Iodine Detection in the Lower Stratosphere

Prof. Rainer Volkamer

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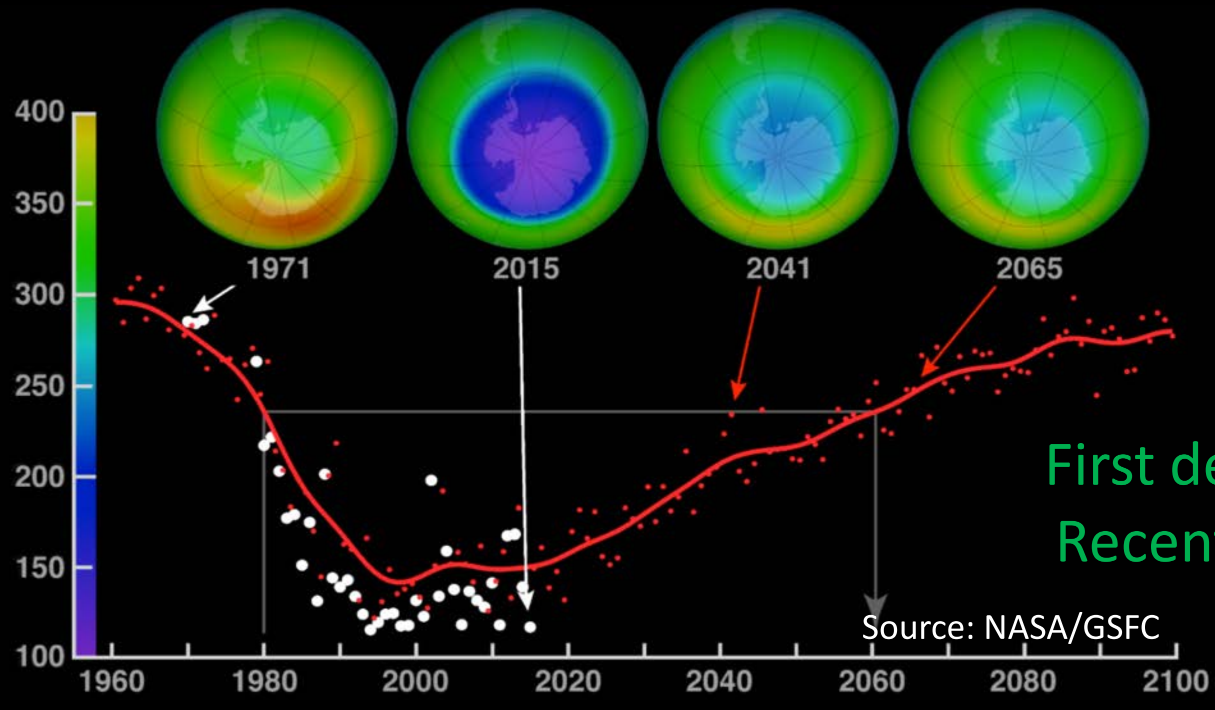
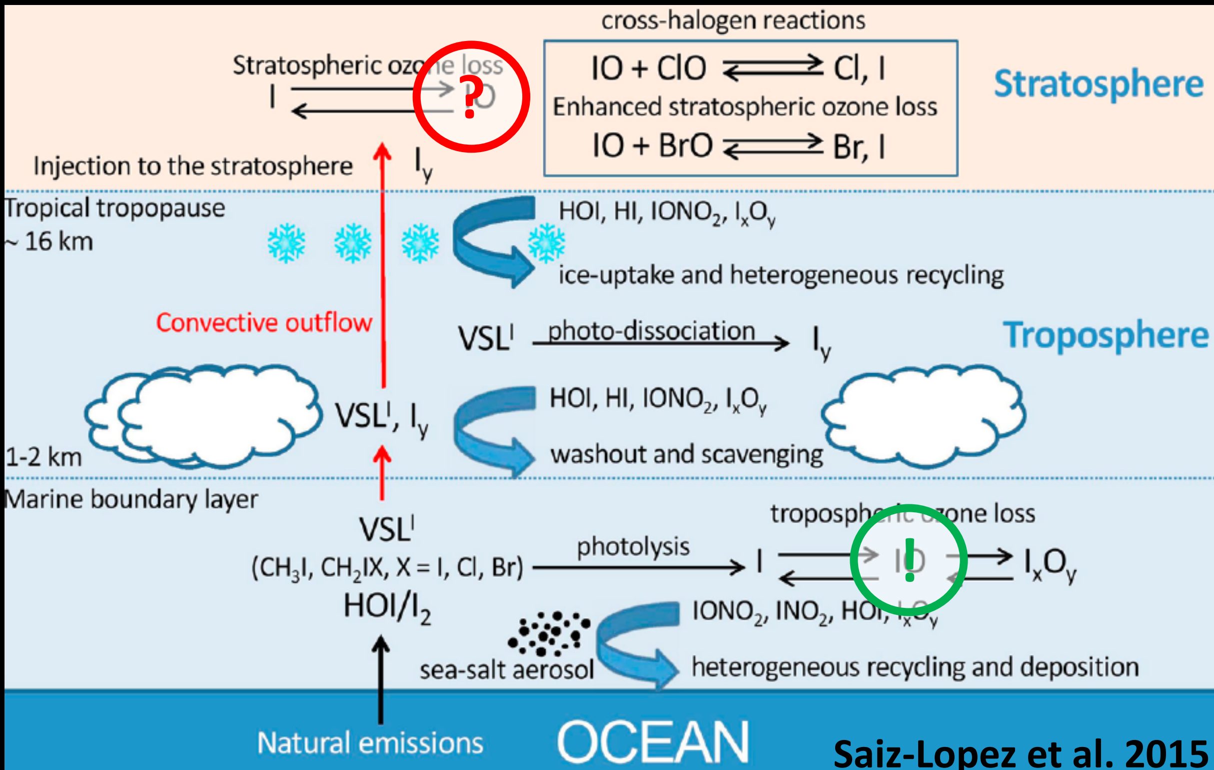


