BROMINE CHEMISTRY IN THE TROPICAL UTLS DURING THE ATTREX EXPERIMENTS

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Motivation

Relative sensitivity of surface temperature upon unit masses of GHG

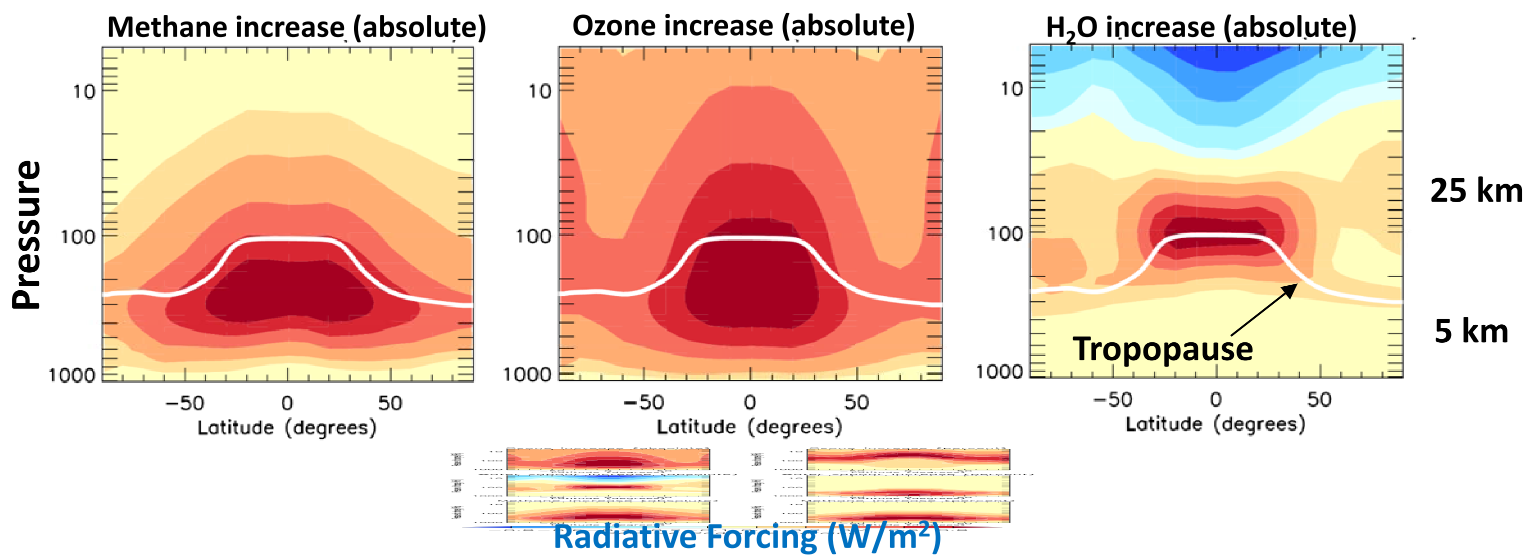


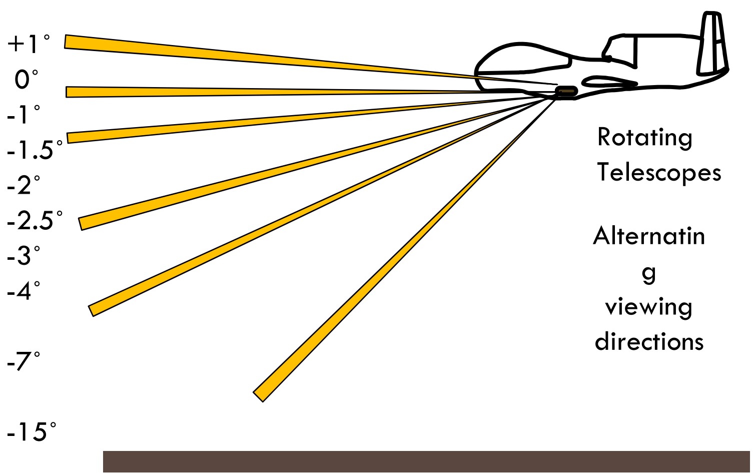
Figure: Illustration of how the surface impact depends on altitude and latitude where the CH_4, O_3 and H_2O changes take place. Shading shows relative surface impact, measured as radiative forcing from a fixed mass increase applied to different altitudes. Red shows where the increase in gas led to maximum surface warming (courtesy P. Foster).

- How does the transport of short-lived halogenated species and their decay products to the stratosphere influence the photochemistry and budget of Bromine (BrO) in the TTL?
- What is the potential of the halogen oxides to directly destroy UT/LS ozone?
- How do cirrus clouds influence chemistry in the UTLS?

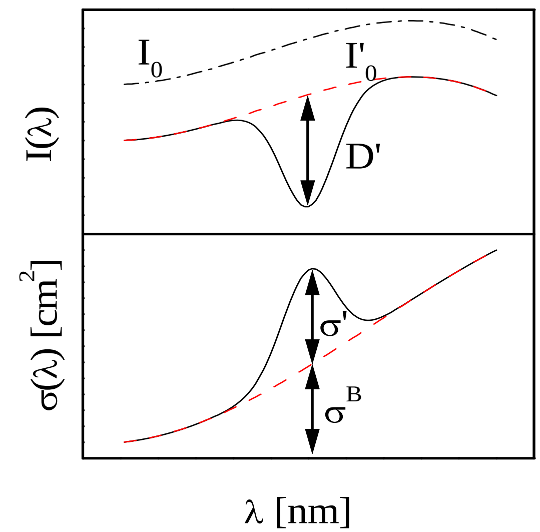
Limb-scanning DOAS Approach

Limb Scanner

(2° off flight direction)



Differential Optical Absorption Spectroscopy



$$I(\lambda) = I_0(\lambda)\cdot e^{-\sigma(\lambda)\cdot SCD}$$

$$D' = \ln\left(-\frac{I(\lambda)}{I_0'(\lambda)}\right)$$

Observation of path-integrated trace gas absorptions using DOAS:

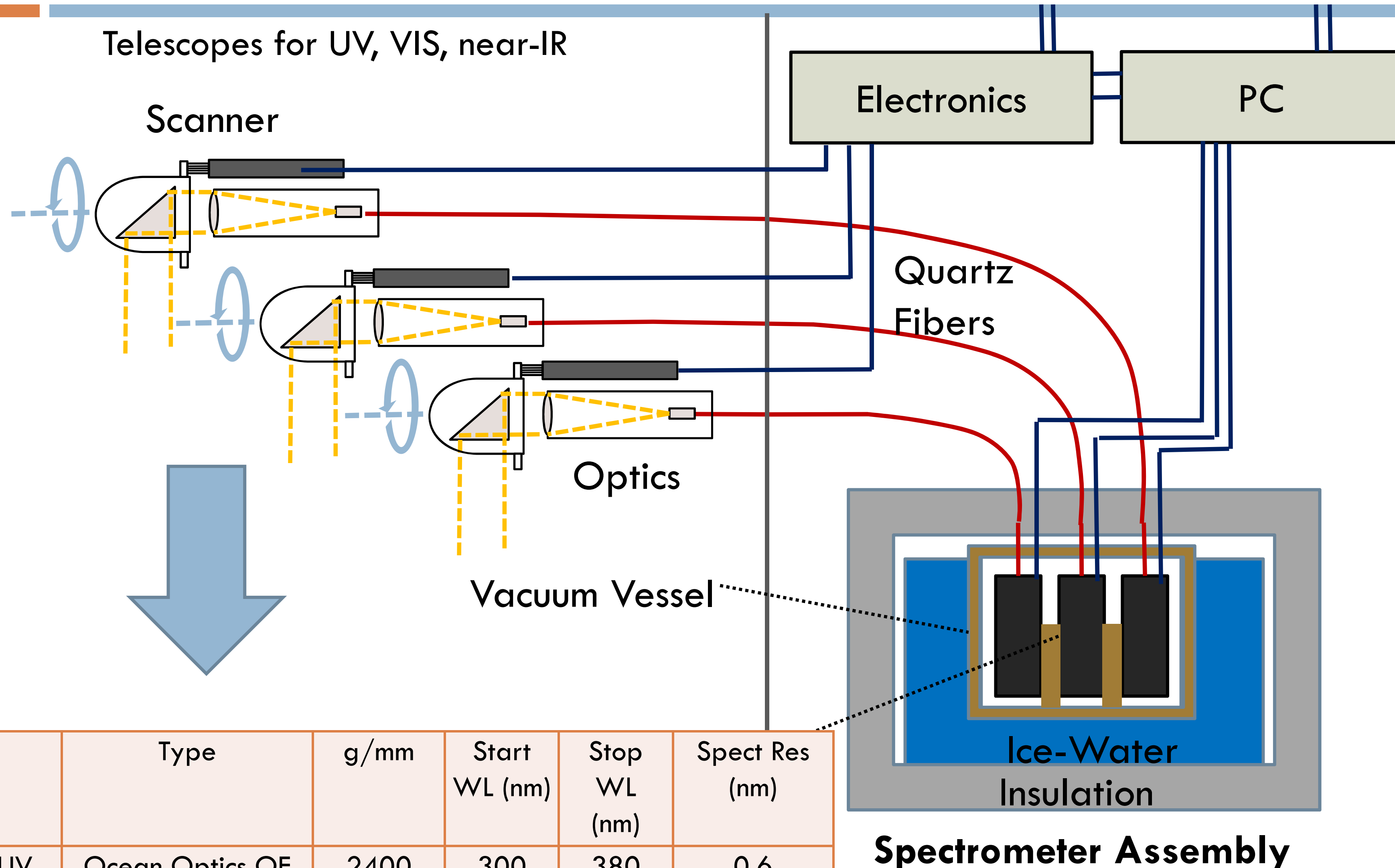
Slant Column Densities:

