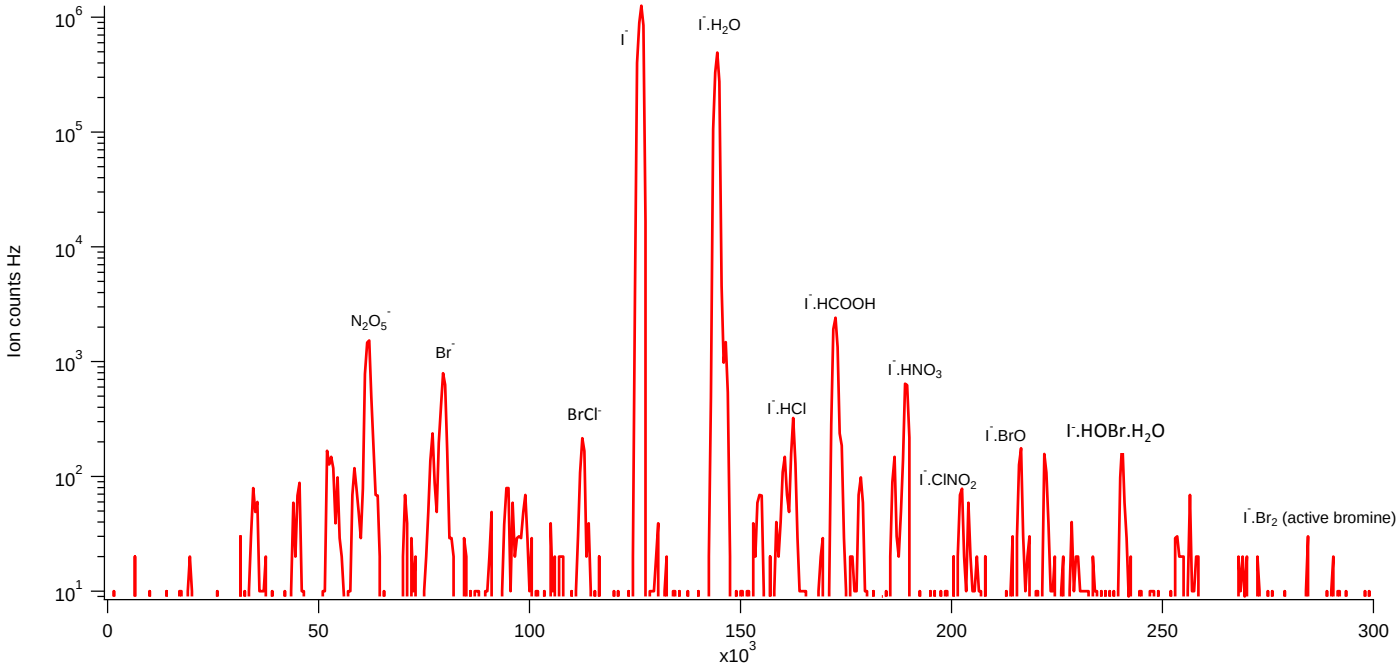
$I^- + HCOOH \rightarrow \mathbf{[HCOOH].I^-}$

Manchester CIMS



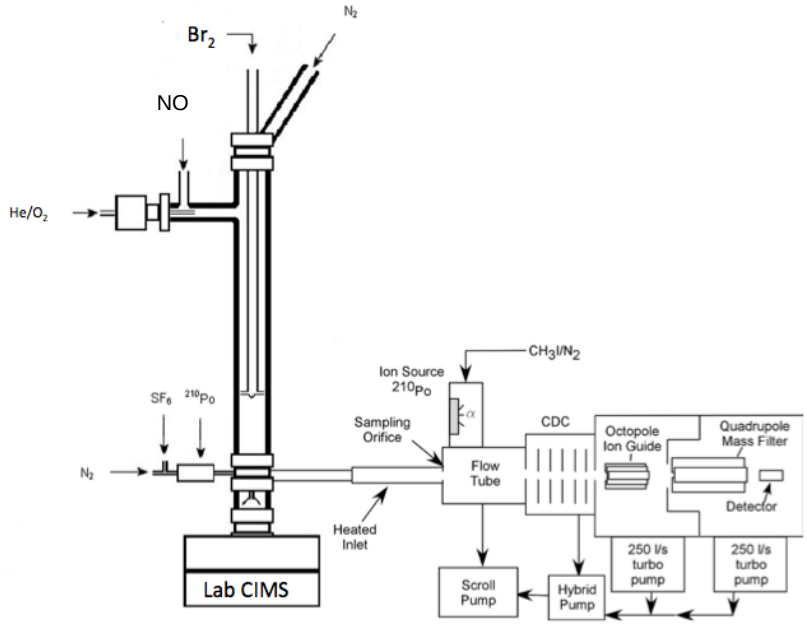


CIMS measurements



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	0.8
Hypobromous acid	I.HOBr.H2O	241	50	0.1
Bromine monochloride	BrCl	113	50	0.1
Bromine	I.Br2	287	100	0.1