Atmospheric iodine
WMO 2014, 2018
First detection of IO in TTL
Recent aircraft campaigns

Br atoms in the stratosphere have ~60 times the O_3 destruction impact of Cl

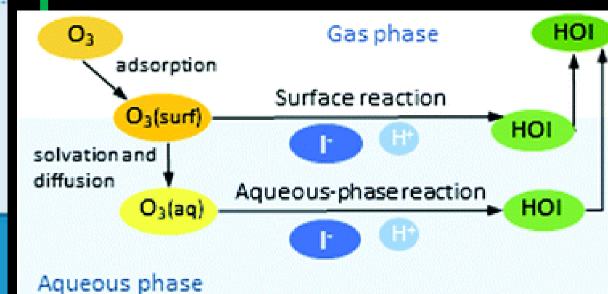
I atoms less certain but estimated at ~600 times the impact of Cl

Atmospheric Chemistry of Iodine



Stratospheric O_3 (Cl,Br)
- **$RF_{St\text{-}O3}$ ~ 0.05 W m^{-2}**
- **Iodine ?**

Tropospheric O_3
- **loss rate: 748 Tg O_X yr^{-1}**
- **O_3 burden: - 9%**
  - **HOI photolysis (78%)**
  - **OIO photolysis (21%)**



Source	Emitted species	Global flux	Lifetime
Organic VSL_I	CH_3I (6.8%), CH_2I_2 (2.8%), CH_2IX(6%)	0.6 Tg I yr^{-1}	mins - days
Inorganic I_y	HOI (76%), I_2 (8.4%)	3.23 Tg I yr^{-1}	seconds - mins
Total source:	Inorganic I_y (~85%), VSL_I (~15%)	3.83 Tg I yr^{-1}	

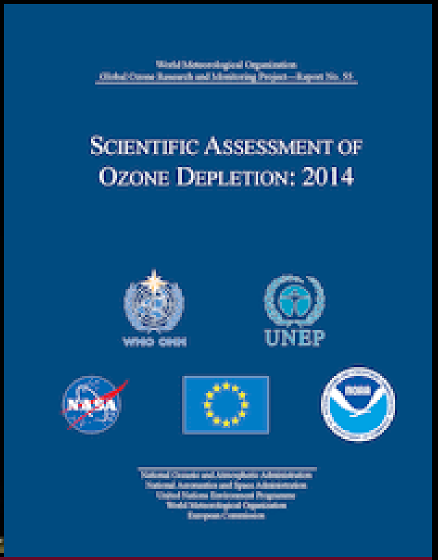
Release atomic I

$I_{y,gas}$ = I, IO, OIO, HOI, I_2, HI, INO_x, I_xO_y $I_{y,part}$ = I^-, IO_3^-

Sherwen et al. 2016; 2017

WMO perspective on iodine in the LS

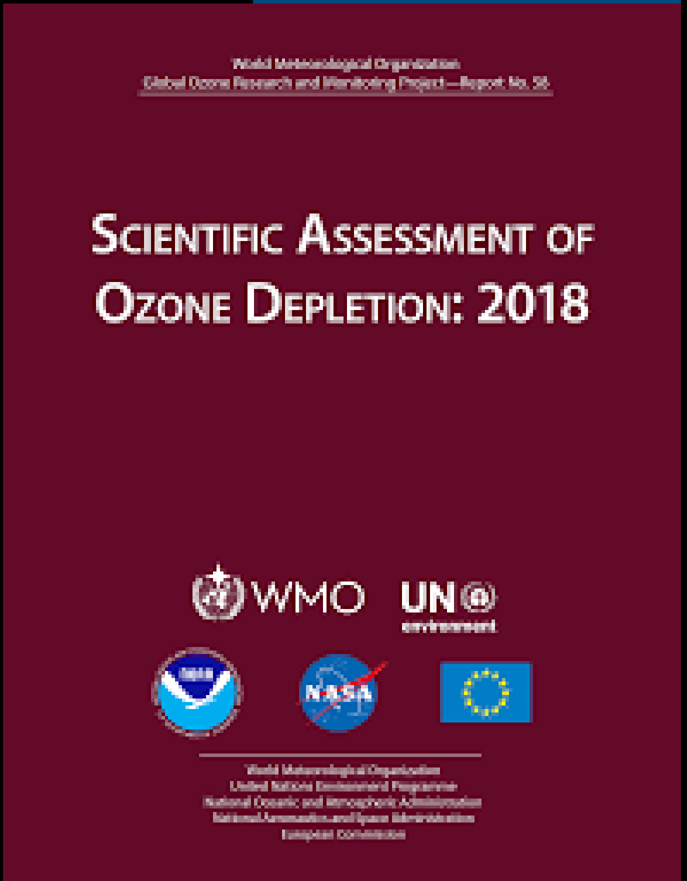
- Iodine Oxide (IO): <0.1ppt, twilight conditions
  (Butz et al. 2009; Boesch et al 2003; Pundt et. al 1998; Wennberg et al 1997)
- Methyl iodide (CH_3I): <0.05 ppt
  (Tegtmeier et al 2013; Saiz Lopez et al 2015)
- Particle Iodine has qualitatively been detected in LS aerosols, but not yet been quantified
  (Murphy and Thomson, 2000; Murphy et. al 2006, 2014)



WMO 2018: Revised I_y estimate

Halogen	X_y (pptv)	O_3 eff. (a.u.)	X_y * O_3 eff. (a.u.)
Chlorine	115	1	115
Bromine	5	60	300
$Iodine_{WMO2014}$	<0.15	600	<90
$Iodine_{WMO2018}$	0 - 0.8	600	0 - 540