$$SCD = \int_0^s c(s)\,ds$$

$$SCD_i = \frac{\ln(D')}{\sigma_i'(\lambda)}$$

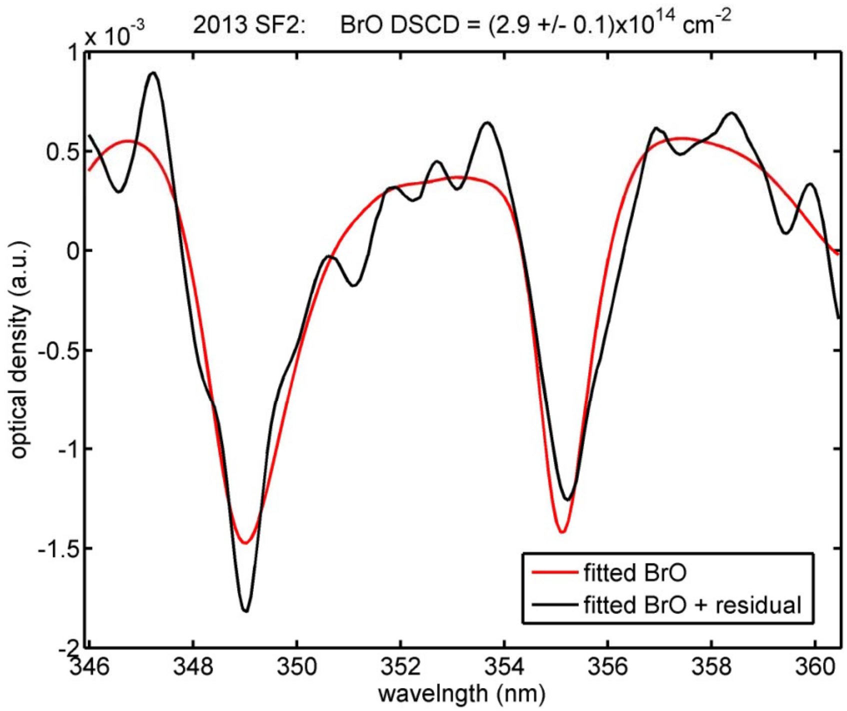
Removal of solar Fraunhofer lines: $DSCD = SCD_{Elev.Angle} - SCD_{solar}$

The Mini-DOAS Instrument



	Type	g/mm	Start WL (nm)	Stop WL (nm)	Spect Res (nm)
UV	Ocean Optics QE	2400	300	380	0.6
Vis	Ocean Optics QE	1800	410	513	0.4
NIR	OO NIRQuest512	150	900	1700	6.6

UV & Vis Analysis of BrO & NO_2



Fit Ranges:

BrO & O_3:	346 – 360.5nm
NO_2:	425 – 446.8 nm
O_3:	346 – 355nm
	437.2 – 485.5 nm

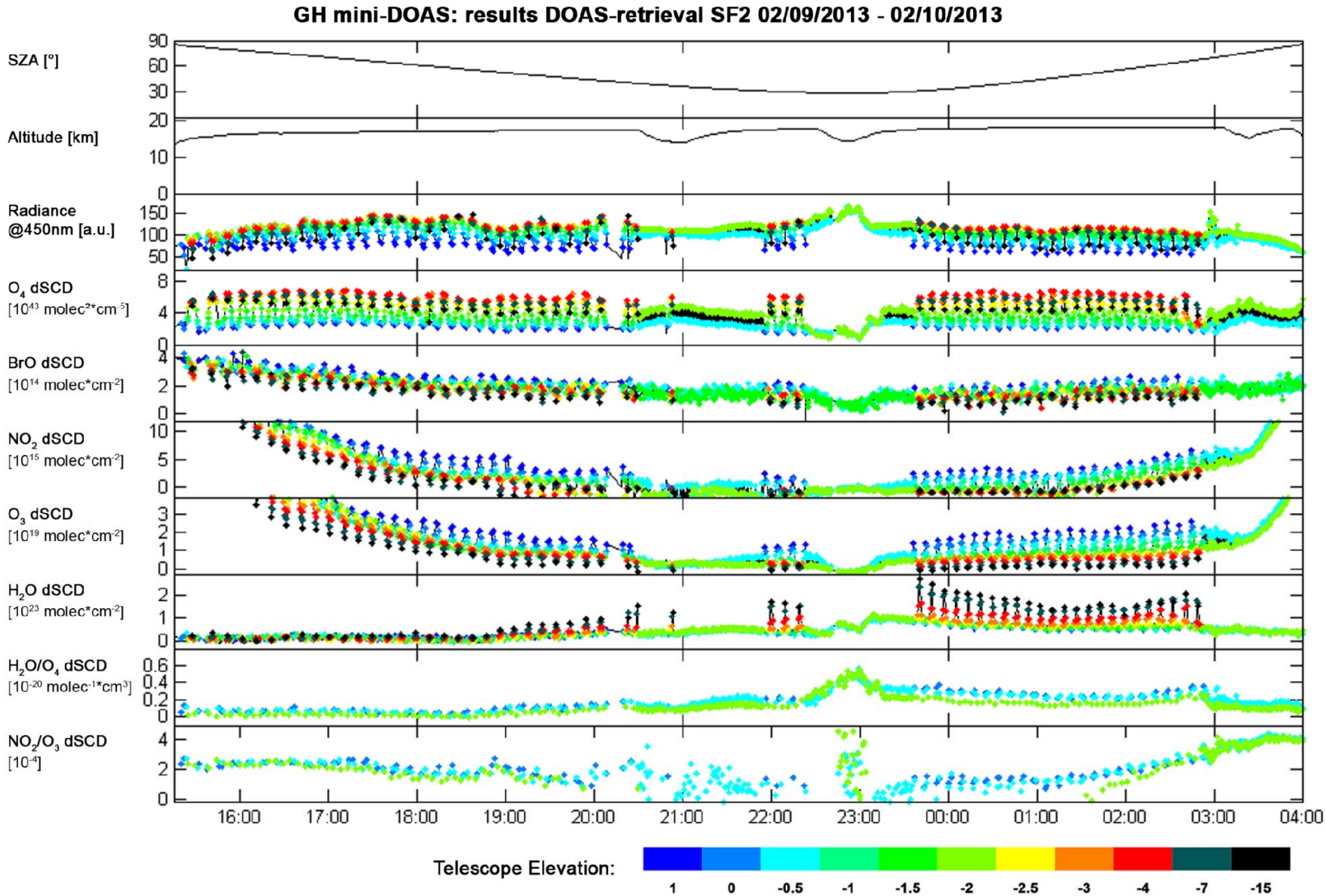
DSCD Detection Limits:

BrO:	2.5×10^{13} molec/cm^2
O_3 :	4×10^{17} molec. cm^{-2}
NO_2:	4.2×10^{14} molec. cm^{-2}

Trace Gas References:

- BrO: Fleischmann et al. 2000
- O_4: Thalman and Volkamer (2013)
- O_3: 203 K and 223 K (Serdyuchenko et al. 2013)
- NO_2 223 K (Bogumil et al., 2002)
- H_2O HITRAN 203 K and 100 mbar (Rothman et al., 2003)
- Ring calculated by DOASIS (Busemer et al).

Example: 2013 Science Flight 2



Data Interpretation: Flight Altitude M.R.

- Focus on -0.5° elevation scans.
- Determine the distance over which the DOAS averages for level flights → use ~1200sec for level flights. 30 sec integration for dives.
- Derive BrO mixing rations using a scaling technique, which relates in-situ O_3 to DOAS O_3 and BrO DSCD.

$$[BrO] = \frac{\alpha_{BrO}}{\alpha_{O3}} \times \frac{DSCD_{BrO}}{DSCD_{O3}} \times [O_3]_{in-situ}$$

RT Model Calculations

DOAS

NOAA

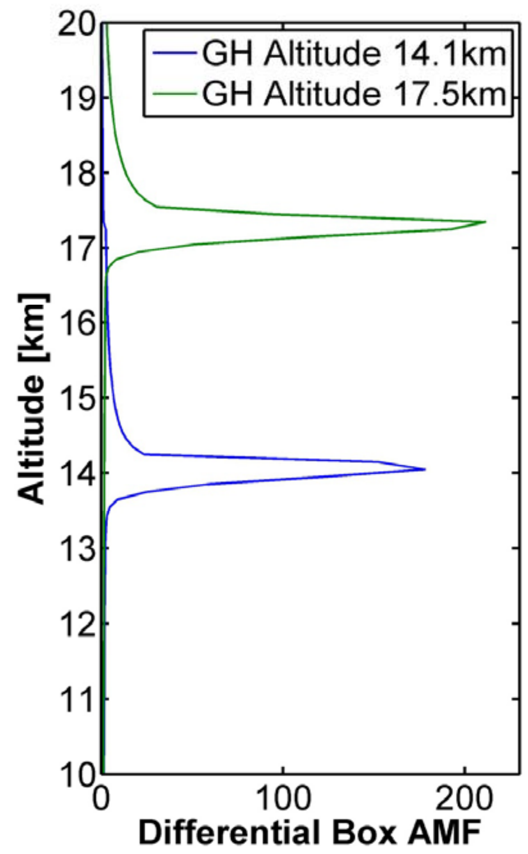
Determination of α Factors

$$\alpha_X = \frac{\sum_{h=Alt-500m}^{h=Alt+500m} [X]_h \times DBAMF_h \times dh}{\sum_h [X]_h \times DBAMF_h \times dh}$$

DBAMF: Differential Box Airmass Factor, relative to solar reference trace gas column (from model).