BrO calibration

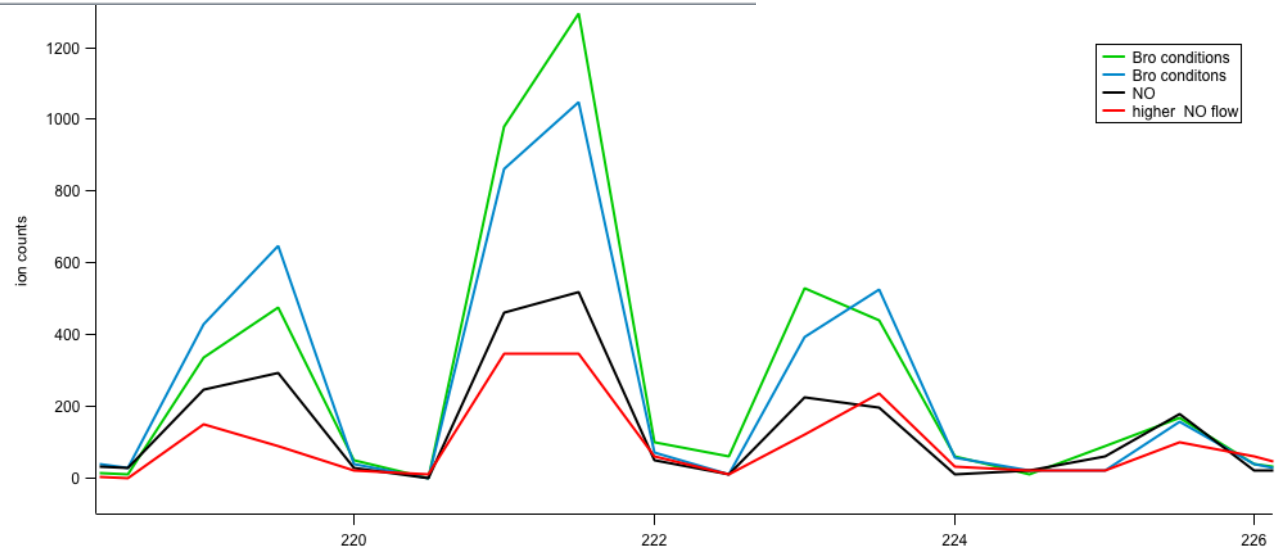


HOBr , BrCl and Br_2 all calibrated on FT

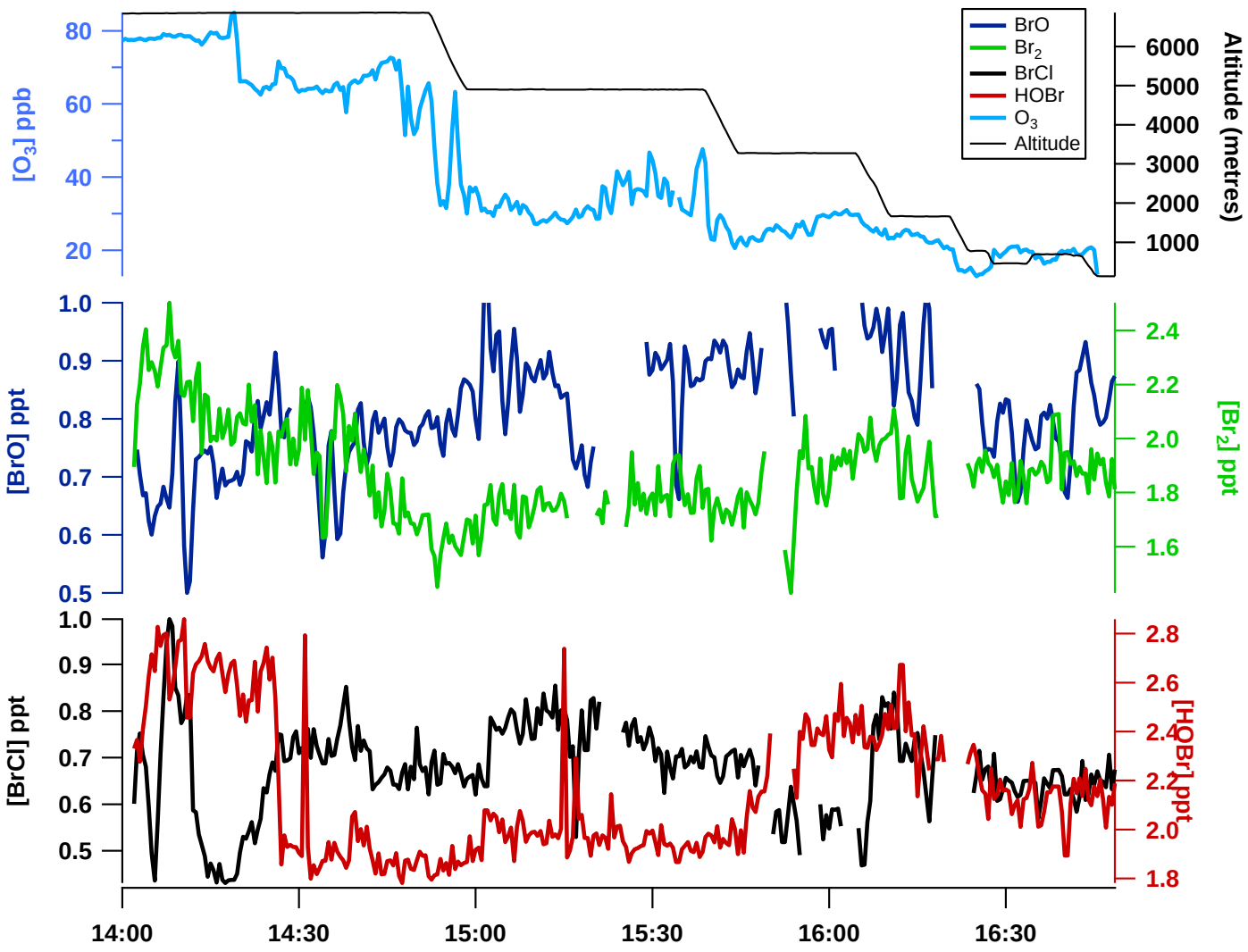
1. BrCl – Cl_2 and Br_2 gas mixture equilibrate

