Measurement and simulation of CH_4, O_3, NO_2, BrO, and major brominated source gases during the NASA-ATTREX Global Hawk deployments in 2013: Implications for the photochemistry and total amount of bromine in the TTL and stratosphere

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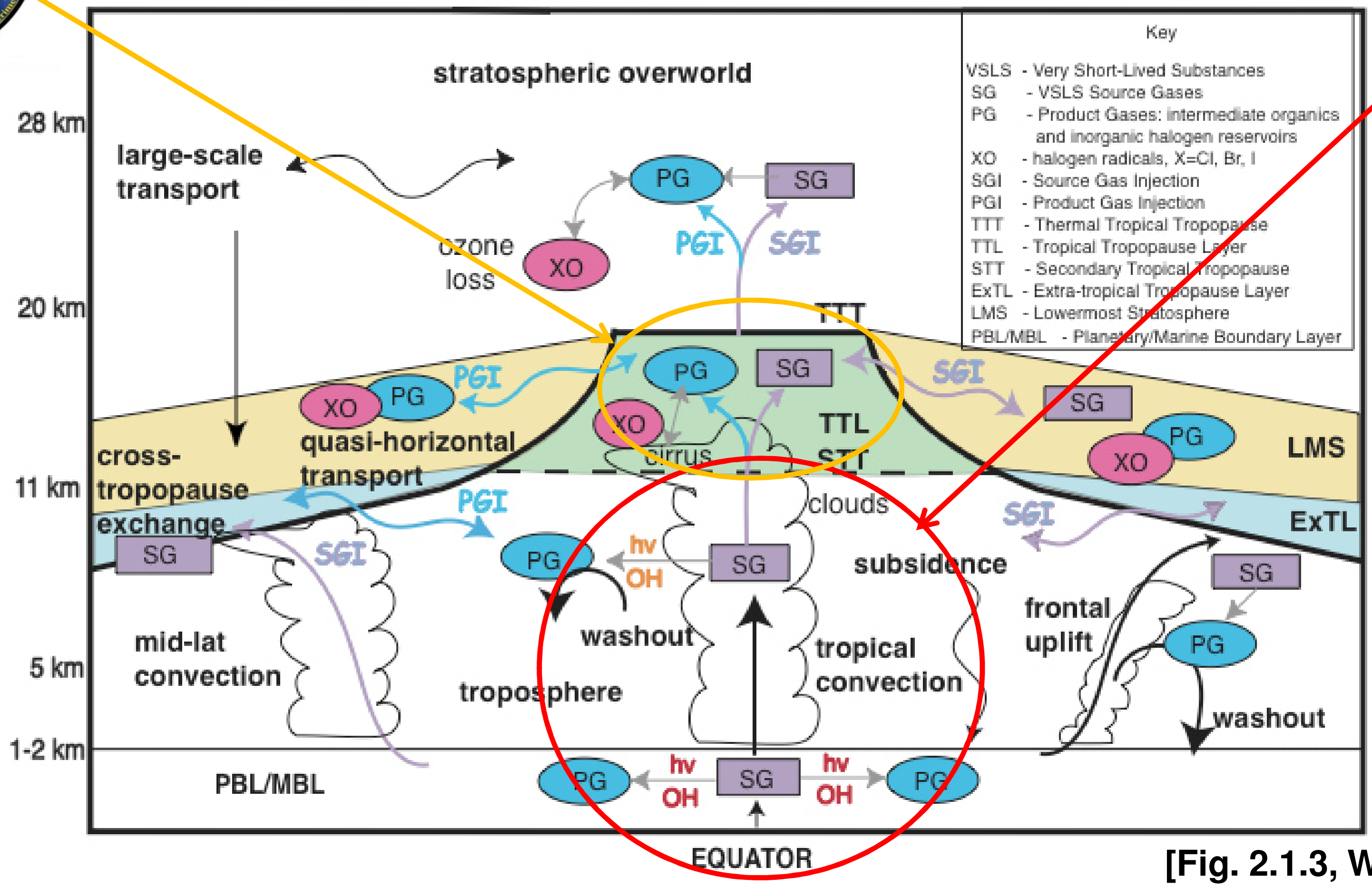
The role of VSLS in stratospheric ozone and climate

Chemical and Dynamical Processes Affecting VSLS

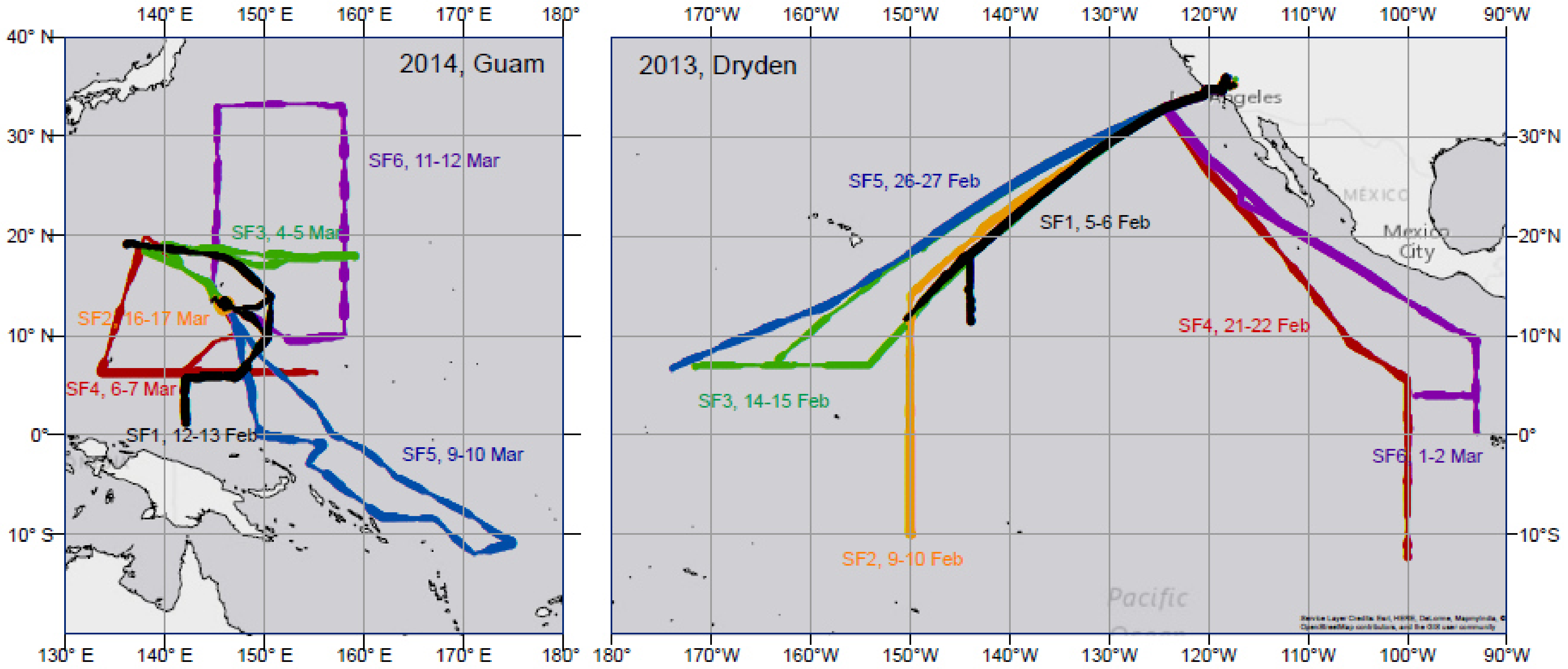


[Fig. 2.1.3, WMO-2007]

➢ Brominated VSLS are known to contribute 1 – 8 ppt to stratospheric Br_y (WMO-2011), but our (IUP-HD) best estimate is 4.1 ± 2.5 ppt (Dorf et al. 2006, and update in WMO-2011).

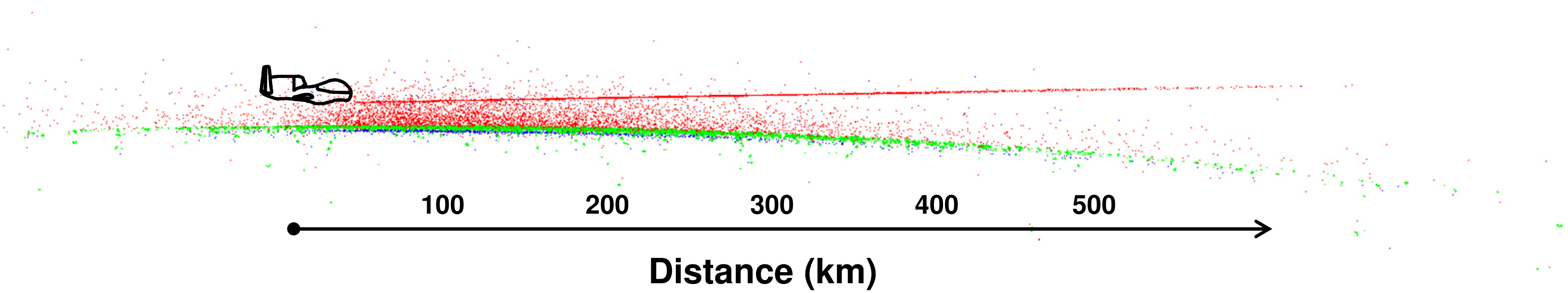
WMO-2007 notation:
VSLS: very short lived species (life times < 6 months)
SG: source gases (e.g. CFC, HCFC, halons, CH3Br, CH3I, CHBr3, CBr2Cl2, etc.)
PG: products gases (e.g. HCl, IO, OIO, BrO, HBr)