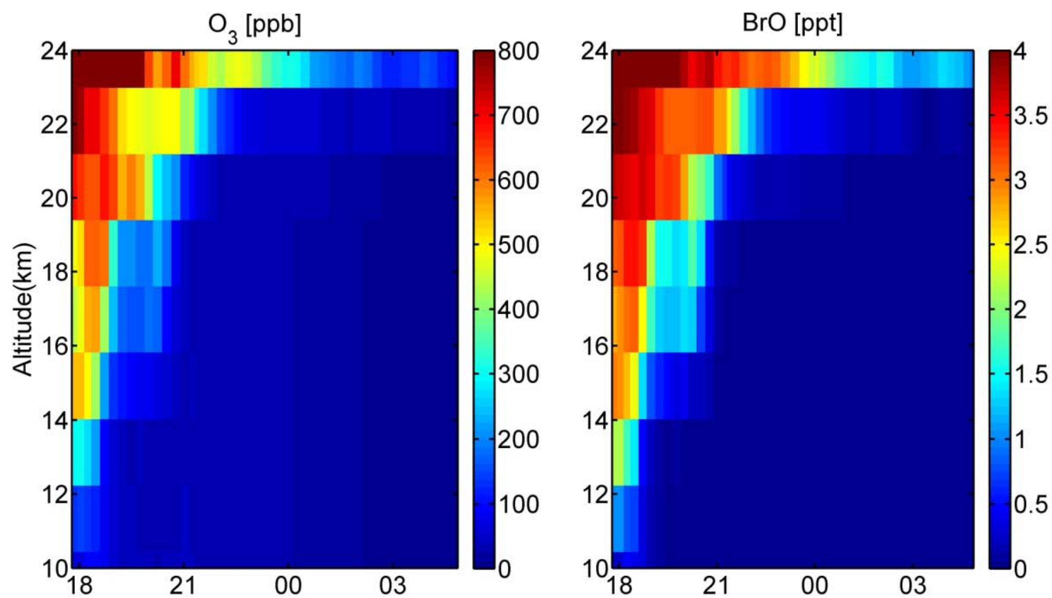
- α_{BrO} and α_{O3} depend on radiative transfer, which depends on:
  - Flight altitude
  - Atmospheric conditions (T, P, aerosol, albedo, etc.)
  - Trace gas vertical profiles
- Calculate α_{BrO} and α_{O3} for the same atmospheric conditions

  → α_{BrO} / α_{O3} ratio is much less sensitive to RT that α itself

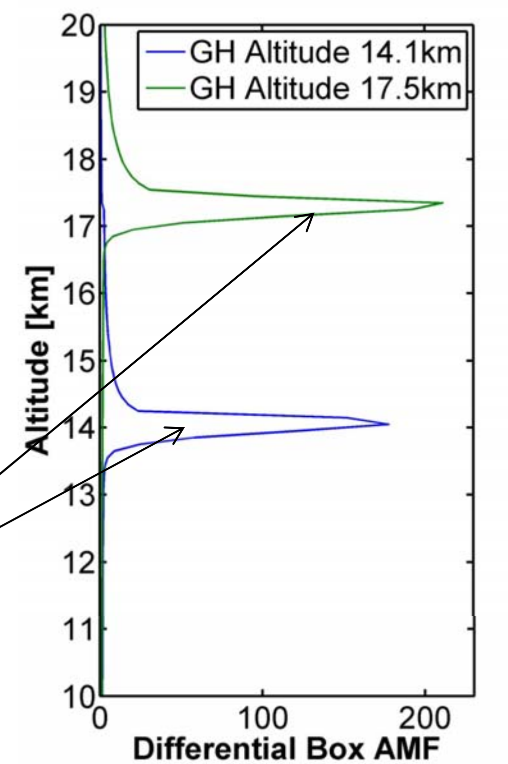


RT Calculations

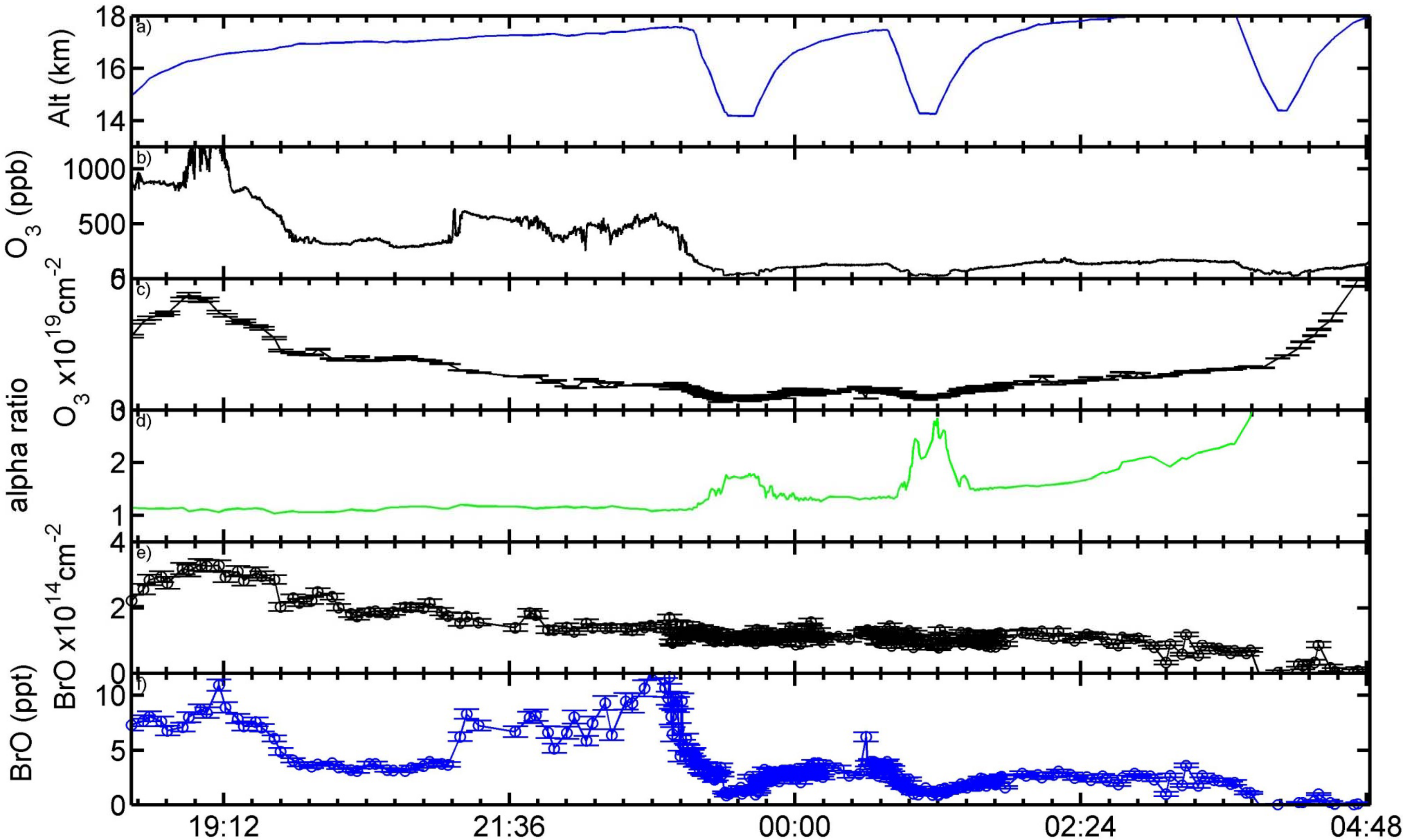
- Use atmospheric profiles from SLIMCAT model



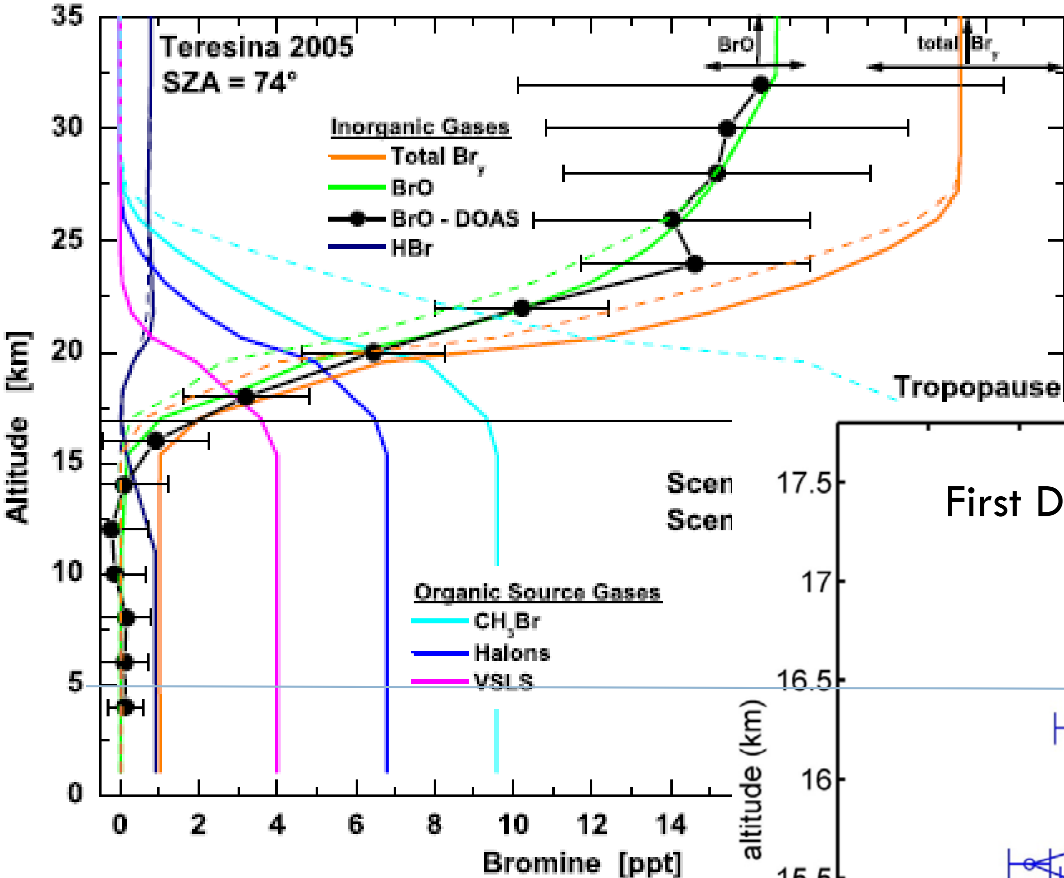
- McArtim Monte Carlo RT
  - 1D with spherical geometry
  - Correction of dynamics/ altitude inaccuracies in SLIMCAT profile through comparison with in-situ O_3
- Sensitivity ±500m around flight altitude