2. HOBr – $AgNO_3$ (liberates Br)
   - Mix with CCl_4 (Removes Br_2)
   - Quantify with H^+ and Br^-

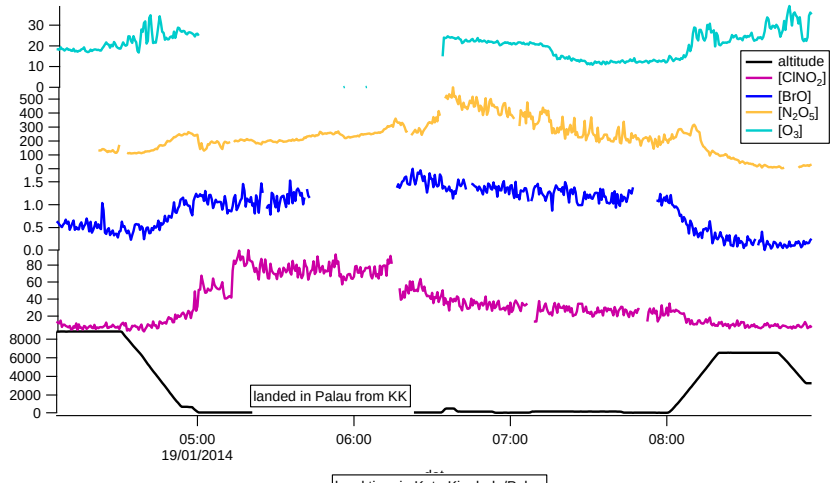
3. Br_2 – gas mixture and perm tube

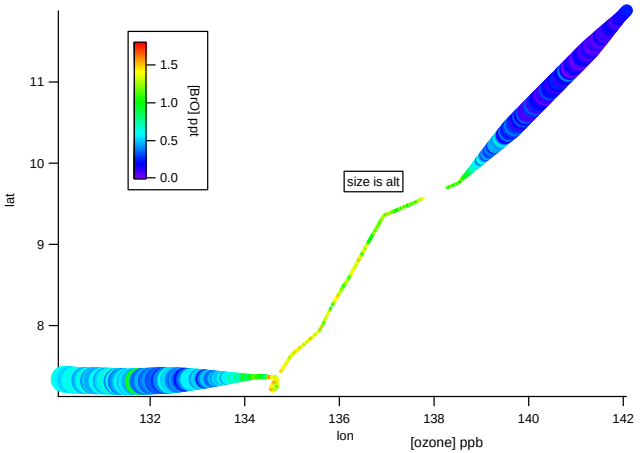


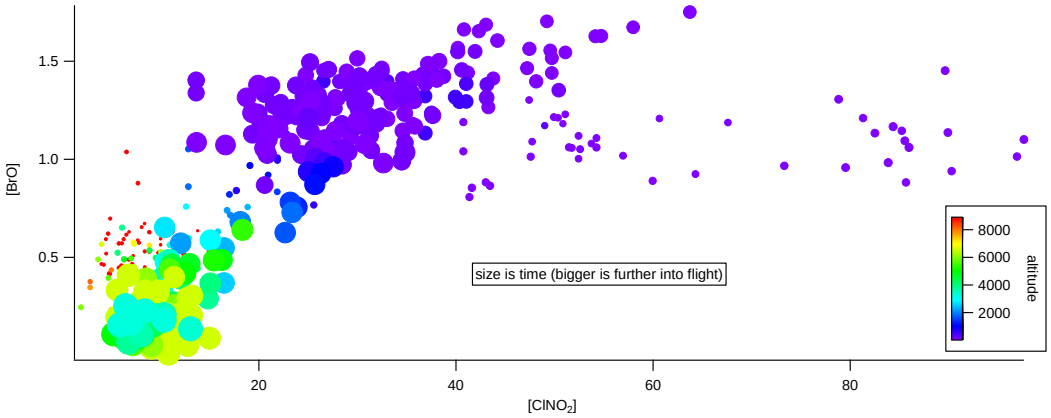
Time series example

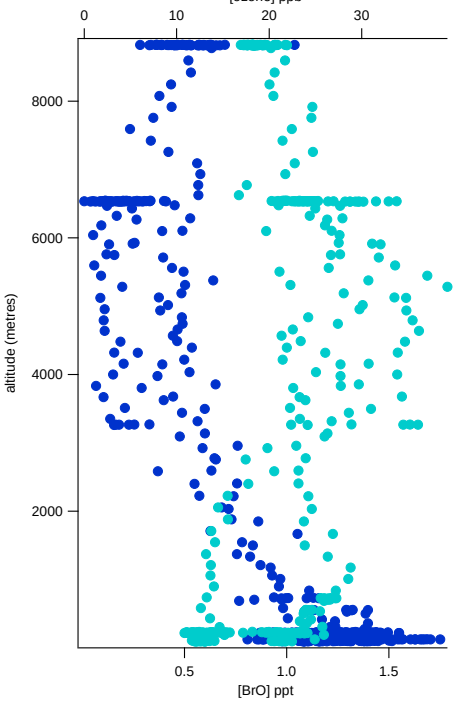


B823 transit

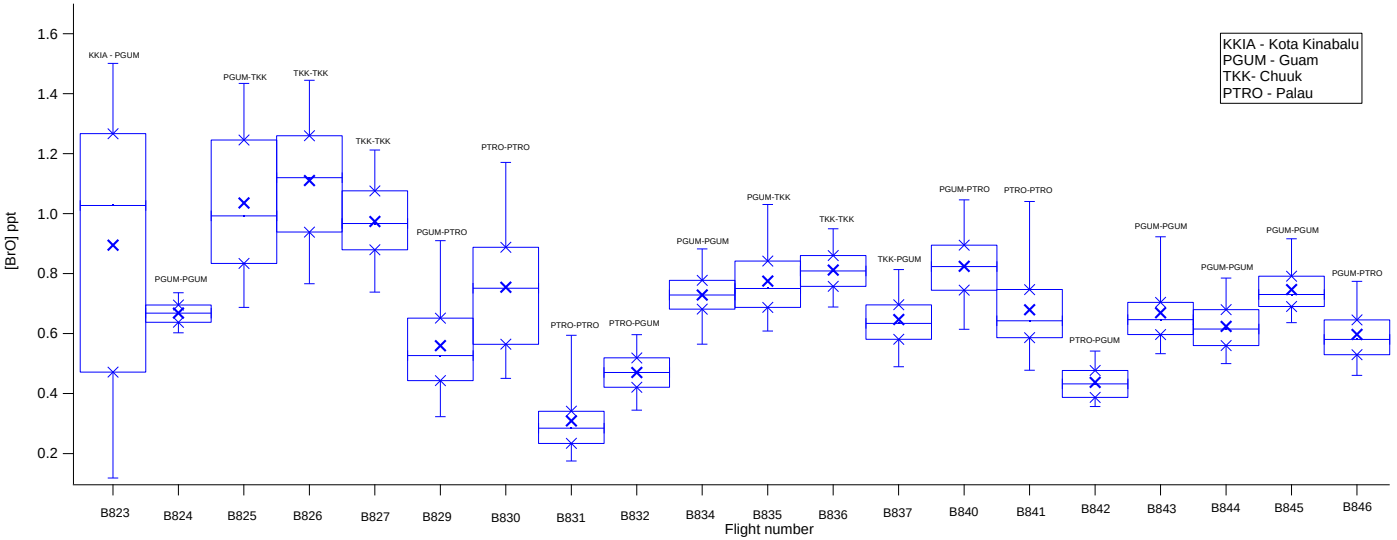


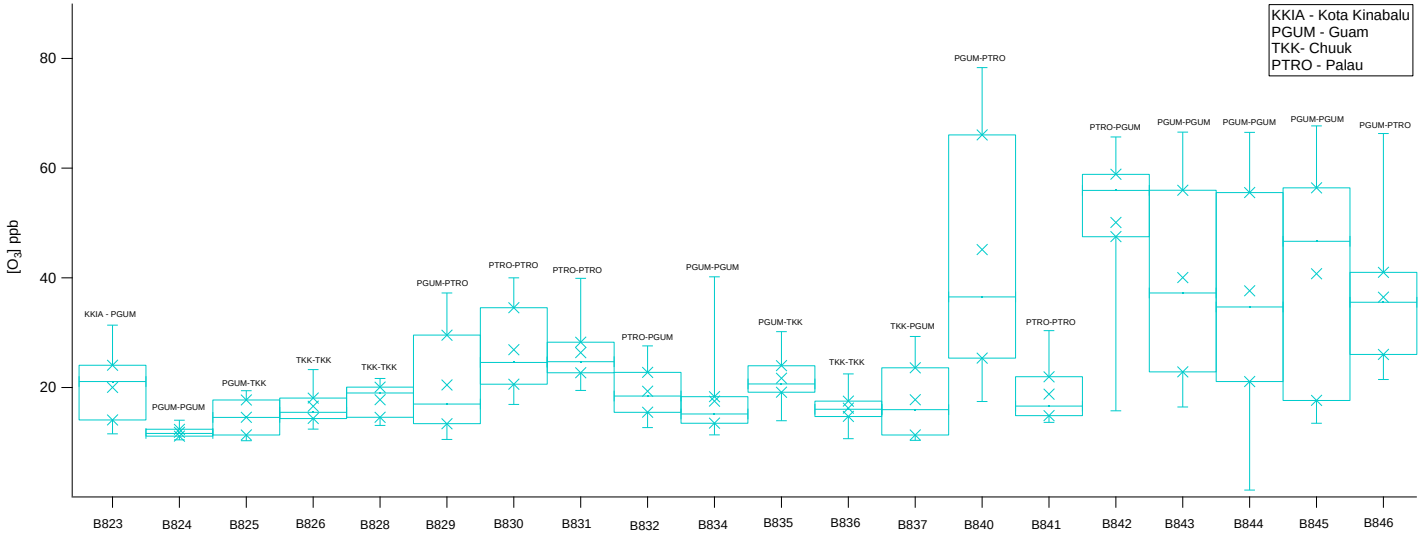




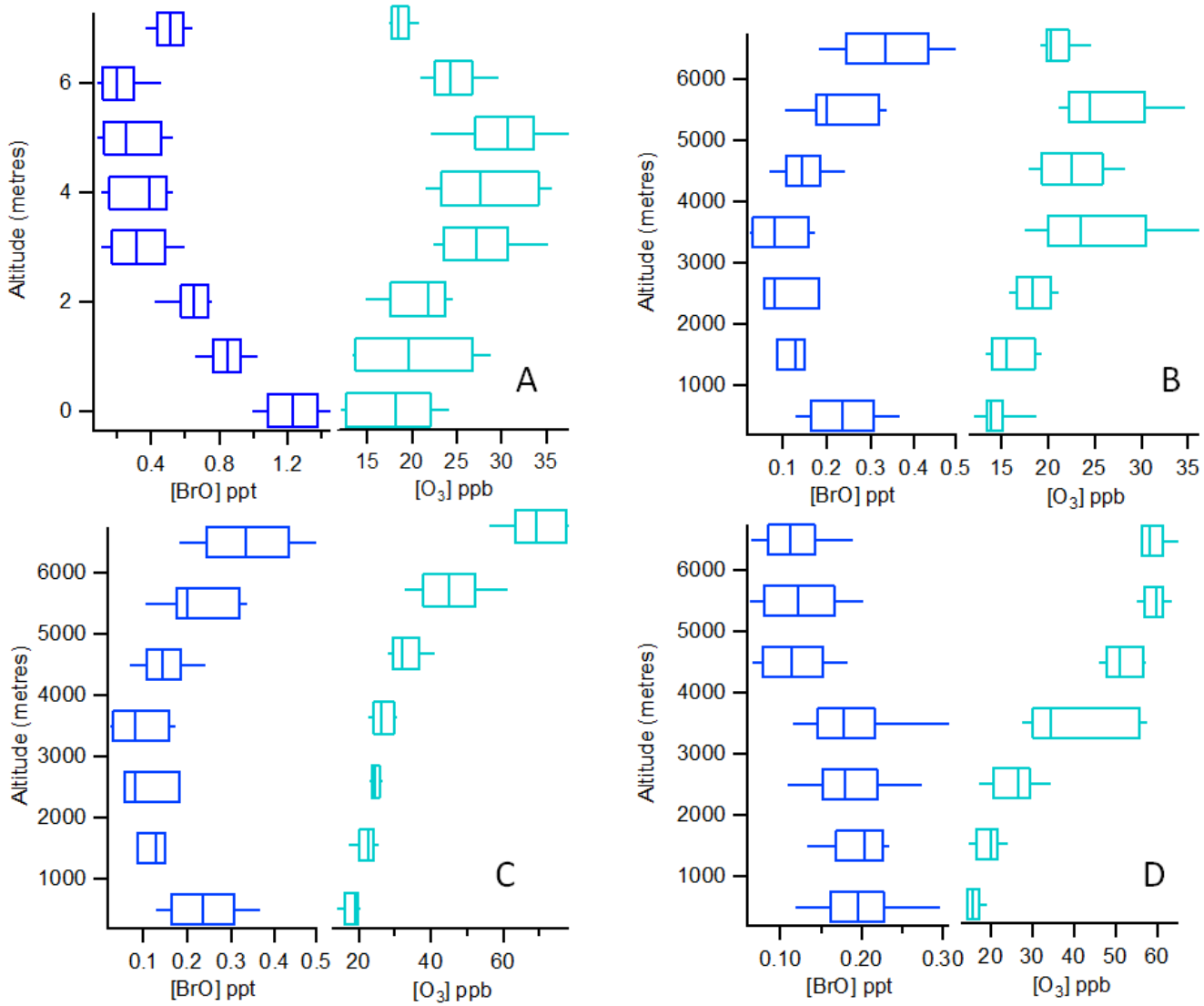


BrO and O_3 data

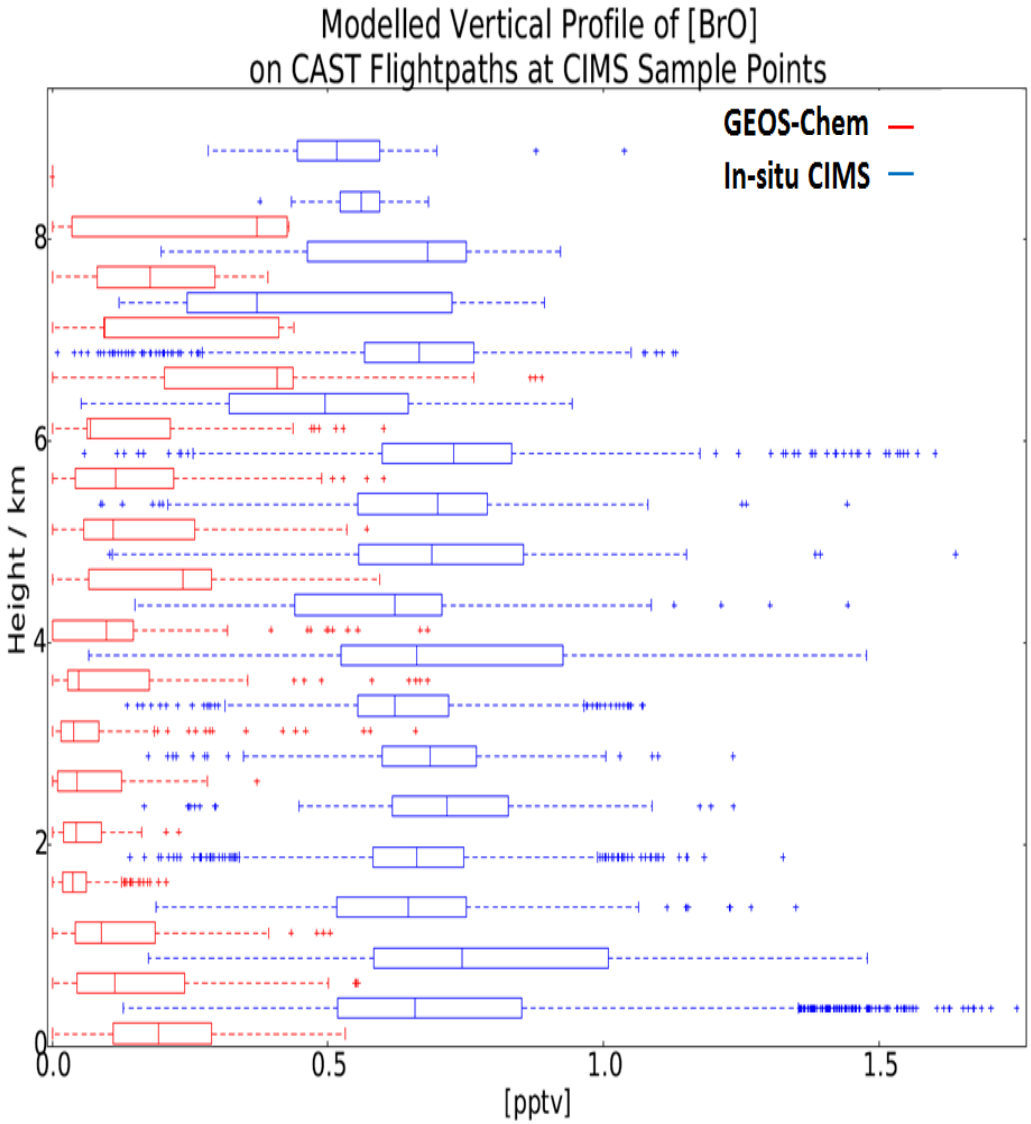