Global Hawk deployments during NASA-ATTREX 2013, and 2014



Observation geometry (at 18 km) and radiative transfer at 350 nm

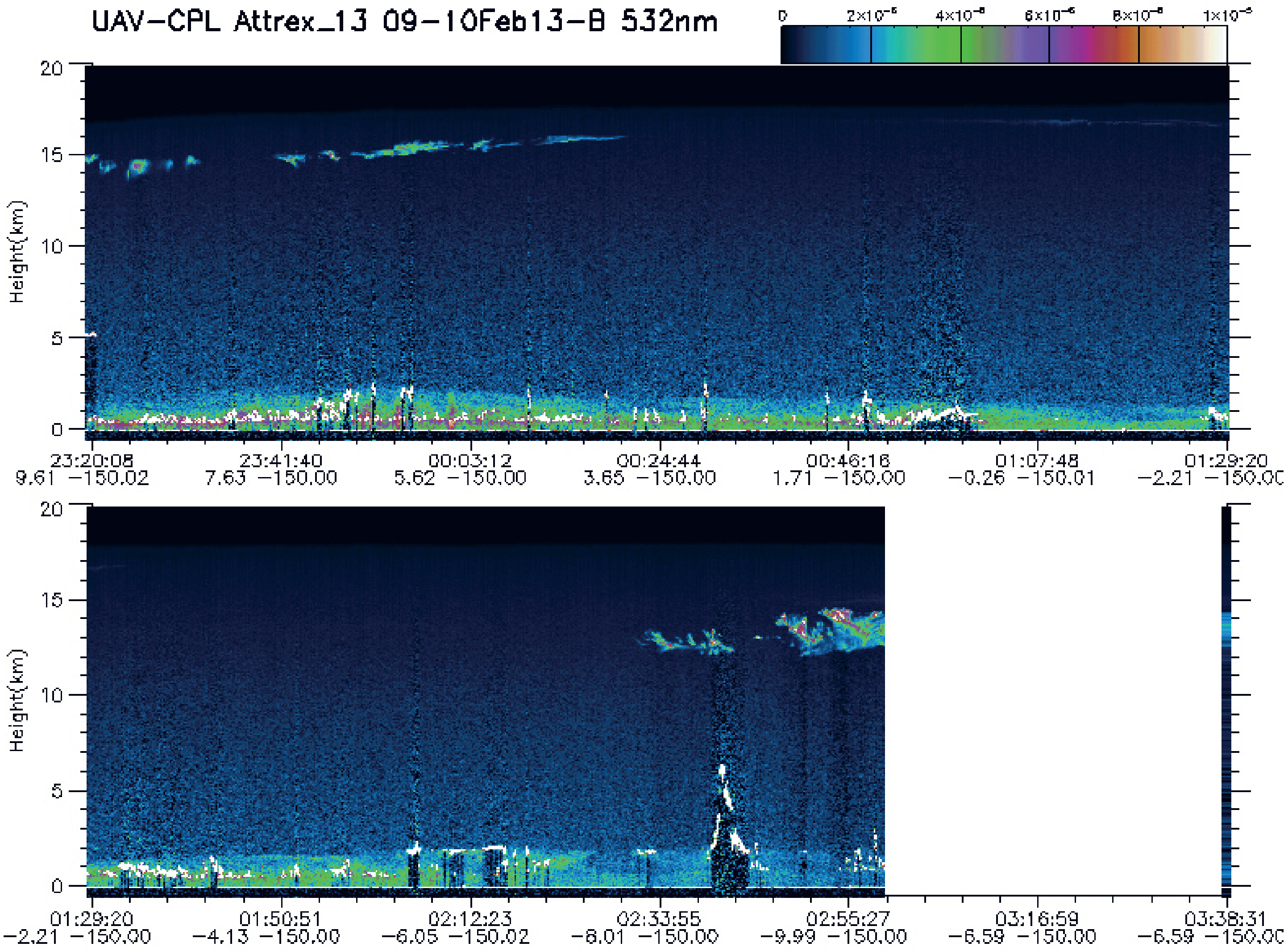
altitude 18km, 350nm, elevation +1 °, cloud layer 30 OD @ 2-3km



red: Rayleigh scattering
green: Mie Scattering
blue: Ground reflection
line of sight: red line (single scattering)

(Tim Deutschmann, PhD thesis, 2015)

Cloud cover during GH SF2-2013 (Eastern Pacific)



Steps to infer concentrations of the targeted gases

1. **DOAS (Differential Optical Absorption Spectroscopy) spectral retrieval to get slant column amounts (SCDs) of the targeted gases (e.g., O_4, O_3, NO_2, BrO, ….**

2. **Retrieval of concentrations**

2.1 Full version (c.f. optimal estimation)

(Non)-linear mathematical inversion of measured slant column amounts with the following major ingredients

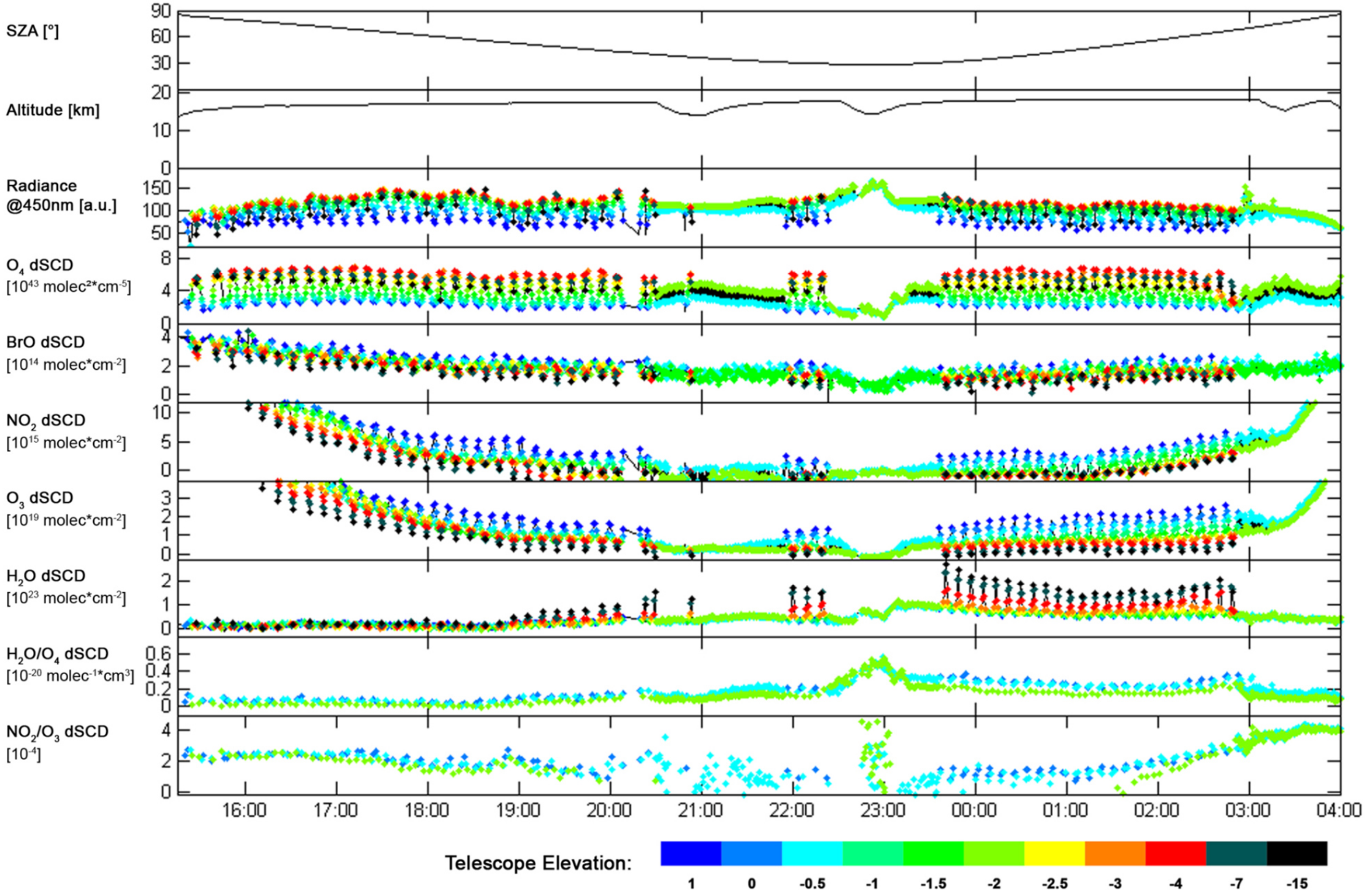
- **A priori fields of T, p, O_3, … from SLIMCAT (ERA interim meteorology)**
- **Aerosol/cloud OD from CPL Lidar and detailed scattering scheme for solid particles with constraints from particle observations on GH or HALO (in future)**
- **RT constraint from measured O_4**
- **Validation with measured in-situ O_3**