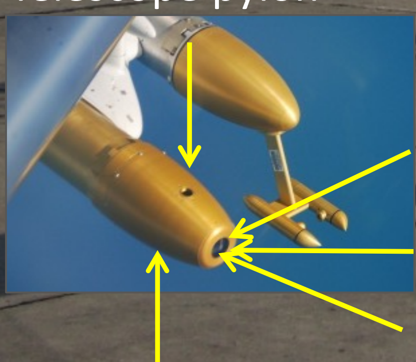
Volkamer et al., 2015; Saiz-Lopez et al. 2015

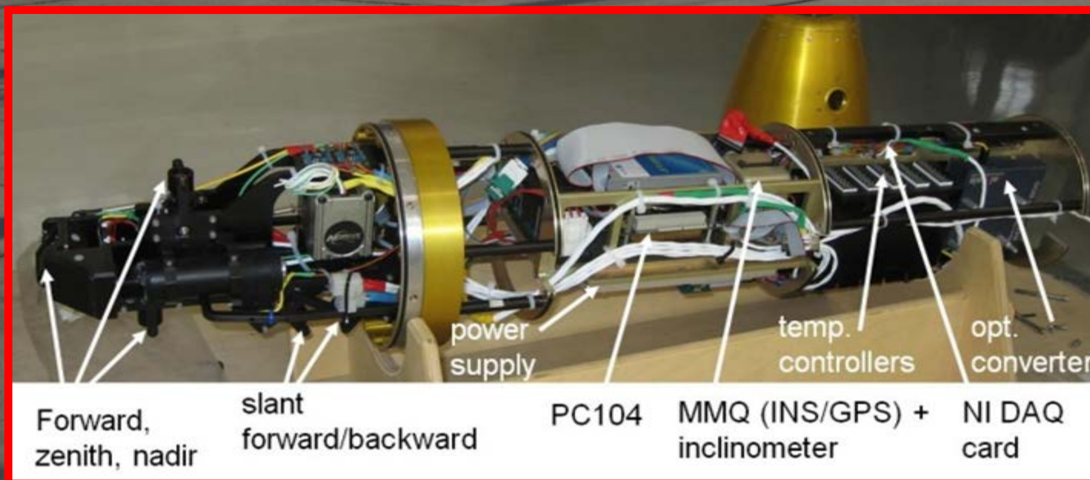


First IO detection in daytime TTL (Volkamer et al 2015)

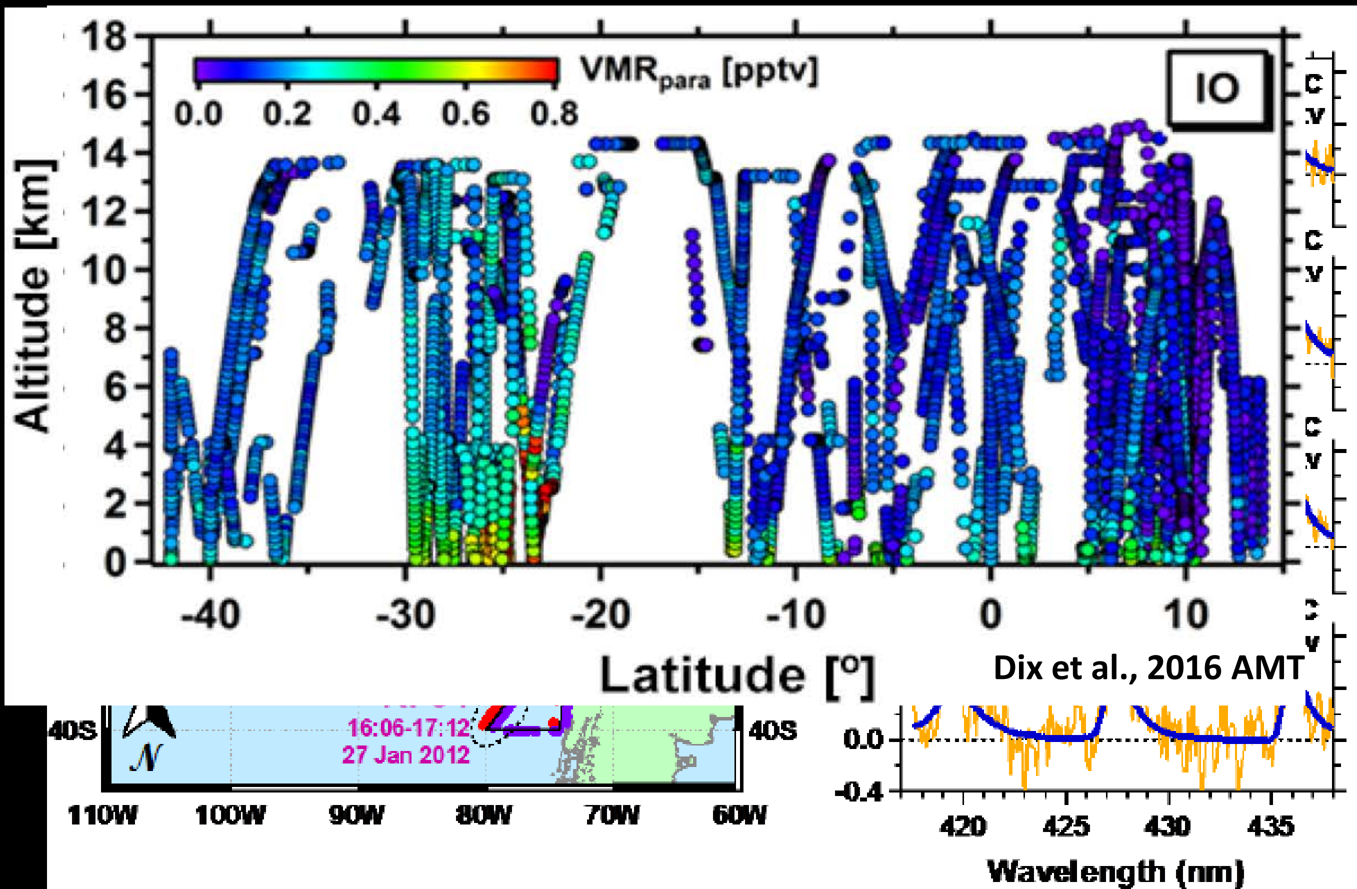
Volkamer et al., 2015 AMT
Wang et al., 2015 PNAS
Saiz-Lopez et al., 2015 GRL
Sherwen et al., 2016 ACP
Schmidt et al., 2016 JGR
Dix et al., 2016 AMT
Koenig et al., 2017 ACP
Wales et al., 2018 JGR
Badia et al., 2019 ACP
Zhu et al., 2019 ACP