Altitude profiles



Model


Modelled Vertical Profile of [BrO]
on CAST Flightpaths at CIMS Sample Points
GEOS-Chem
In-situ CIMS
Height / km
0
2
4
6
8
0.0
0.5
1.0
1.5
[pptv]

O_3 loss reactions

1. $Br + O_3 \rightarrow BrO + O_3$
2. $Br + DMS \rightarrow$ products
3. $BrO + HO_2 \rightarrow HOBr$
4. $BrO + DMS \rightarrow Br + DMSO$
5. $HOBr + hv \rightarrow OH + Br$
6. $Br_2 + hv \rightarrow Br + Br$
7. $BrCl + hv \rightarrow Br + Cl$
8. HOBr (wet deposition)→
9. BrCl (wet deposition)→
10. Br_2 (wet deposition)→

11. $O_3 + HO_2 \rightarrow OH + 2O_2$
12. $O_3 + hv \rightarrow O(^1D) + O_2$
13a $O(^1D) + N_2 \rightarrow O(^3P) + N_2$
13b $O(^1D) + O_2 \rightarrow O(^3P) + O_2$
13c $O(^1D) + H_2O \rightarrow OH + OH$
14 $BrO + CH_3O_2 \rightarrow HOBr + CH_2OO$
15a $CH_2OO \rightarrow OH + HO_2$
15b $CH_2OO + H_2O \rightarrow HCOOH + H_2O$

O_3 loss reactions

Consider the four loss reactions

11.	$O_3 + HO_2 \rightarrow OH + 2O_2$	$O_{3\ HO2+O3} = k_{11}[HO_2][O_3]$
16.	$O_3 + OH \rightarrow HO_2 + O_2$	$O_{3\ OH+O3} = k_{16}[OH][O_3]$