2.2 O_3 (and O_4) scaling technique

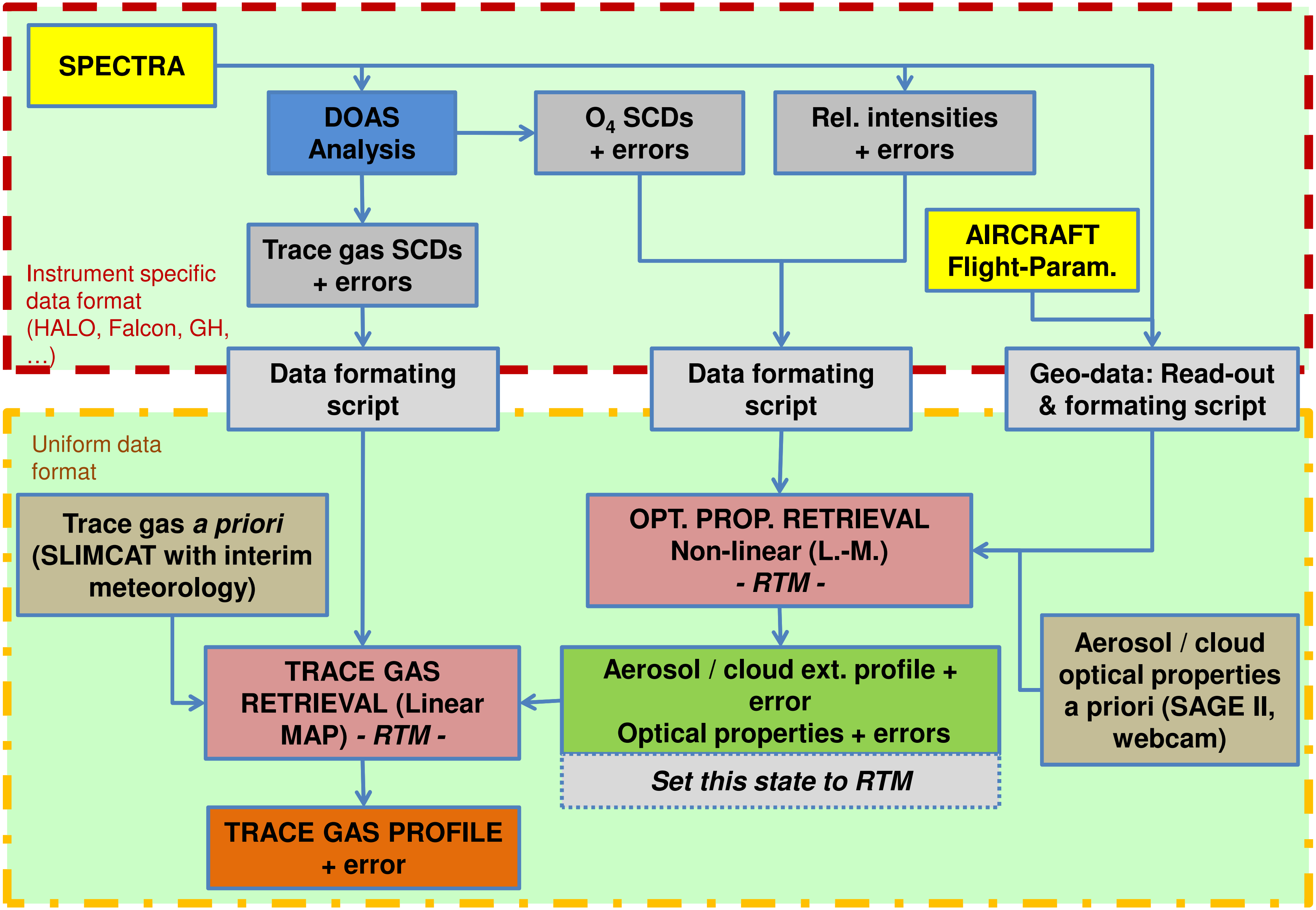
Relevant photon path length for the targeted gases ….. is inferred from in-situ measured O_3 (c.f., by NOAA on the GH) and/or calculated O_4 and by comparison with DOAS measured O_3 (O_4) for similar wavelength intervals

Science Flight 2 in 2013 (SF2-2013)

GH mini-DOAS: results DOAS-retrieval SF2 02/09/2013 - 02/10/2013



2.1 Optimal estimation (OE): Retrieval (MaRS) Flow Chart



SPECTRA

DOAS Analysis

O_4 SCDs + errors

Rel. intensities + errors

Trace gas SCDs + errors

AIRCRAFT Flight-Param.

Instrument specific data format (HALO, Falcon, GH, …)

Data formating script

Data formating script

Geo-data: Read-out & formating script

Uniform data format

Trace gas *a priori* (SLIMCAT with interim meteorology)

OPT. PROP. RETRIEVAL Non-linear (L.-M.) *- RTM -*

TRACE GAS RETRIEVAL (Linear MAP) *- RTM -*

Aerosol / cloud ext. profile + error Optical properties + errors

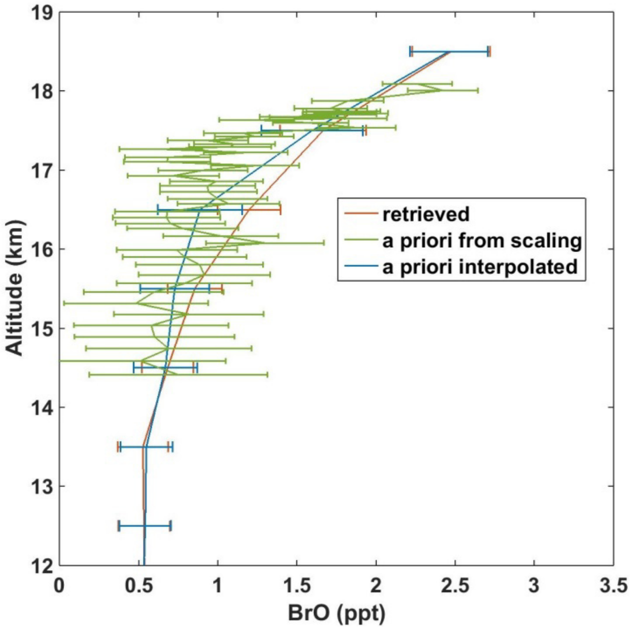
Set this state to RTM

Aerosol / cloud optical properties a priori (SAGE II, webcam)