Telescope pylon

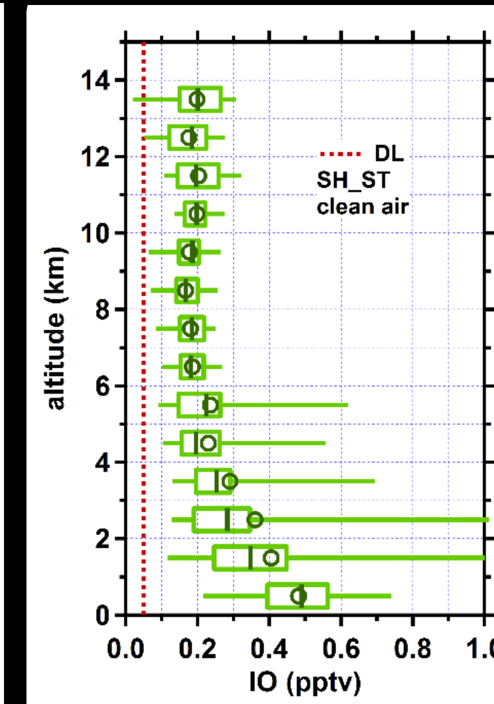




First IO detection in daytime TTL (Volkamer et al 2015)



Wang et al. 2015 PNAS



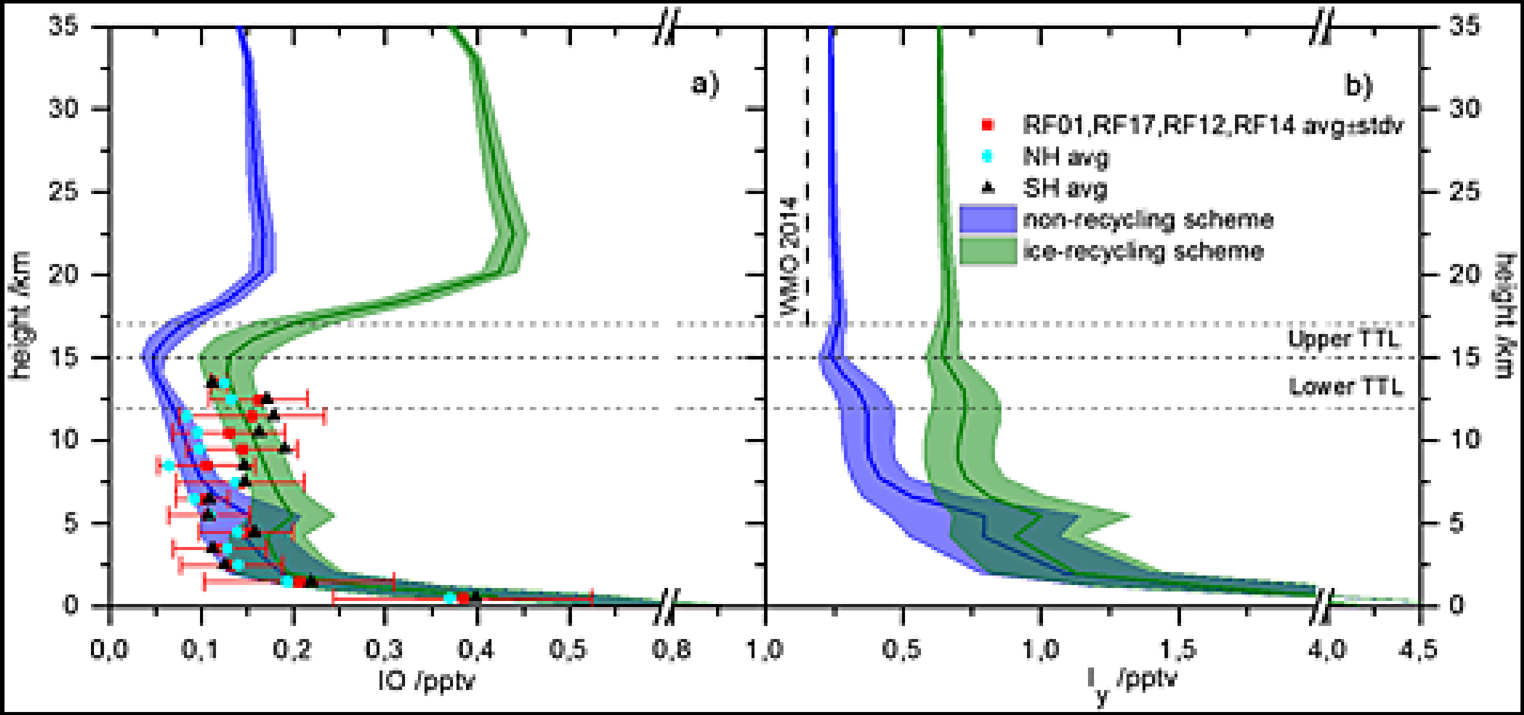
Dix et al. 2016 AMT

0.13-0.15 pptv IO in the Tropical Transition Layer (both hemispheres)

"Our understanding of the chemical processes involving halogens and organic carbon species in the tropics seems incomplete."