12	$O_3 + h\nu \rightarrow O(^1D) + O_2$	$O_{3O1D} = F1*J_{12}[O_3]$
13c	$O(^1D) + H_2O \rightarrow OH + OH$	$F1 = k_{13C[H2O]} / k_{13a[N2]} + k_{13b[O2]} + k_{13C[H2O]}$
1.	$Br + O_3 \rightarrow BrO + O_3$	$O_{3\ Br+O3} = k_1[Br][O_3]$

SS approx for HO_2

$[HOBr] = k_3[BrO][HO_2] / J_5 + J_8]$ **SS1**

$[HO_2] = J_5[HOBr] / K_3[BrO]$ **SS2**

We don't know the wet deposition rate underestimate of HO_2 or lower limit.

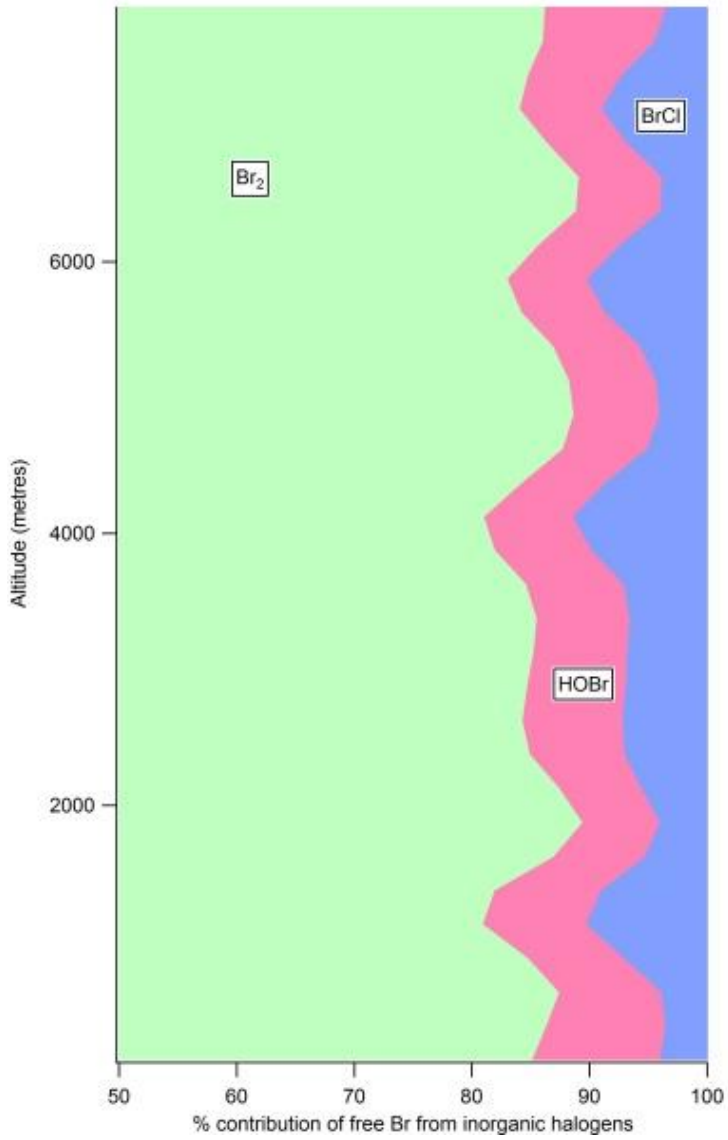
$[HO_2] = J_5 [HOBr] / K_3[BrO]$ **SS3**