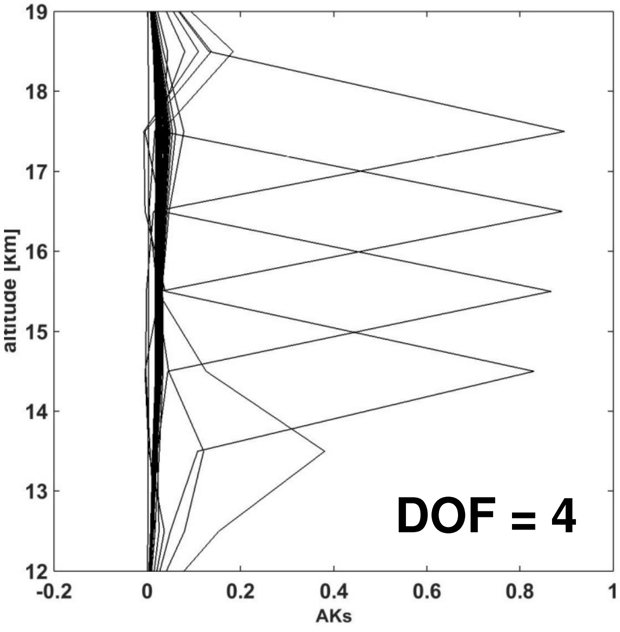
TRACE GAS PROFILE + error

2.1 Profile inversion by optimal estimation

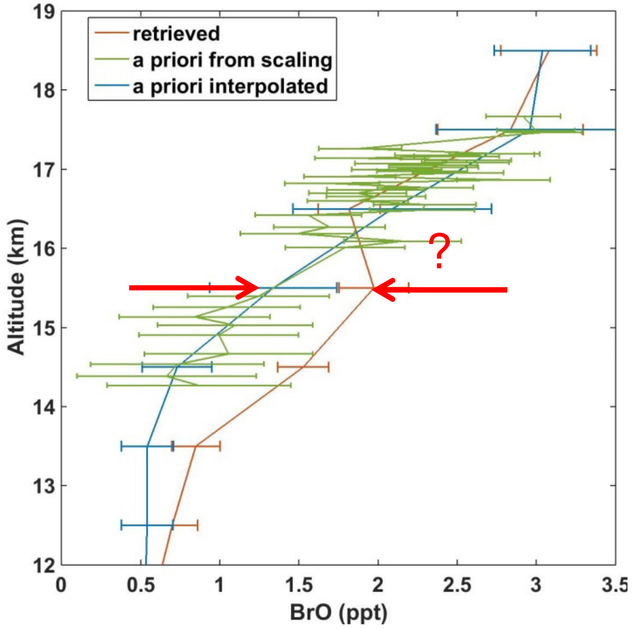
SF1 ascent 2



Averaging kernels



SF3 ascent 2

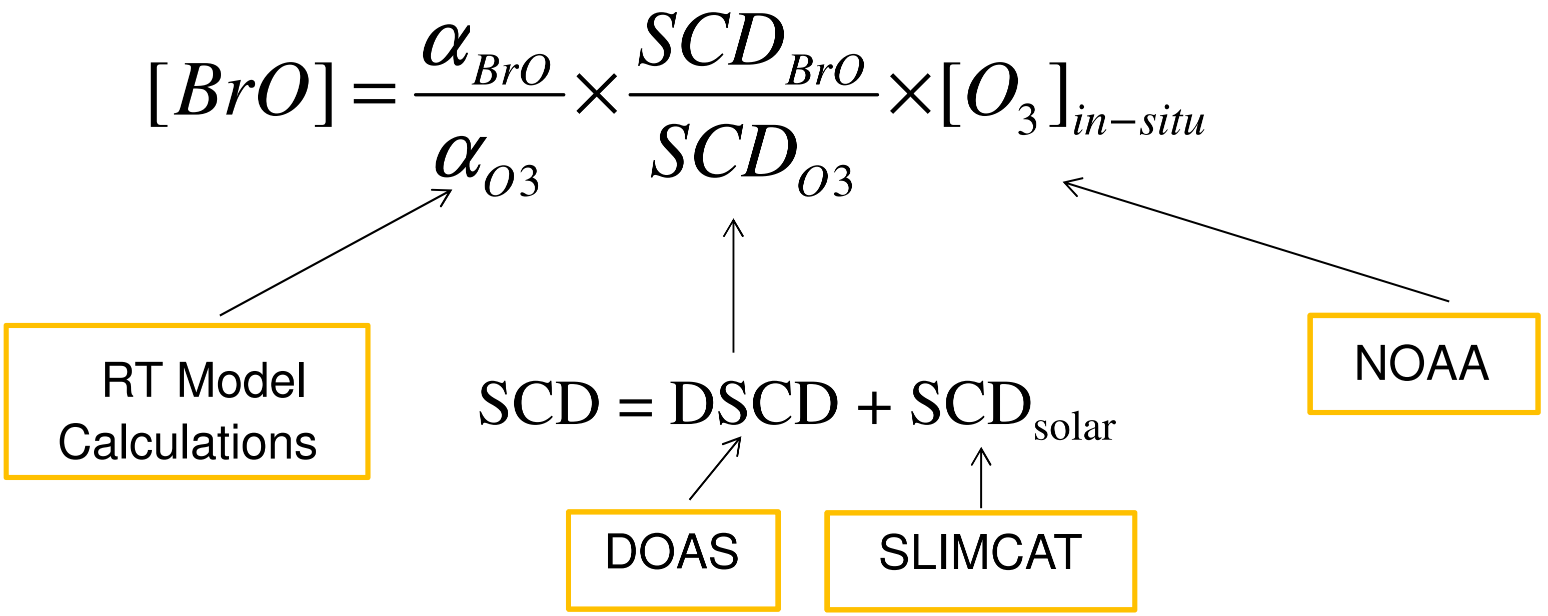


Problems:

- OE depends on some assumptions, i.e. overhead and below profile,…….
- Quality of RT including its assumptions (e.g. aerosol profile, clouds, ..)
- OE only provides profiles at little temporal (for dives) and spatial resolution (with DOF~4)
- Accuracy is rather limited (see below), due mostly to Mie scattering contribution by aerosols and clouds not properly accounted for.
- …

2.2. Concentration retrieval using the scaling method

- **Infer the concentration of the targeted gas X**
  - **Use the differential absorption measured adjacent to an O_3 absorption band**
  - **Scale concentration of X to the in-situ measured [O3] (or [O4], ..) concentration, via**



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

$$\mathrm{SCD} = \mathrm{DSCD} + \mathrm{SCD}_{\mathrm{solar}}$$

- ➢ **Major advantage of the scaling technique as compared to OE is to largely remove uncertainties in assumptions regarding the RT, via the use of α-factor ratios!**

Determination of α factors

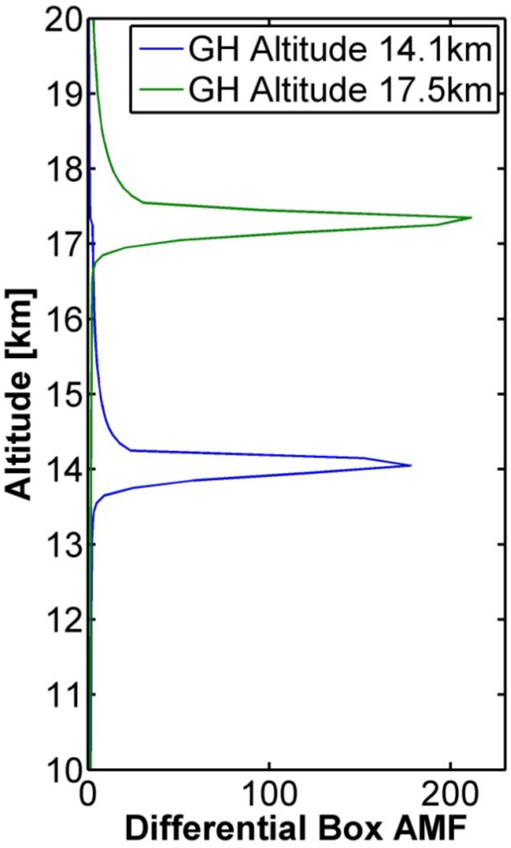
- α-factors are calculated from

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

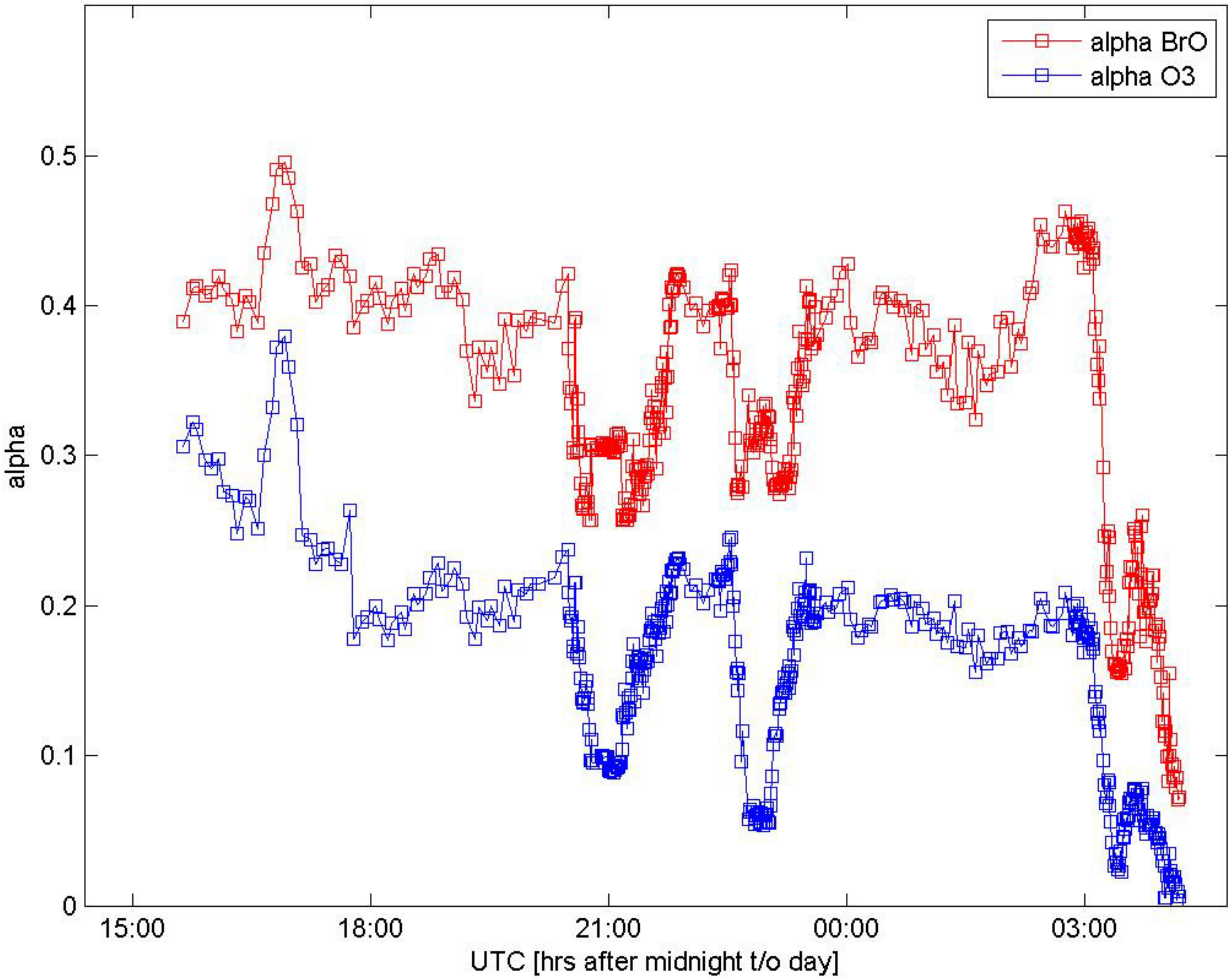
where $BAMF_h$ (Box Airmass Factor) for the layer dh are calculated in 1D (or 3D) using SLIMCAT curtains in the RT model McArtim