Volkamer et al. 2015 AMT

Stratospheric I_y injection inferred from TTL-IO



Saiz Lopez et al. 2015 GRL

Daytime TTL-IO suggests 0.25 to 0.70 pptv I_y are injected into the LS

Previous measurements had found <0.1 pptv IO at twilight in the LS (Butz et al. 2009; Wennberg et al 1997).

There is no previous daytime detection of IO in the LS.

CONTRAST RF15: Bromine injection to the stratosphere

We have re-visited this case study to measure iodine oxide radicals

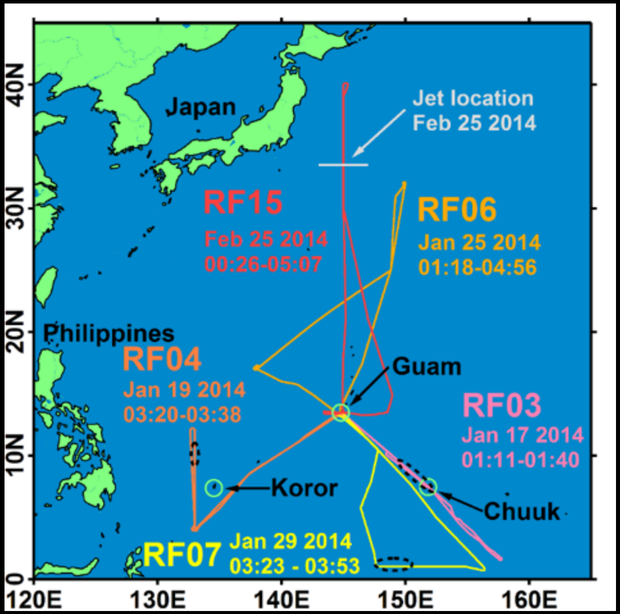
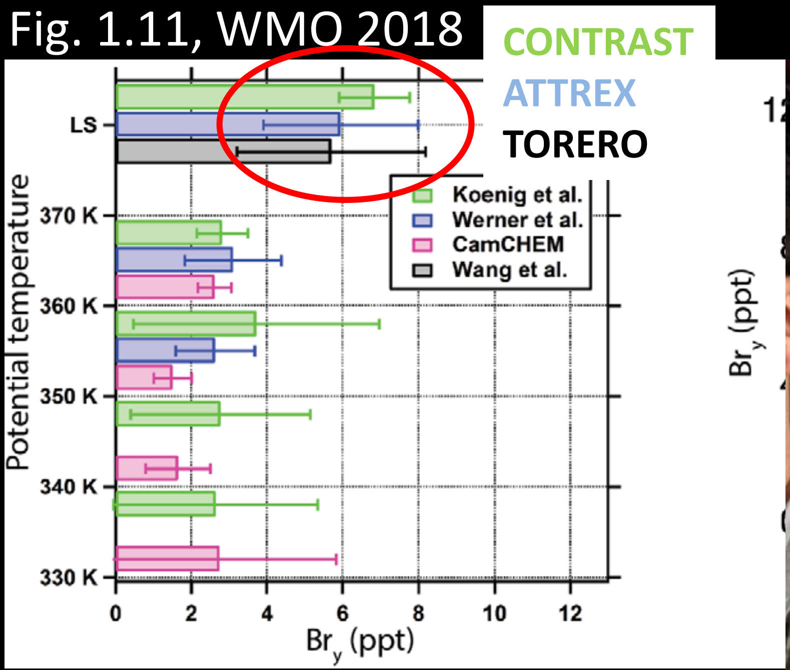