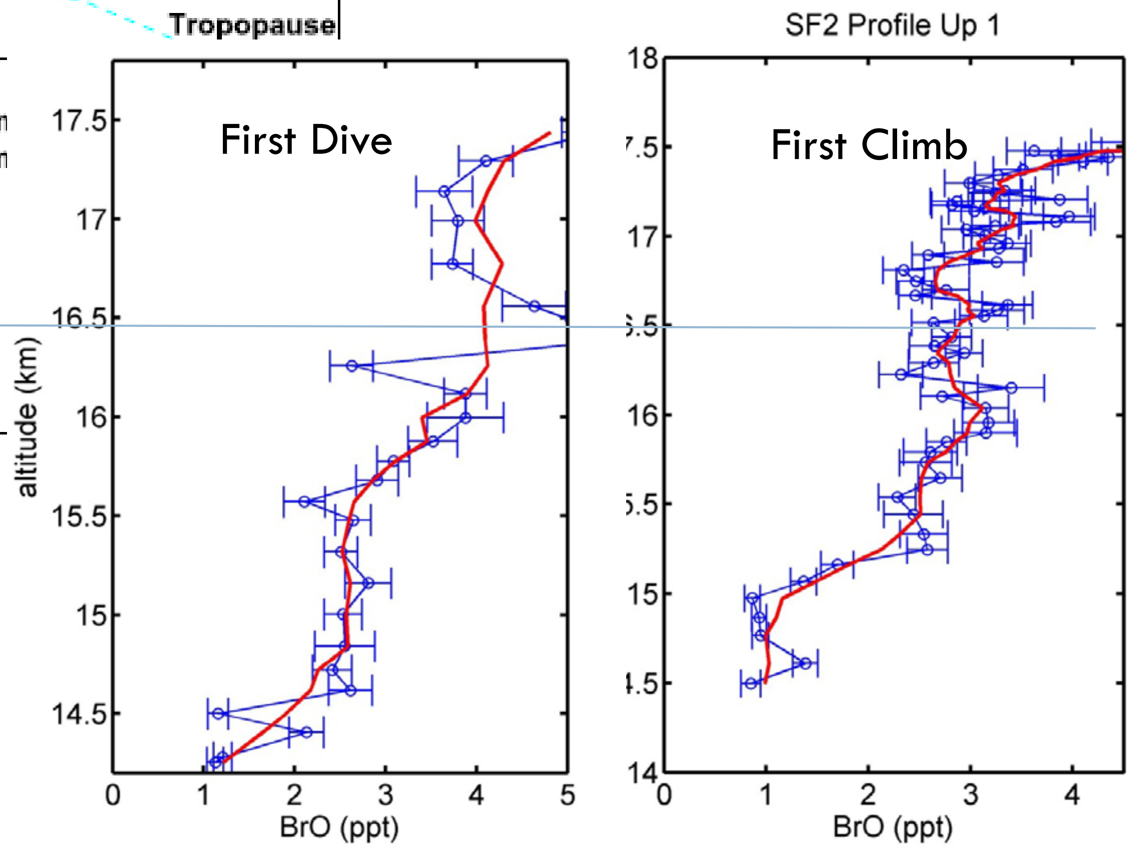
Example of Calculations



Vertical BrO Profiles from SF2



Dorf et al, 2008

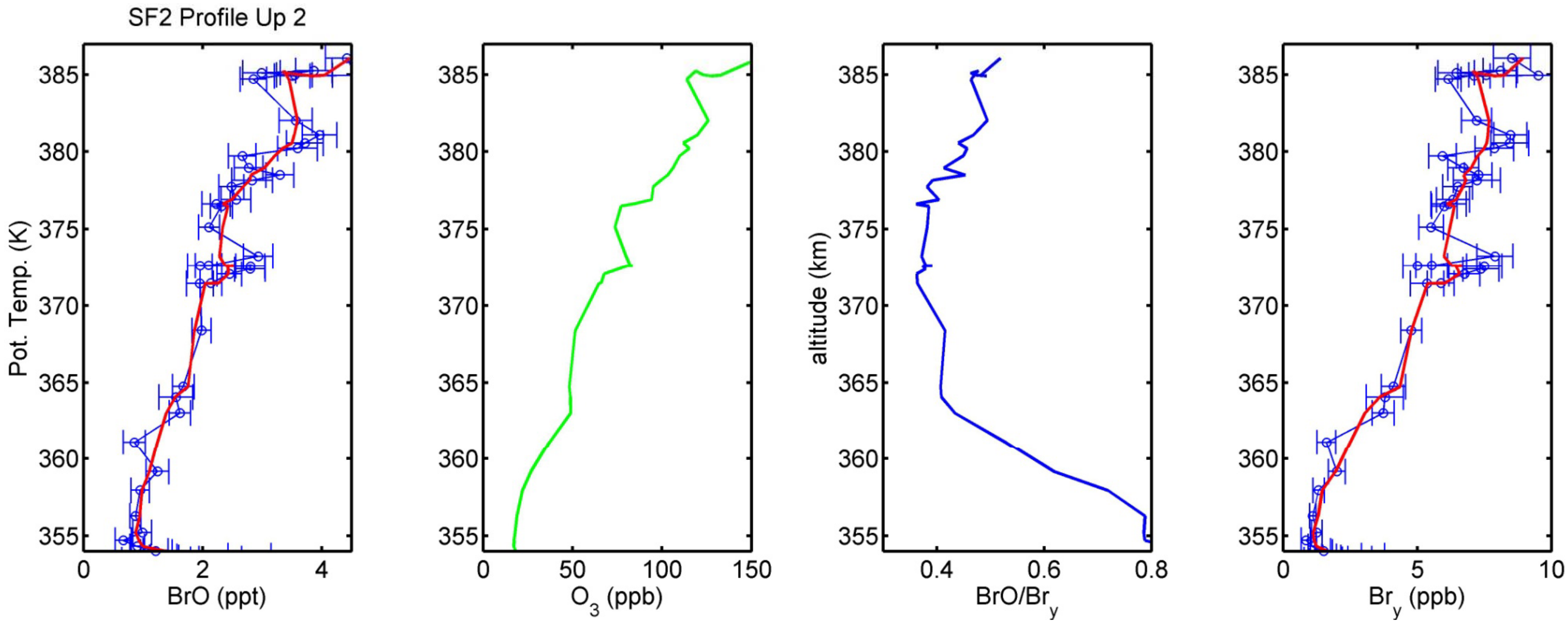


Br_y and total Bromine

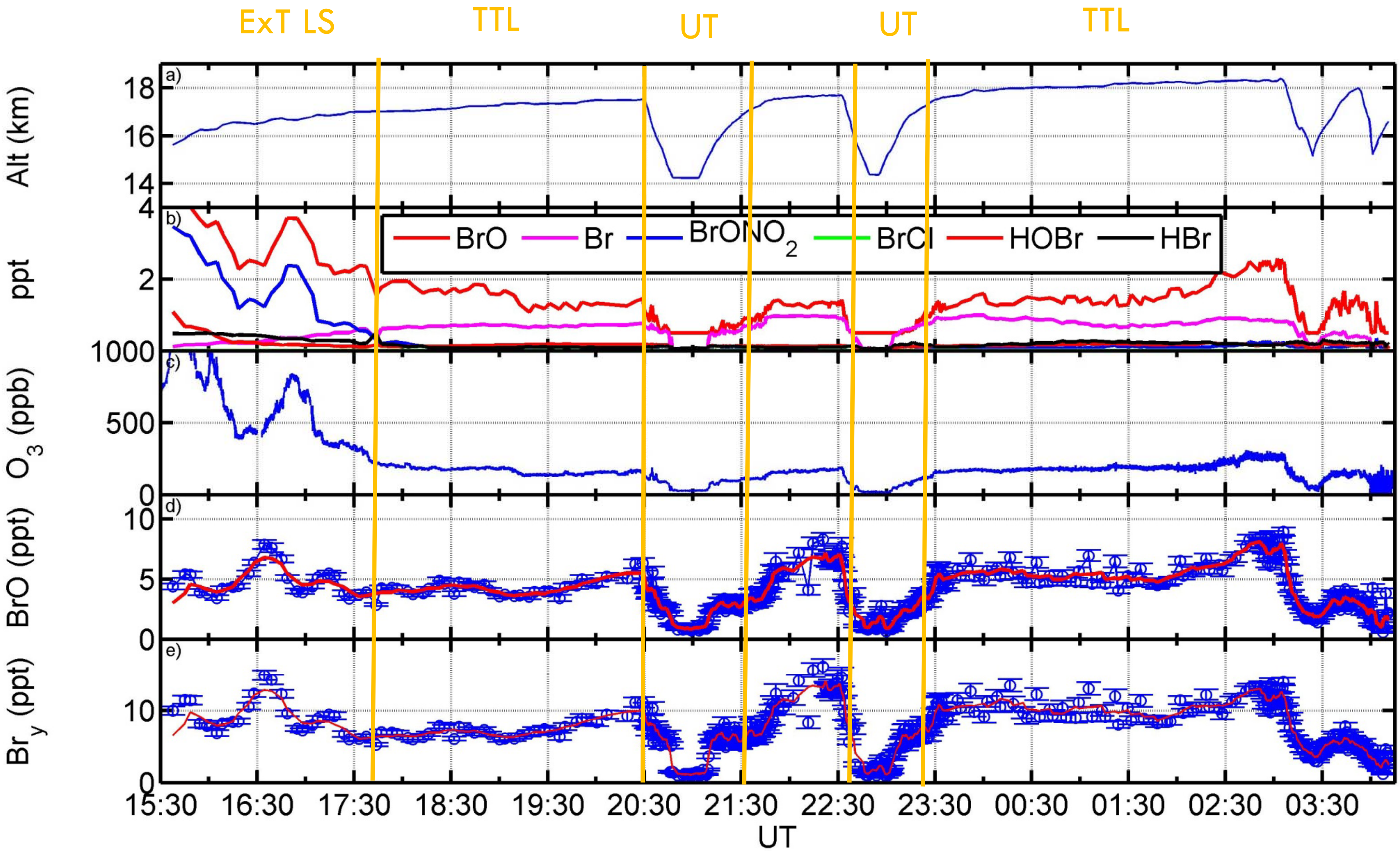
- BrO to Br_y
  - Use SLIMCAT
  - BrO/Br_y between 0.3-0.8, in the expected range