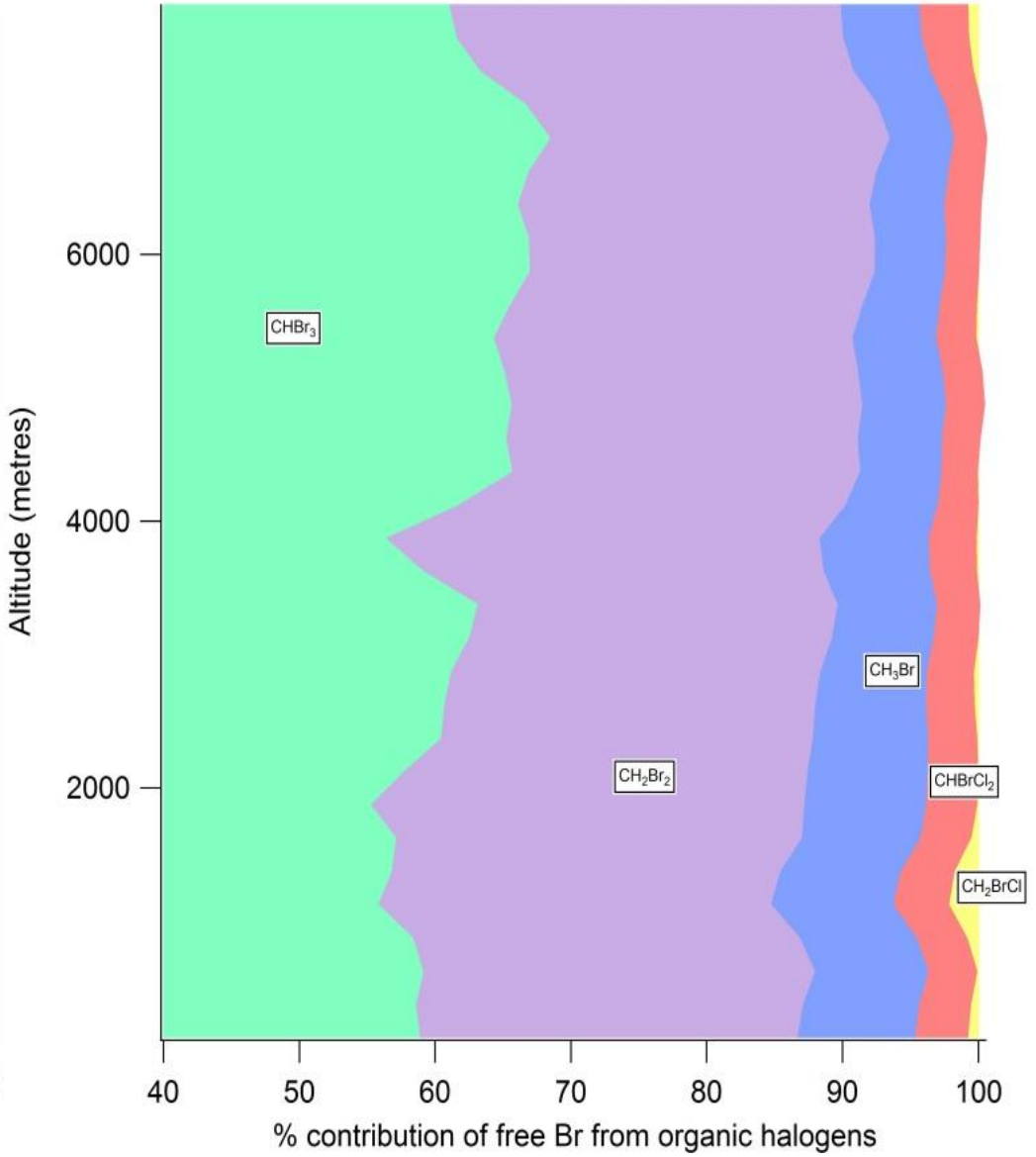
$$[BrO] = \frac{k_1[O_3][Br]}{k_4[DMS] + k_3[HO_2]} = \frac{k_4[BrO][DMS] + J_5[HOBr] + 2J_6[Br_2] + J_7[BrCl]}{k_4[DMS] + k_3[HO_2]} \quad \textbf{SS5}$$

$$[HO_2] = \frac{J_5[HOBr] + 2J_6[Br_2] + J_7[BrCl]}{k_3[BrO]} \quad \textbf{SS6}$$