Fig. 1.11, WMO 2018



Koenig et al., 2017

Br_y injection = 5 ± 2 pptv WMO 2018

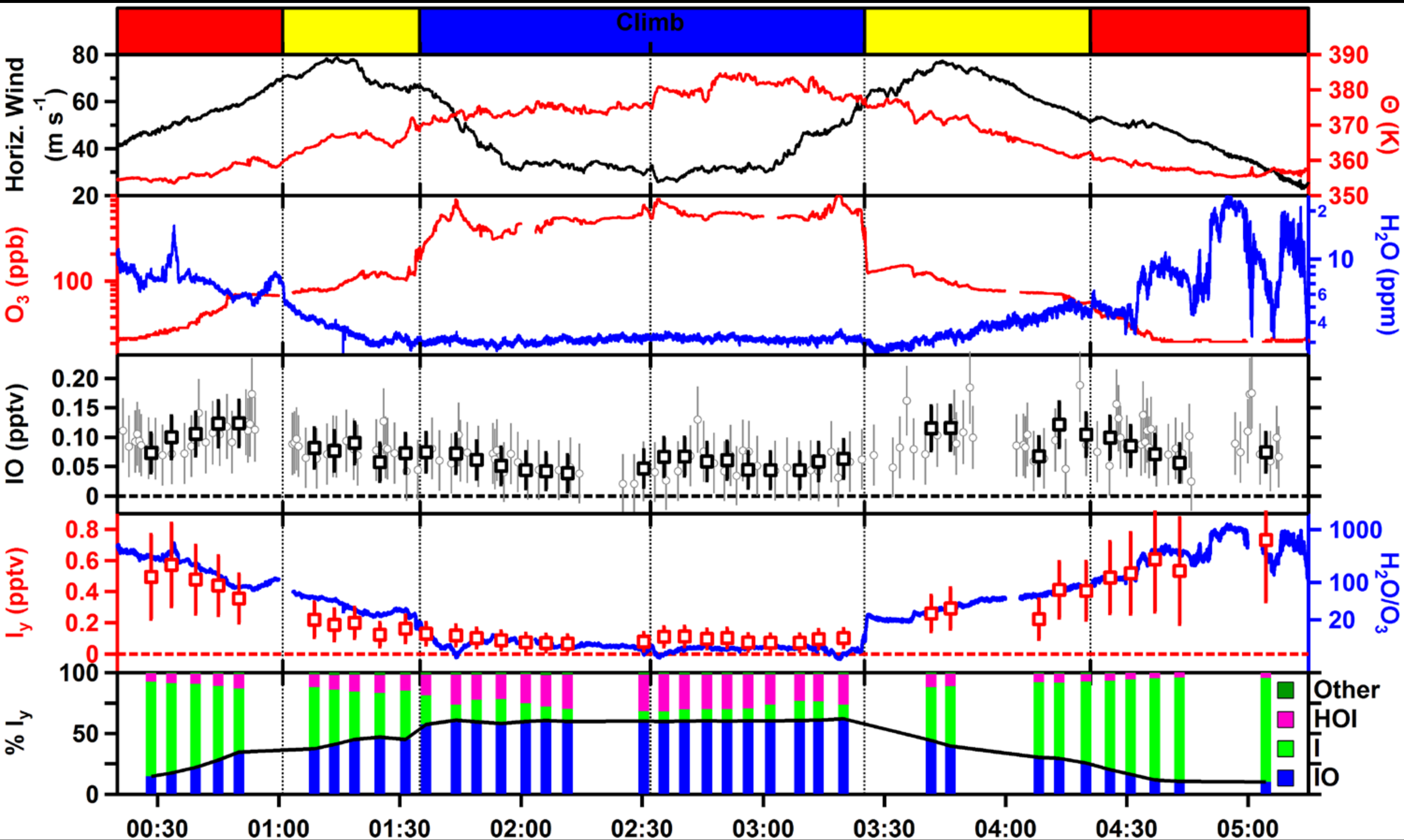
~5 pptv WMO 2014 (confirmed)

SGI = ~3 pptv Br_y based on VSL_{Br} observations

PGI = 2-4 pptv Br_y inferred from BrO observations

Good consistency for Br_y in LS, incl. several recent aircraft datasets (i.e., TORERO, CONTRAST, ATTREX)

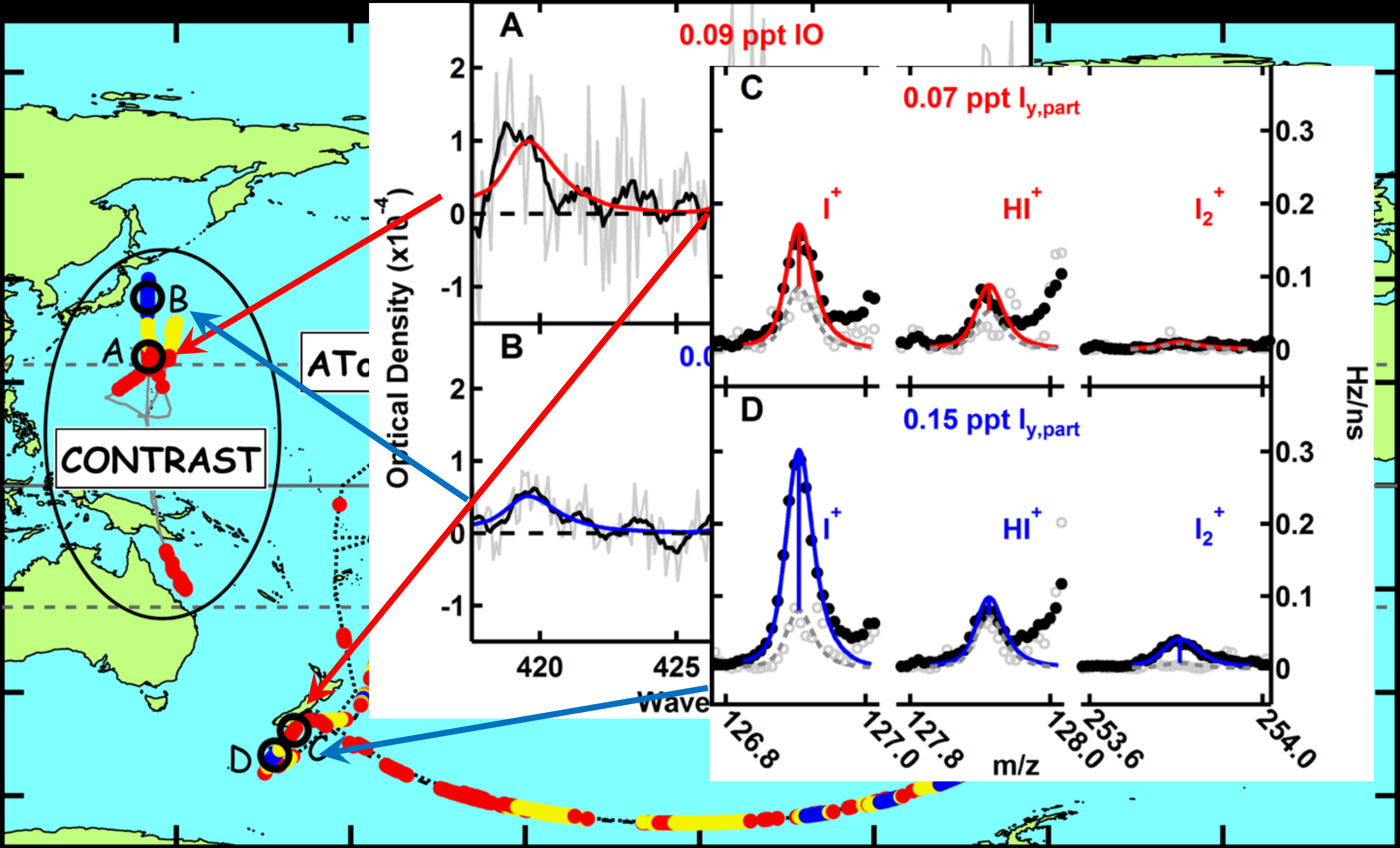
CONTRAST RF15: Jet crossing into NH mid latitude LS