- **α-factors express how much of the total measured absorption comes from individual layer *dh.***

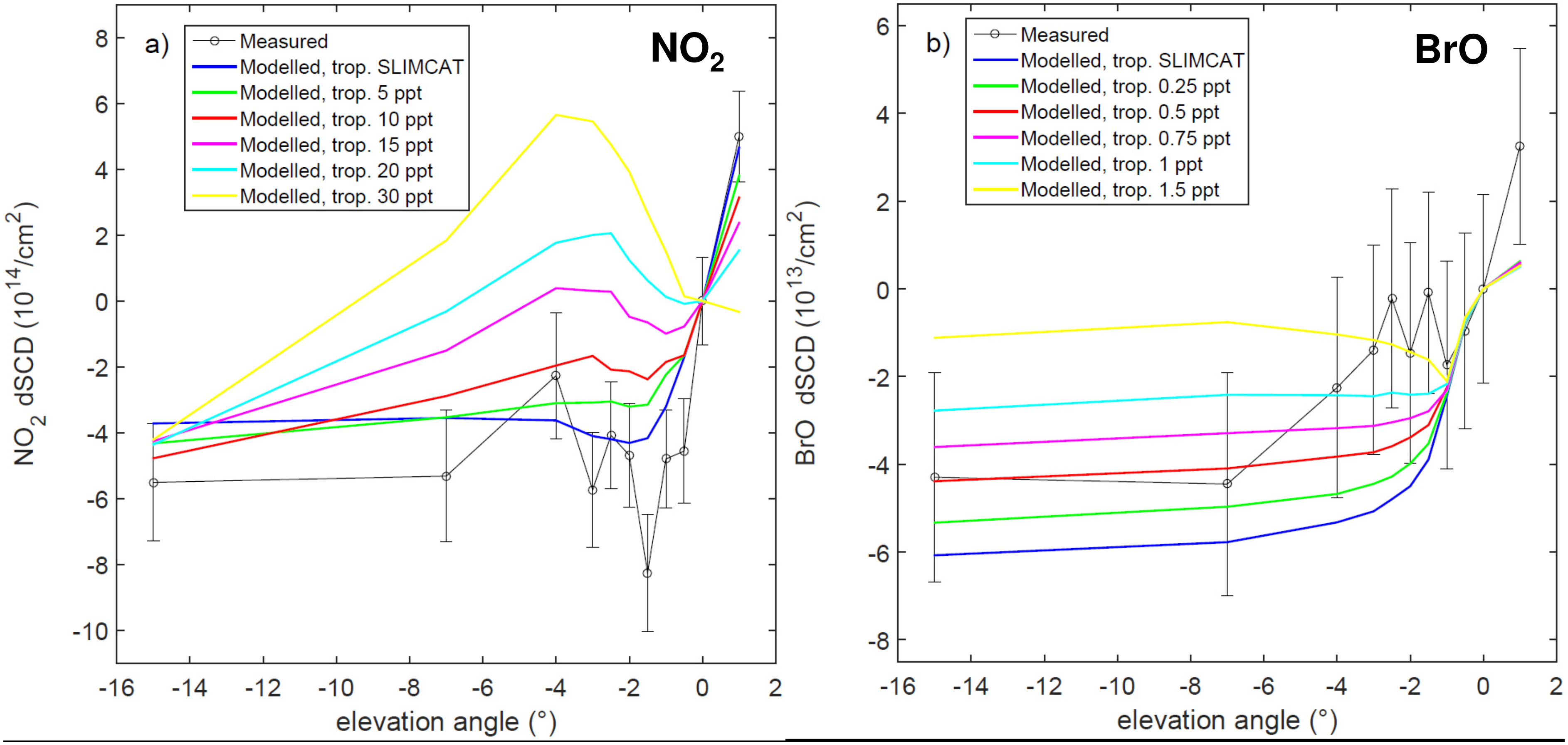
- **RT simulations indicate that, for gases with similar shaped profiles (e.g., O_3, NO_2, BrO. ..), ratios of α-factors (α_{BrO}/α_{O3}) for adjacent wavelengths are only little sensitive on assumptions regarding the RT (aerosols, clouds, …)!**



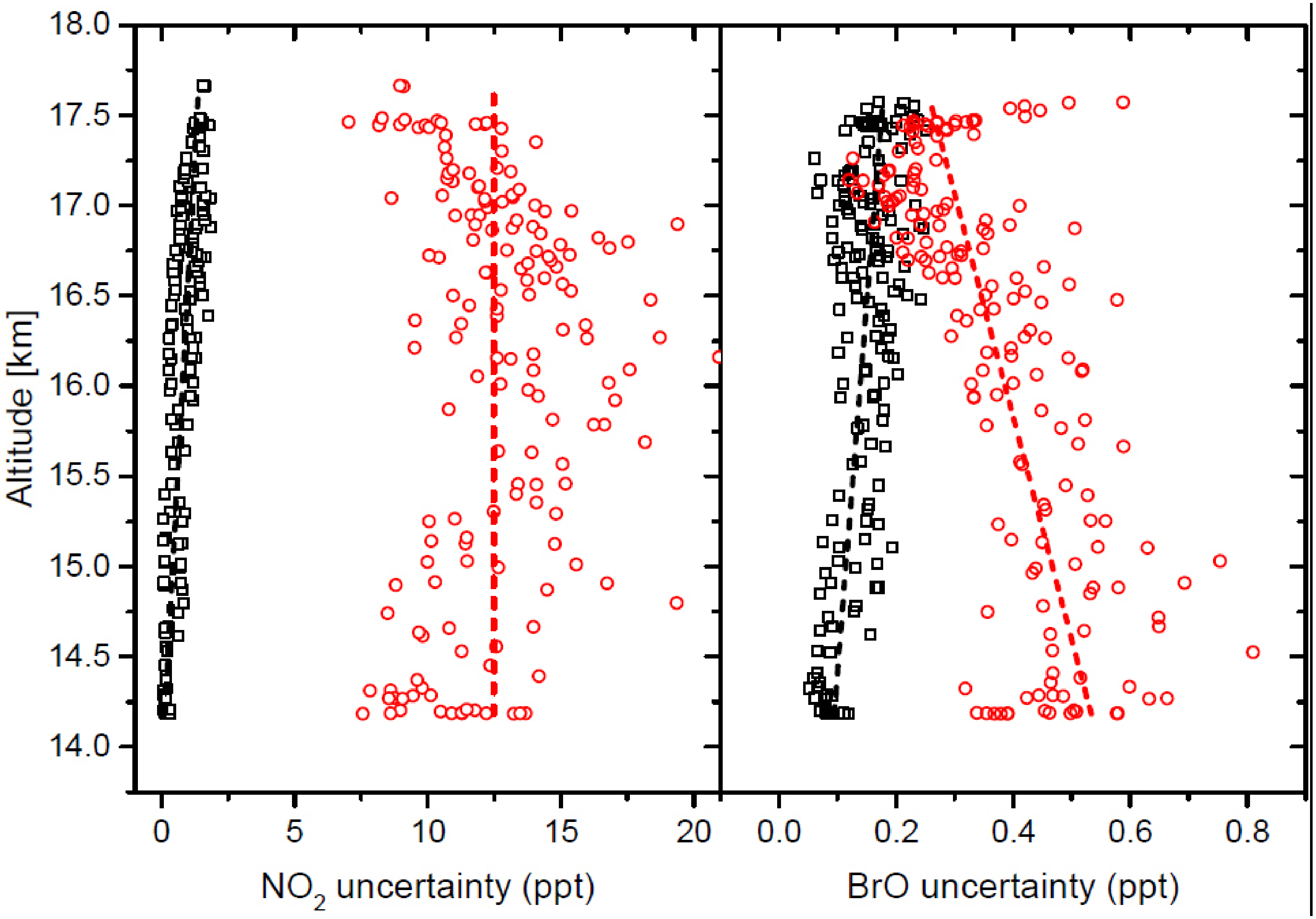
α- factors for O_3 and BrO (SF2-2013)