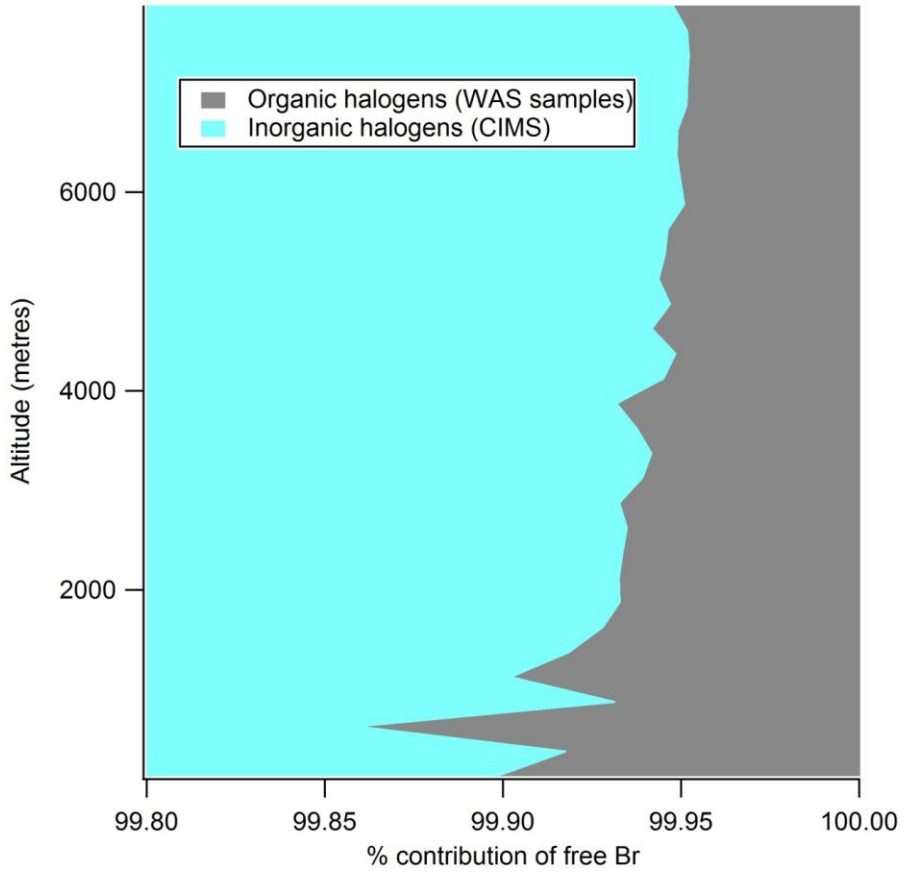
$$J_8 = \frac{2J_6[Br_2] + J_7[BrCl]}{[HOBr]}$$

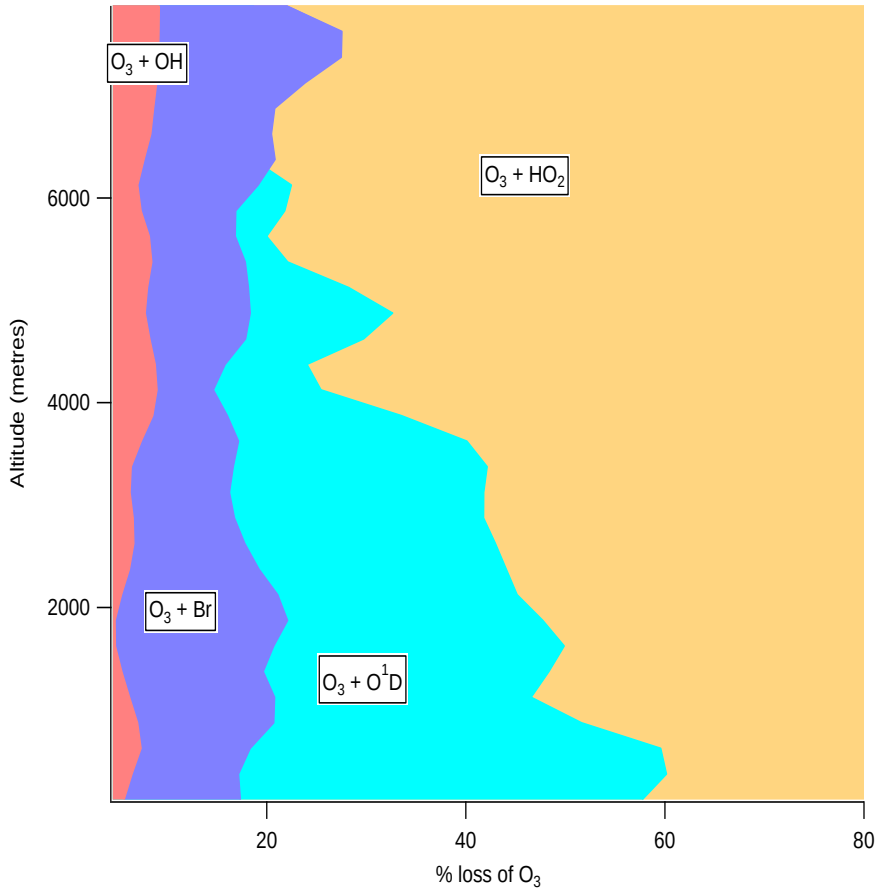
BrO Altitude profiles





CIMS case studies





Summary and further work

- A suite of inorganics simultaneously measured in tropics on aircraft
- Also have measurements of formic, butanoic, nitric, HCN, $ClNO_2$ and N_2O_5
- CIMS measurements indicate model underestimates BrO by a factor of 3/4
- Other inorganic halogens underestimated by similar factor
- Free Br dominated by inorganic photolysis
- Inorganic halogen photolysis responsible for up to 20% O_3 loss in TMBL