$I_{y,gas}$ decreases from ~0.6 pptv in UT to ~0.1 pptv in LS

0.055 pptv IO in the daytime LS is compatible with previous upper limits (twilight)

Iodine in the UTLS – a global perspective



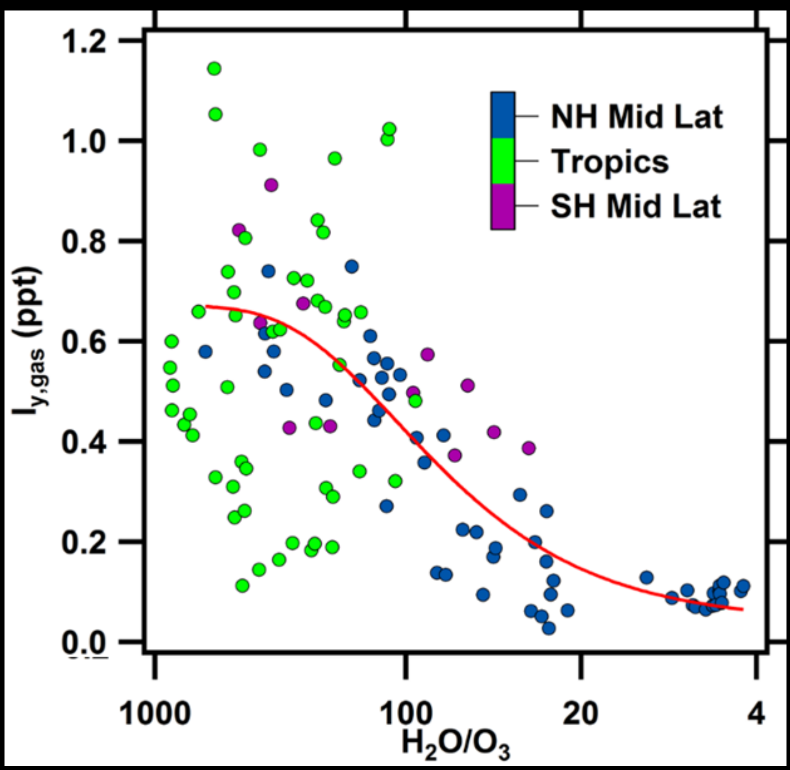
First IO detection in daytime LS.

First quantitative $I_{y,part}$ detection in the UTLS.

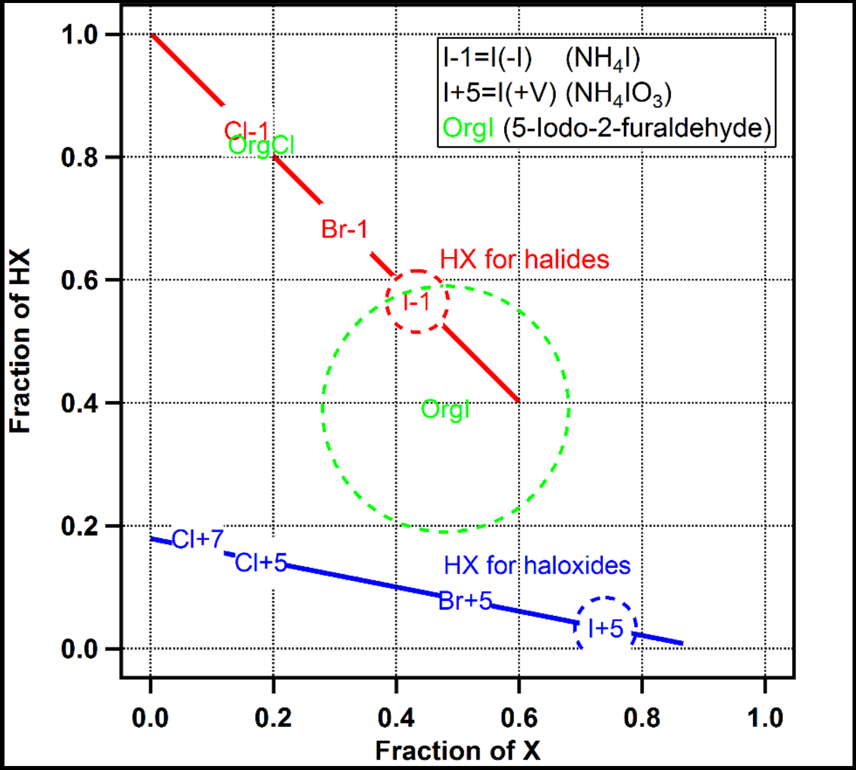
Heterogeneous O_3 loss due to the I^- + O_3 reaction

Altitude (km)	$I_{y,gas}$ (ppt)	$I_{y,part}$ (ppt)	$I^-/I_{y,part}$ (%)	$[I^-]$ (mmol/kg)	γ
11.7	0.64	0.13	50	14.7	9.2e-6
13.7	0.25	0.52	30	10.7	5.7e-6
15.5	0.09	0.68	12	9.19	4.9e-6