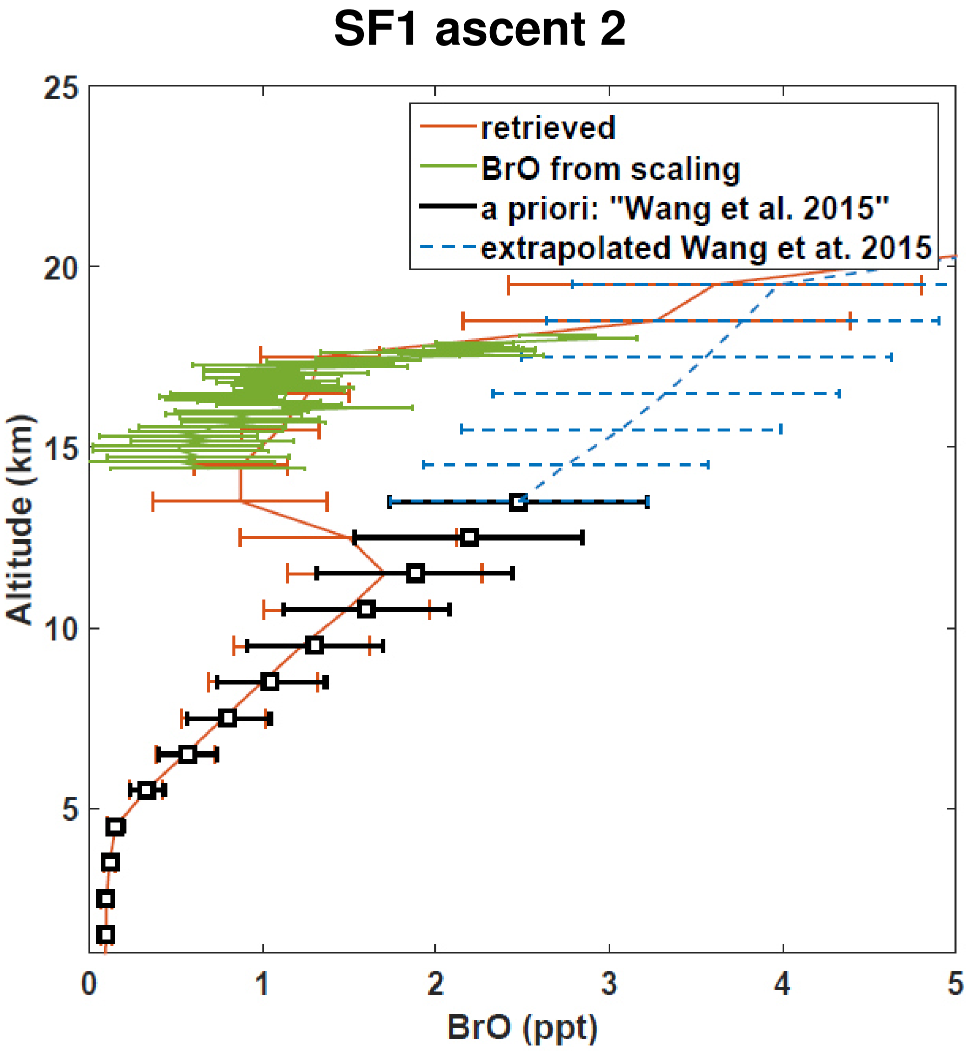
Contribution of tropospheric NO_2 and BrO to the measured limb absorption



Combined uncertainties of overhead (black) and tropospheric (red) contributions



Consistency of our BrO measurements with Wang et al., 2015



- Constraining the OE profile retrieval to the Wang et al., (2015) BrO profile (i.e. as a priori) indicates some inconsistency with our data!

Approach/steps to inter-compare measured and predicted (CTM SLIMCAT/TOMCAT) traces gases for assessing total bromine and its photochemistry in the TTL/exLS

1. **Test of dynamics by comparison of measured (UCATS, and HUPCRS) and modelled CH_4**

2. **Test of photochemistry by comparisons of measured and modelled**
   - ✓ **O_3, and NO_2**
   - ✓ **Amount of brominated source gases, in particular the VSLS i.e., Br_y^{org}**
   - ✓ **BrO, and inferred Br_y^{inorg}**
   - ✓ **Test of photochemical constants (e.g. J/k for $BrONO_2$ and k_{Br+O3})**

   - ➢ **Br_y^{inorg} is inferred from measured BrO, and the predicted BrO/Br_y^{inorg} partioning**

3. **Consequences for ozone photochemistry and RT heating**

SLIMCAT/TOMCAT simulations

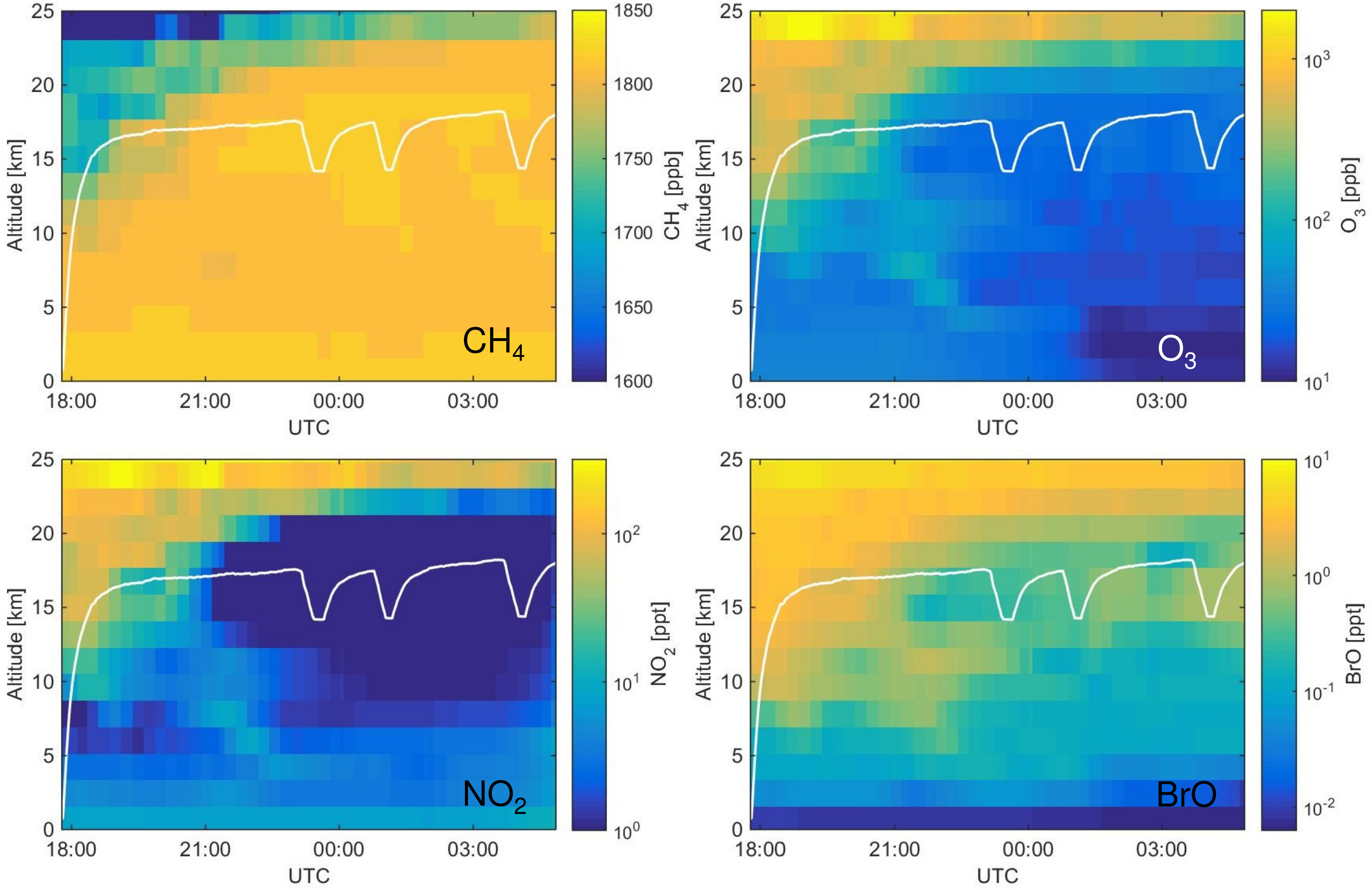
1. Dynamics: ECMWF with archived ERA-Interim convective mass fluxes
2. Kinetic and photochemical data: JPL-2011 with recent updates
3. Trace gases:
   - CH_4: AGAGE https://agage.mit.edu/ and NOAA
   - Surface concentration of brominated source gases (20.55 ppt)
     - CH_3Br: 6.9 ppt
     - Halons: 7.99 ppt
     - $CHBr_3$: 1.4 ppt
     - CH_2Br_2: 1.05 ppt
     - ∑ $CHClBr_2$, $CHCl_2Br$, CH_2ClBr, .. : ~1 ppt (Sala et al., 2014)
     - No other (c.f., inorganic) sources of bromine are assumed (e.g., Wang et al., 2015)
4. Run #583: Standard run with spin-up since 1979, and 1.2 x 1.2 degrees resolution from 1/1/2013 on
5. Runs #584&585; High resolution sensitivity runs starting from 1/1/2013

➢ with J/k for $BrONO_2$ increased by 1.75 (#584) (Kreycy et al. 2013)