- Br_{org} from GWAS samples

$$[Br_{tot}] = [Br_{org}] + \left.\frac{[Br_y]}{[BrO]}\right|_{calc} [BrO]$$

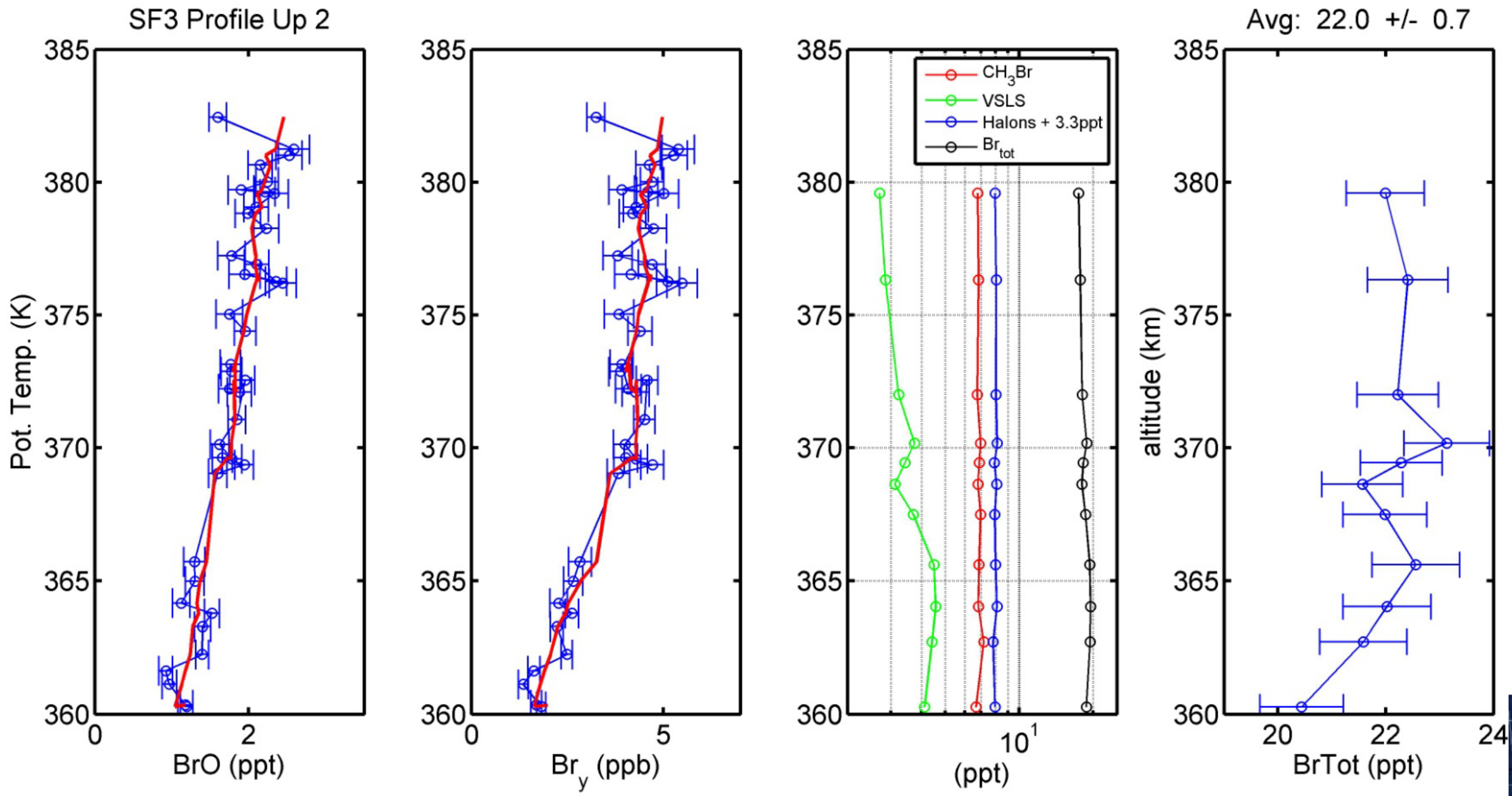
$Br_y = Br + BrO + BrONO_2 + BrCl + HOBr + HBr$
$Br_{org} = CH_3Br + CH_2BrCl + 2 \times CH_2Br_2 + CHBrCl_2 + 2 \times CHBr_2Cl + 3 \times CHBr_3 + \text{halons}$