$I_{y,gas} = f(H_2O/O_3)$



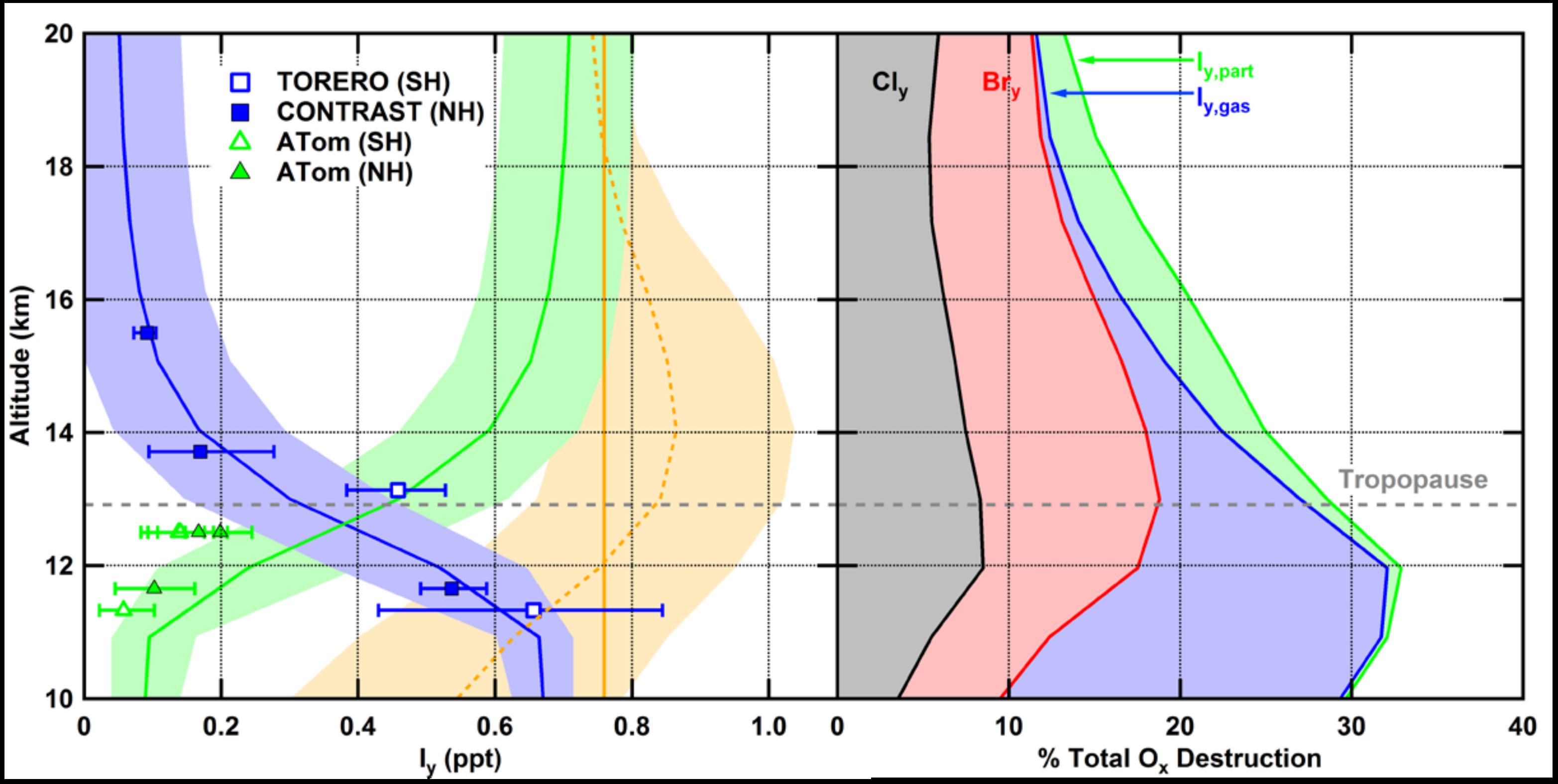
$I_{y,part} = f(I^-, IO_3^-)$ lab calib.



Model comparison and LS O_3 loss

I_y vertical distribution

LS O_3 loss: I_y >= Br_y & Cl_y



Measurements support I_y injection >0.6 pptv; rapid conversion to $I_{y,part}$ (Compare WMO 2018: 0 – 0.8 pptv I_y), but $I_{y,gas}$ remains detectable

O_3 loss: $I_{y,part}$ is competitive with $I_{y,gas}$. I_y is comparable to Br_y, Cl_y

Conclusions

- TORERO: First IO detection in the daytime TTL (Volkamer et al., 2015) suggested 0.25 to 0.70 pptv I_y are injected into the LS (Saiz Lopez et. al 2015). Revised WMO2018 estimate of 0 to 0.8 pptv I_y injection to LS inferred from TTL.
- CONTRAST: First IO detection in the daytime LS. The values are low (0.06 pptv IO) and compatible with previous IO upper limits measured at twilight.
- ATom-1 & ATom-2: First quantification of aerosol iodine in the LS. The fraction $I^-/I_{y,part}$ decreases in the LS, but is non-zero, suggesting heterogeneous re-cycling.
- Our measurements support 0.76 ± 0.15 pptv I_y are injected into the LS

Halogen	X_y (pptv)	O_3 eff. (a.u.)	X_y * O_3 eff. (a.u.)	O_3 loss (%)
Chlorine	115	1	115	16%
Bromine	5	60	300	43%
Iodine	*0 - 0.8*	*~600*	*0 - 540*	
Total I_y	**0.76**	**375**	**285**	41%
- Gas	0.11	960	105	
- Particle	0.65	280	180	

- LS-O_3 loss: Br ~ I >> Cl
- Gas-phase more efficient than particulate iodine at destroying O_3
- Heterogeneous O_3 loss dominates over gas-phase, and is responsible for >60% of iodine O_3 loss in LS.

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