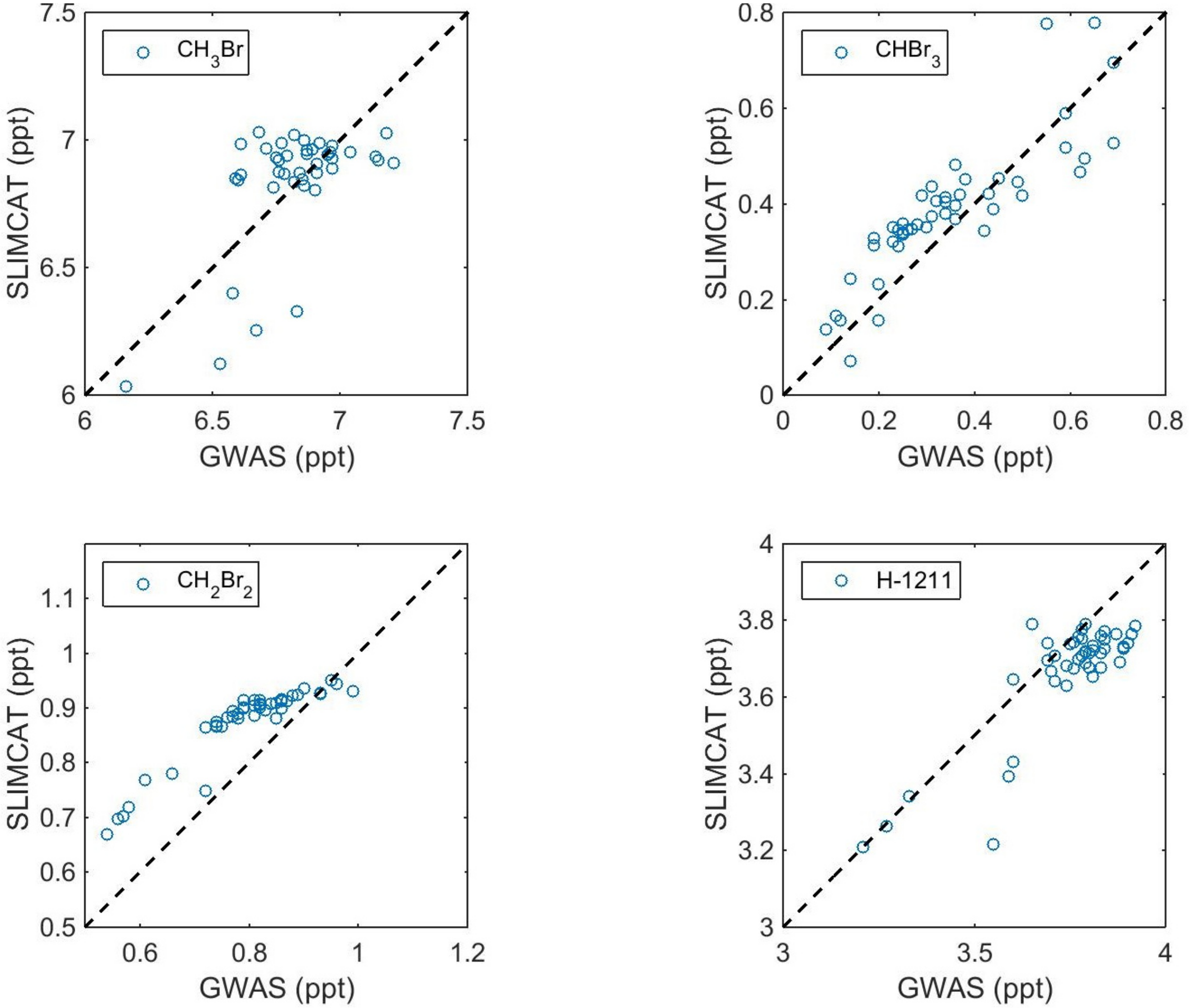
or

➢ Br + O_3 increased to the upper limit of JPL uncertainties (#585)

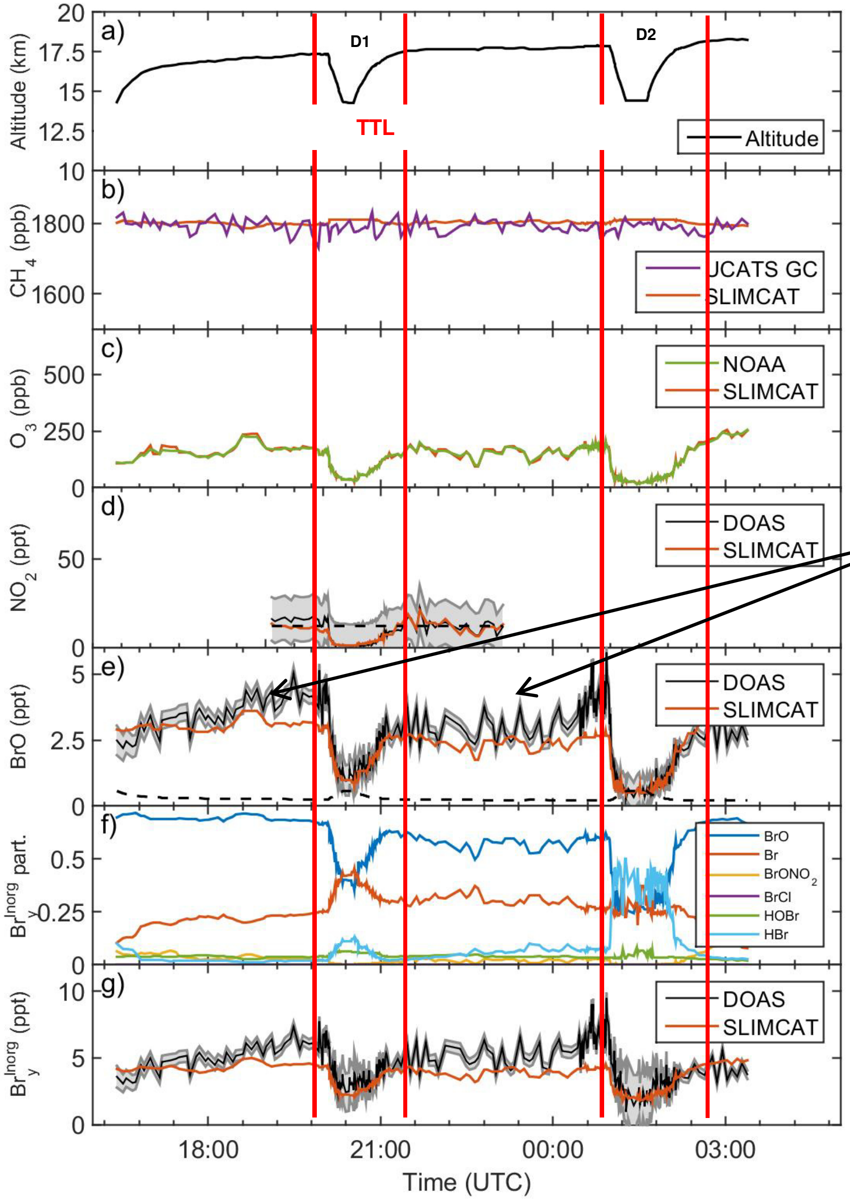
SLIMCAT simulation of CH_4, O_3, NO_2 and BrO curtains (SF3 on Feb. 14, 2013)



Comparison of measured and modelled brominated source gases for SLIMCAT control run #583

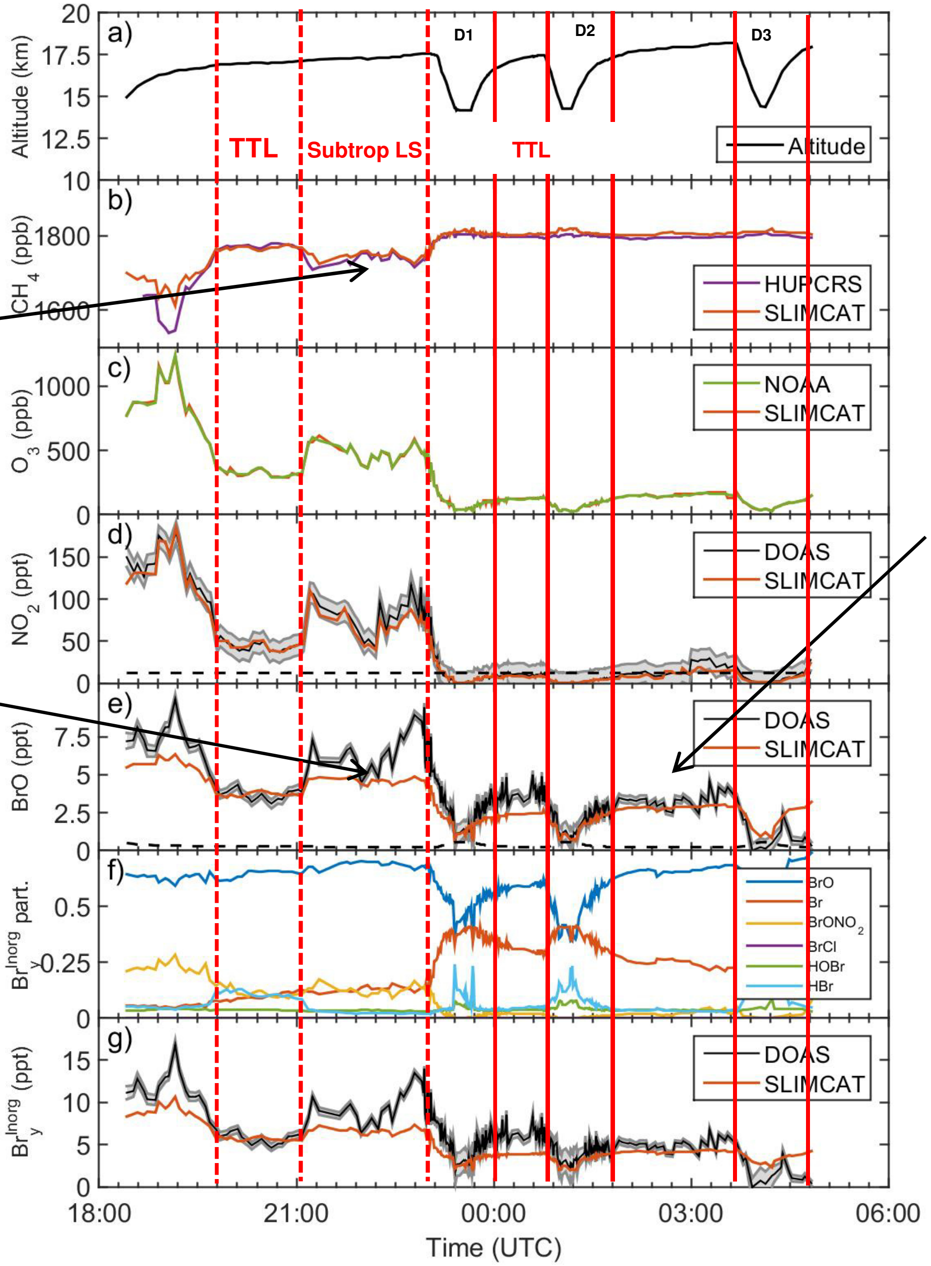


Measurement vs control run #583 (SF1 on Feb. 6/7, 2013)