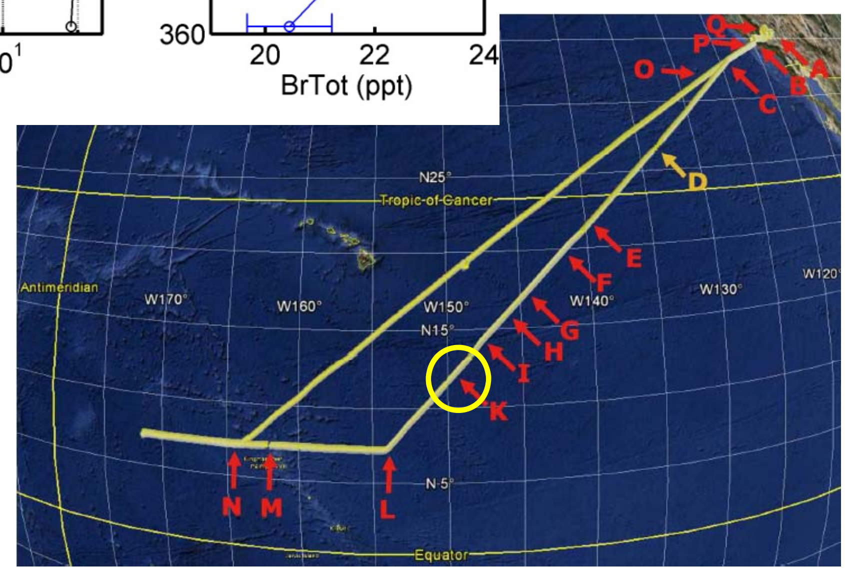


BrO/Br_y in SF2



Science Flight 3, Second Climb

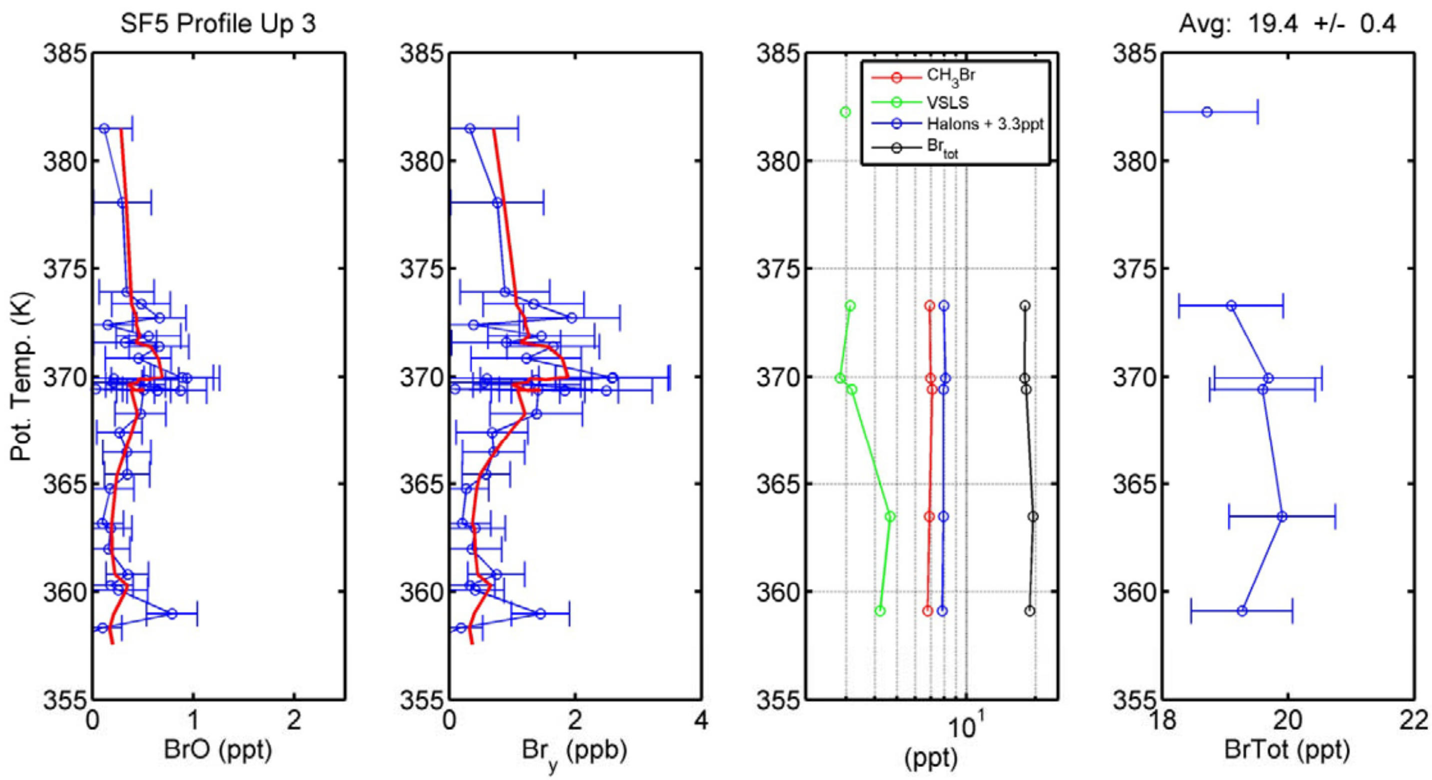


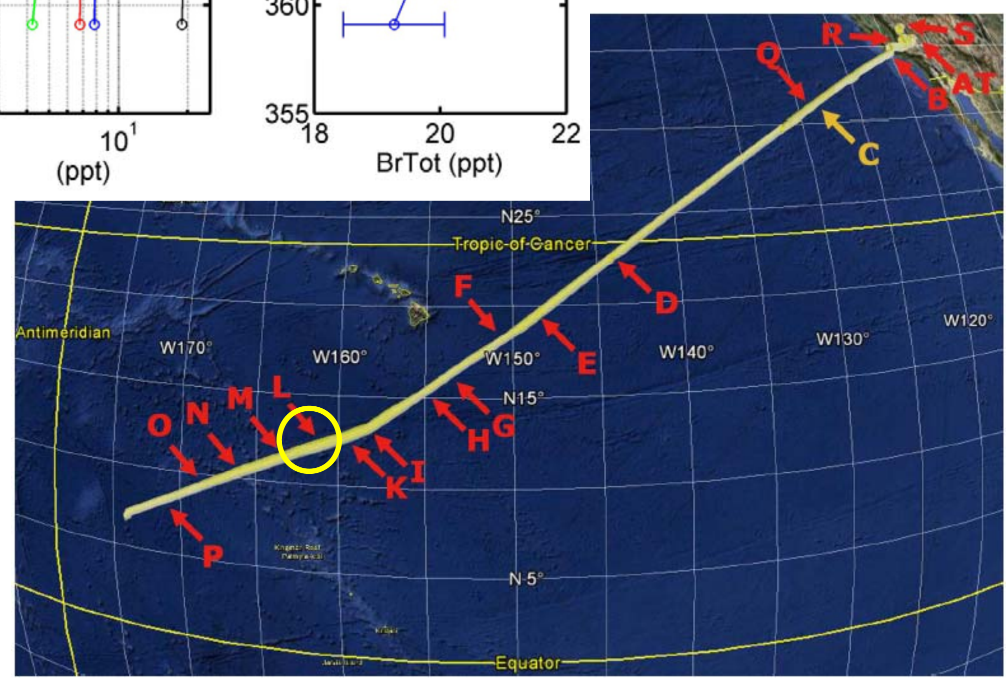


Average total Br: 22.0 ± 0.7ppt

12°N 150°W

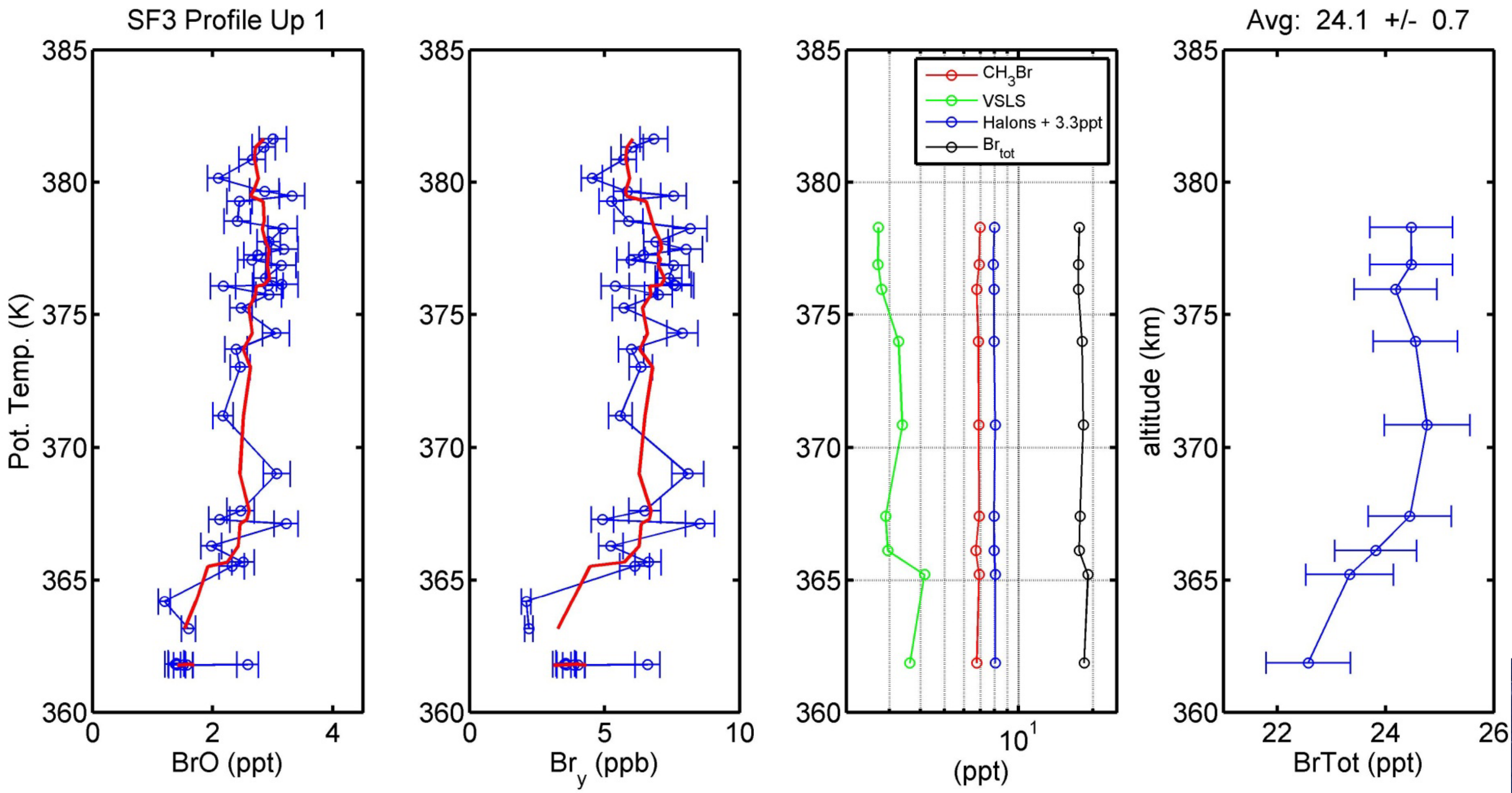
Science Flight 5, Second Climb





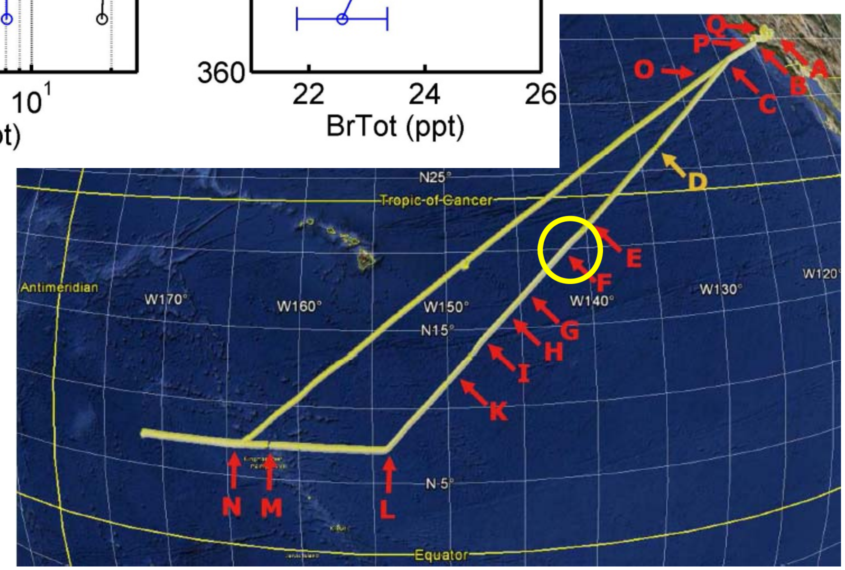
Average total Br: 19.4±0.4ppt

Science Flight 3, First Climb



Average total Br: 24.1±0.7 ppt

20°N 142°W

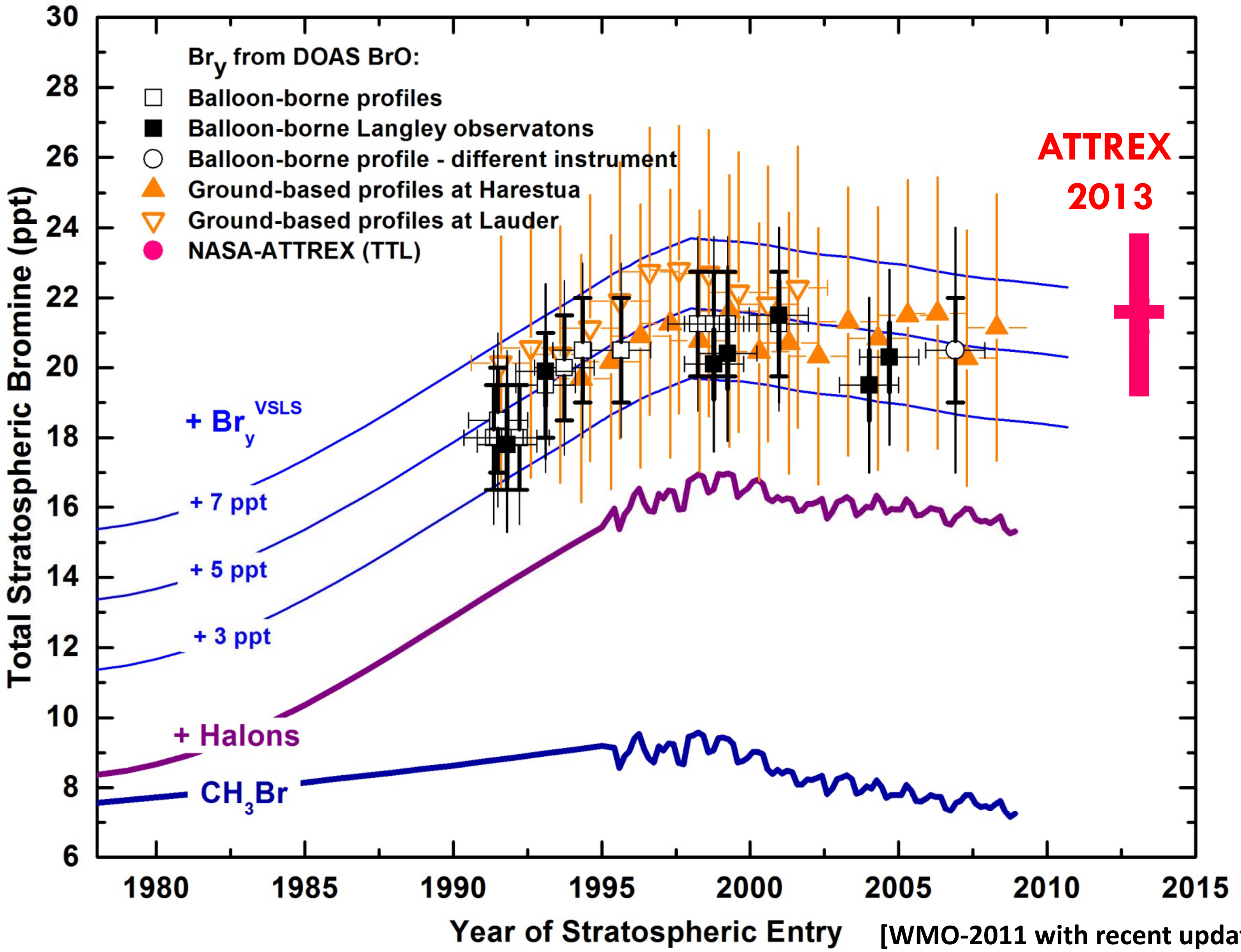


Total Bromine all Profiles in 2013

	Lat	Long	Br_{Tot} (ppt)	Br_{Org} (ppt)
SF1/1	24	-136	21.3 ± 0.3	19.2 ± 0.4
SF3/1	19	-142	24.1 ±0.7	18 ± 0.5
SF3/2	14	-148	22 ± 0.7	18.5 ± 0.7
SF5/1	17	-152	22.1 ± 1.1	18 ± 0.5
SF5/2	12	-162	20.8 ± 0.5	18.1 ± 0.6
SF5/3	8	-170	19.4 ± 0.4	18.4 ± 0.6
SF6/1	18	-111	22 ± 1.2	17.3 ± 0.3
SF6/2	15	-106	23.4 ± 0.9	18.3 ± 0.7
SF6/3	8	-93	21 ± 0.7	18.2 ± 0.8

Errors are standard deviation of values in profile
Uncertainty from individual observation ~1ppt

Bromine Budget

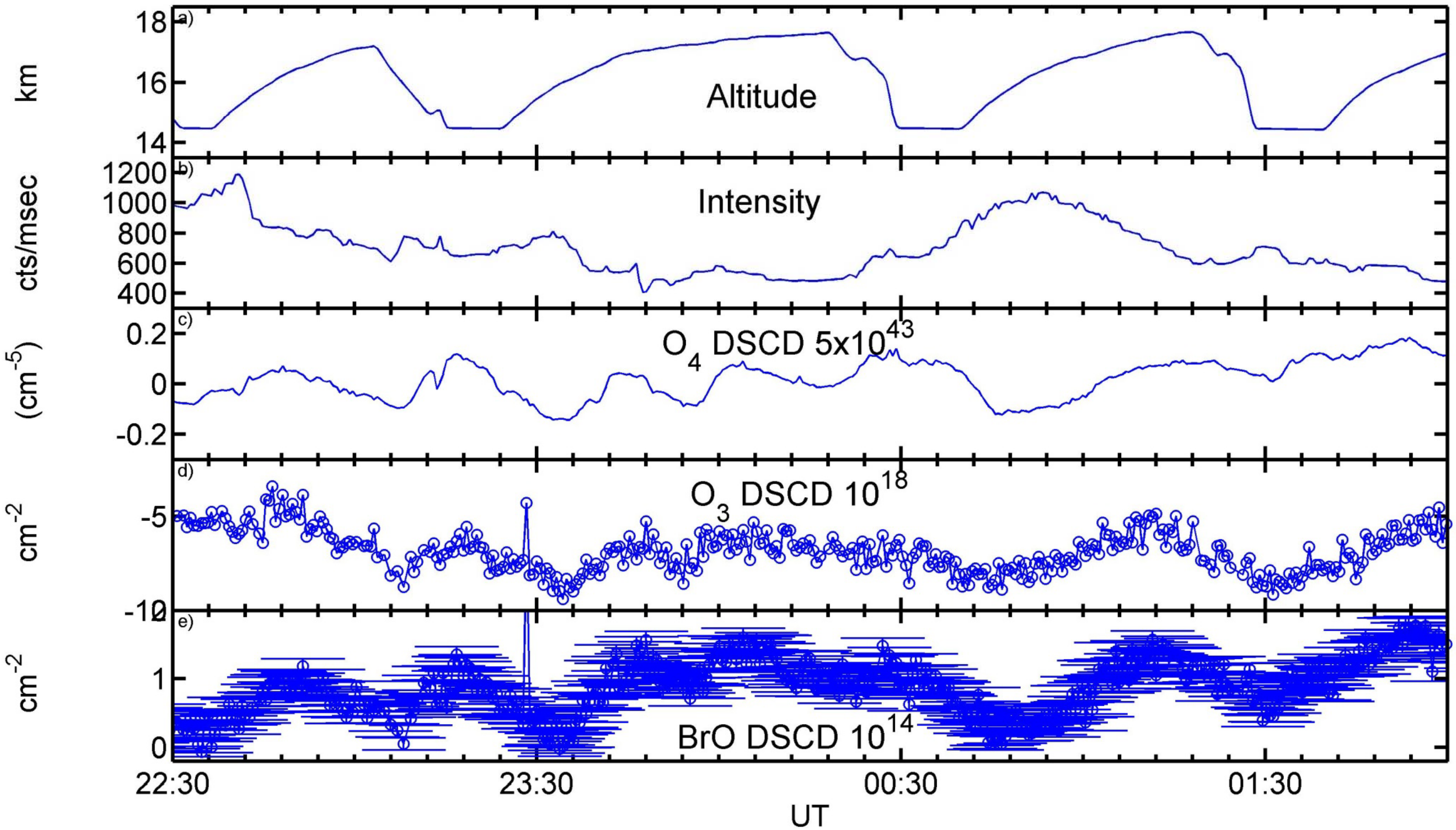


[WMO-2011 with recent updates]

Conclusions & Outlook

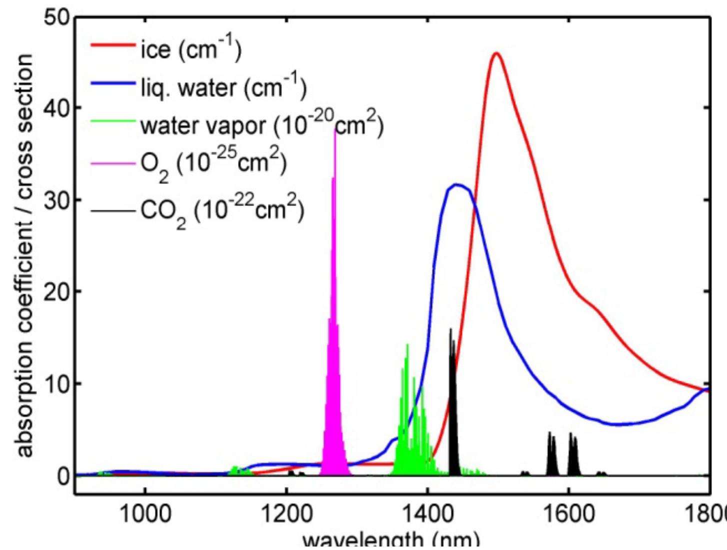
- DOAS instrument measured BrO, O_3, and NO_2 differential slant column densities.
- An ozone scaling technique has been applied to convert path-integrated BrO DSCD to mixing ratios using SLIMCAT output and McArtim RT calculations.
- BrO mixing ratios varied from up to 10ppt in the lower stratosphere to below 1ppt in the troposphere.
- Total bromine (DOAS + GWAS) budget varies between 19.5 and 24ppt, with an average of 21.8ppt
  - Variation stems from the reactive bromine
  - Cause if the variation is currently unclear
    - Still a problem with the DOAS/RT retrievals
    - Horizontal averaging?
    - Unrecognized sink/source of reacive bromine
- Outlook
  - Further improve profile retrievals → full inversions
  - Finalize total bromine calculation
- So what about Guam 2014?

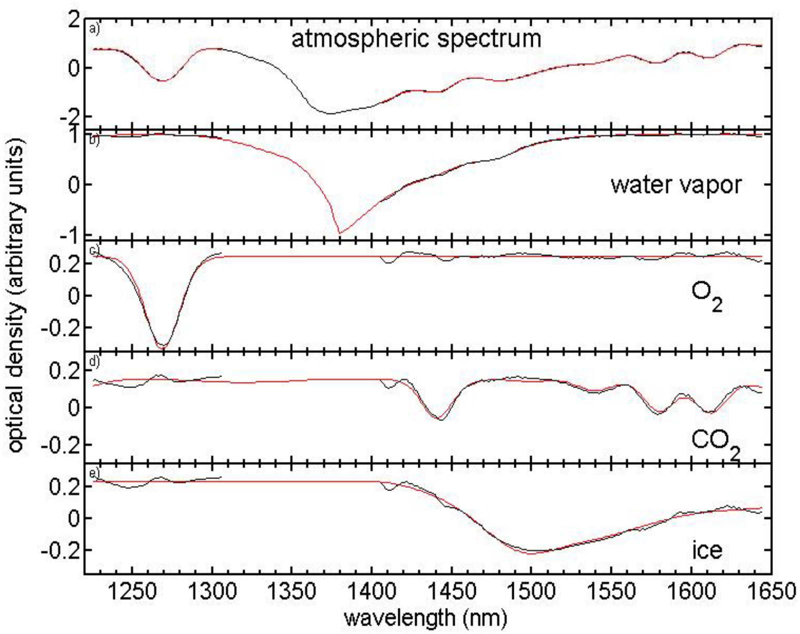
BrO SF3 Guam 2014

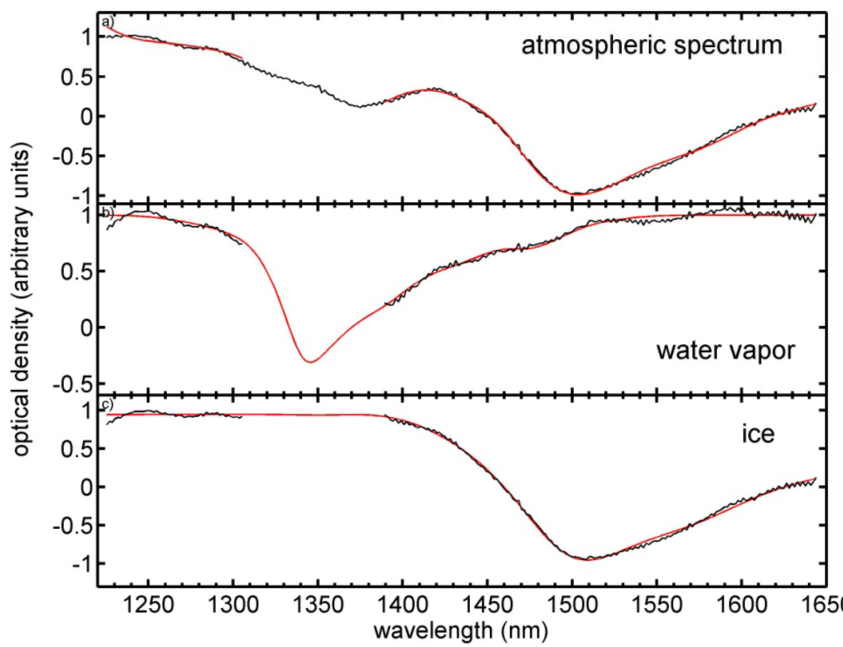


Cirrus Ice during ATTREX

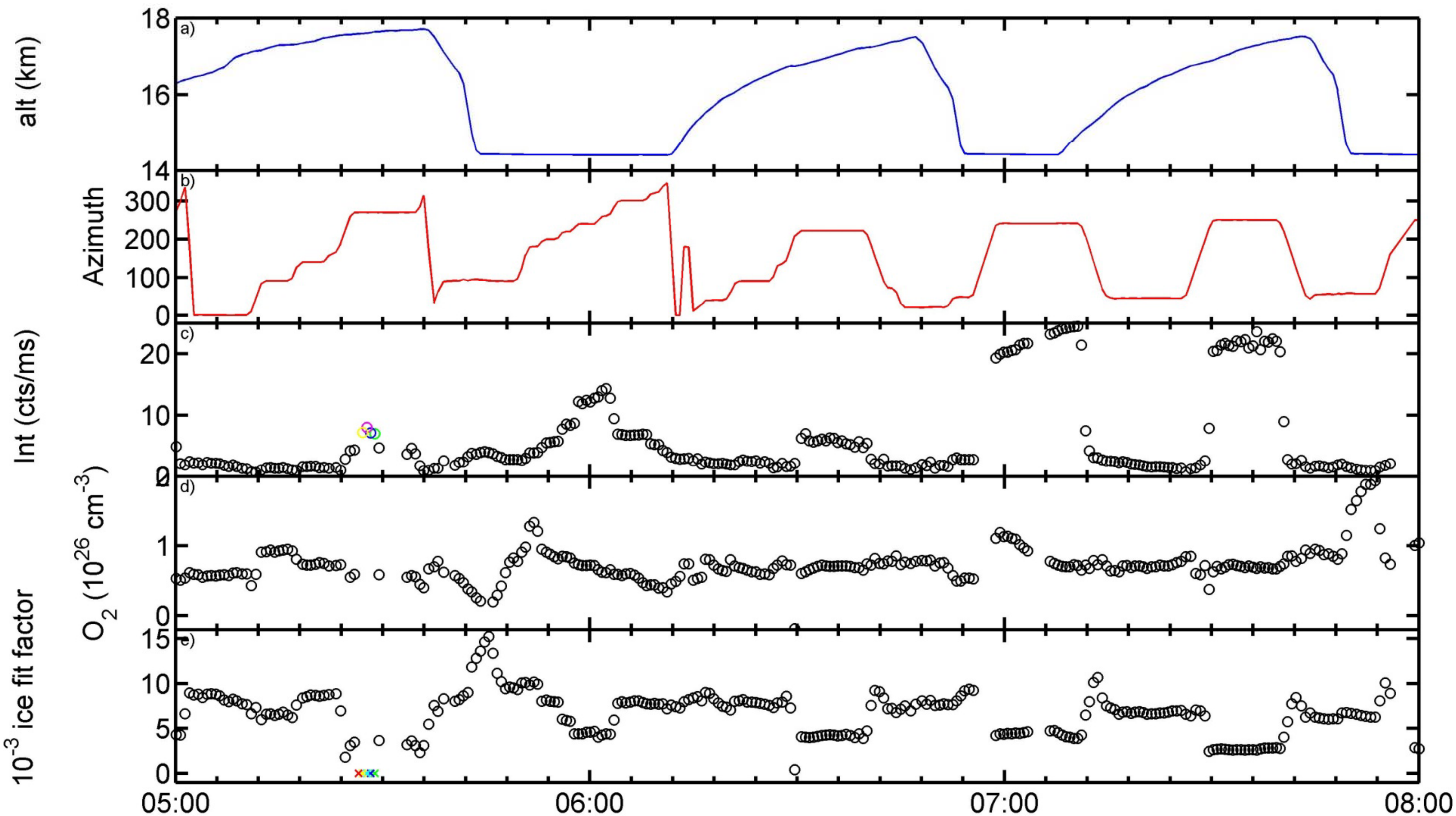
GH flew in clouds most of the times







Cirrus Ice SF2 Guam 2014



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