Small underprediction (< 1 ppt) of measured BrO within the TTL

Measurement vs control run #583 (SF3 on Feb. 14/15, 2013)

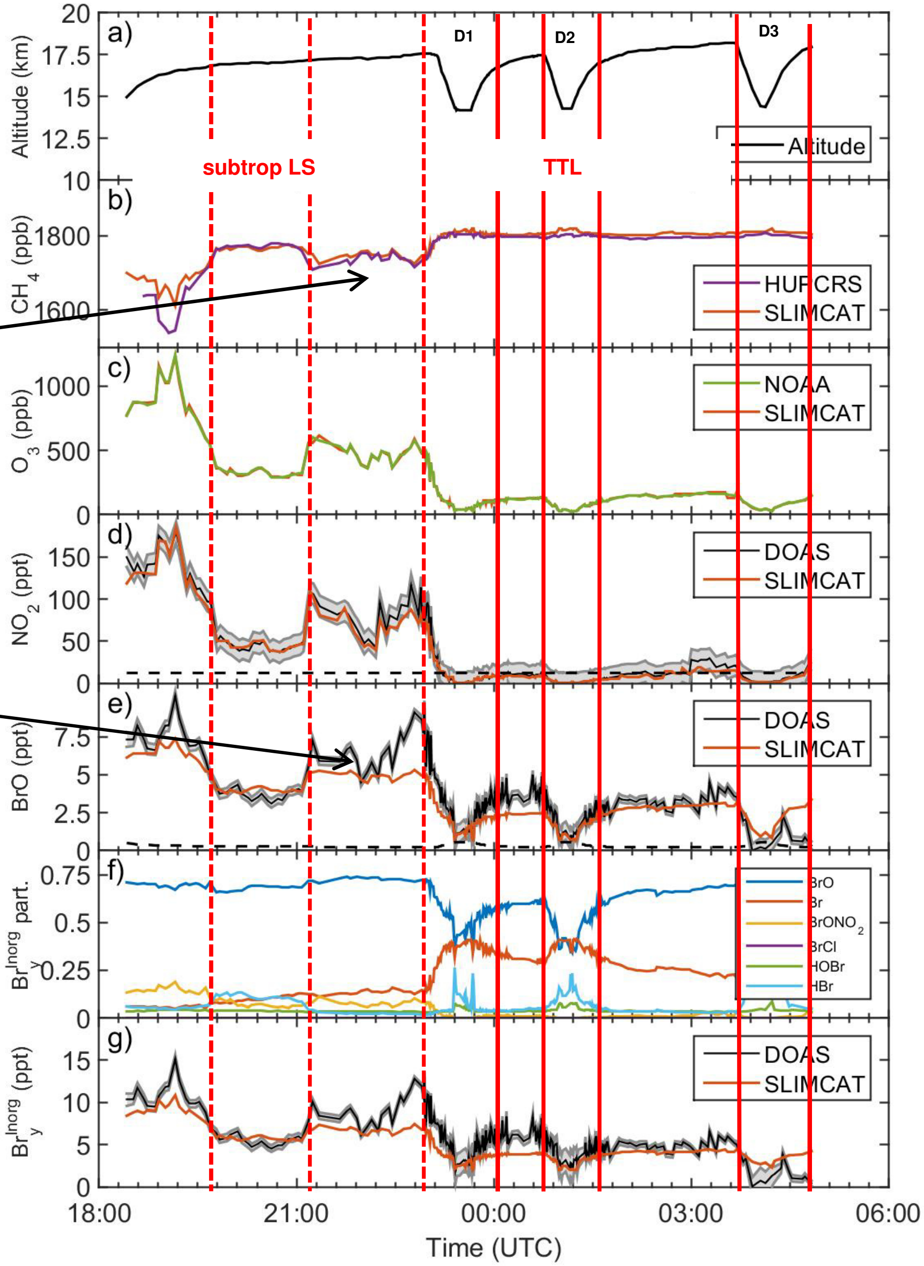


Mixing of TTL air into the subtropics

Small under-prediction (< 0.5 ppt) of measured BrO within the TTL

Significant underprediction (< 2.5 ppt) of measured BrO within the subtropical LS

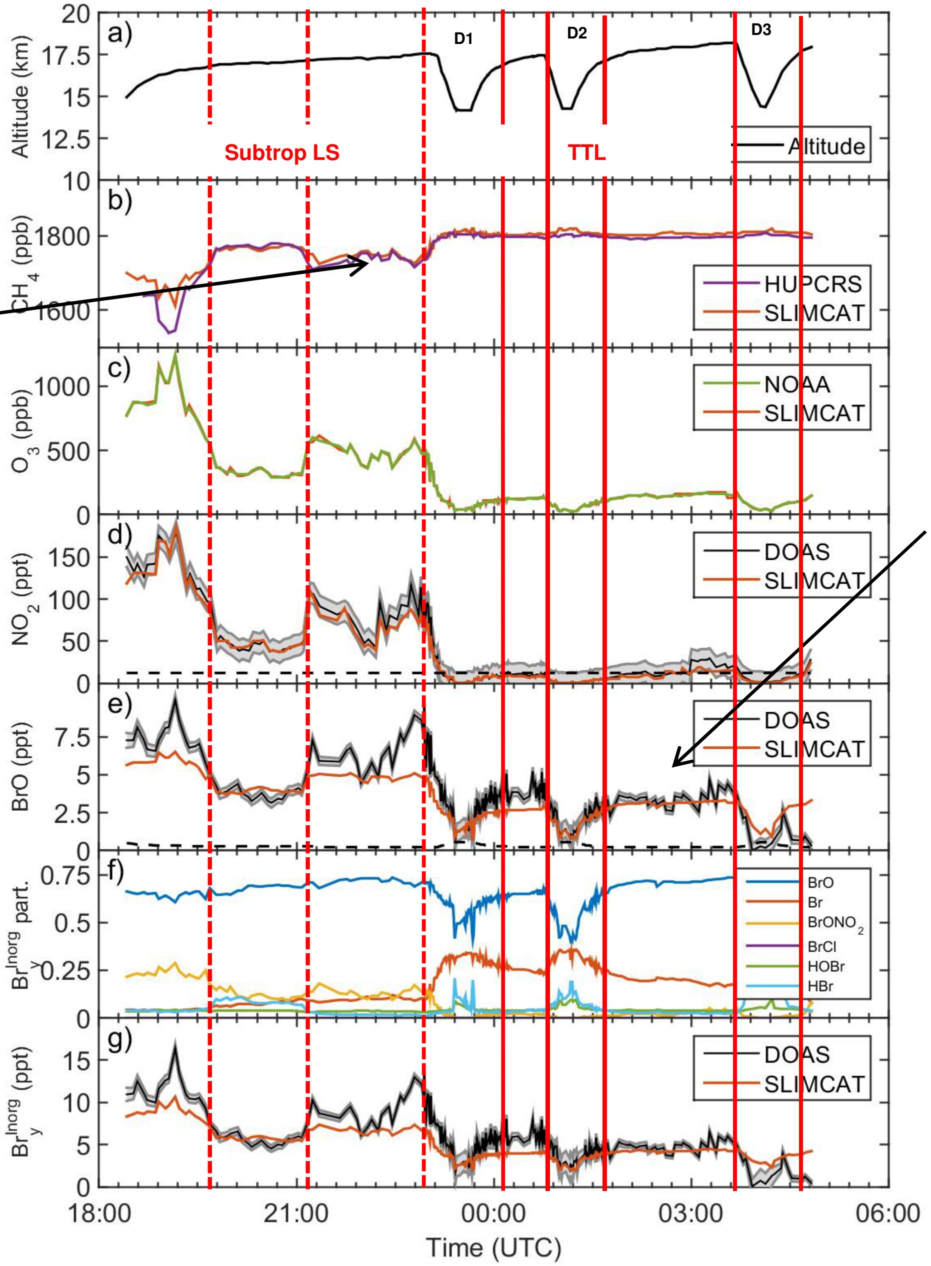
Measurement vs run with J/k$_{BrONO2}$ increased (SF3 on Feb. 14/15, 2013)



Mixing of TTL air into the subtropics

Reduced underprediction (< 2.0 ppt) of measured BrO within the subtropical LS

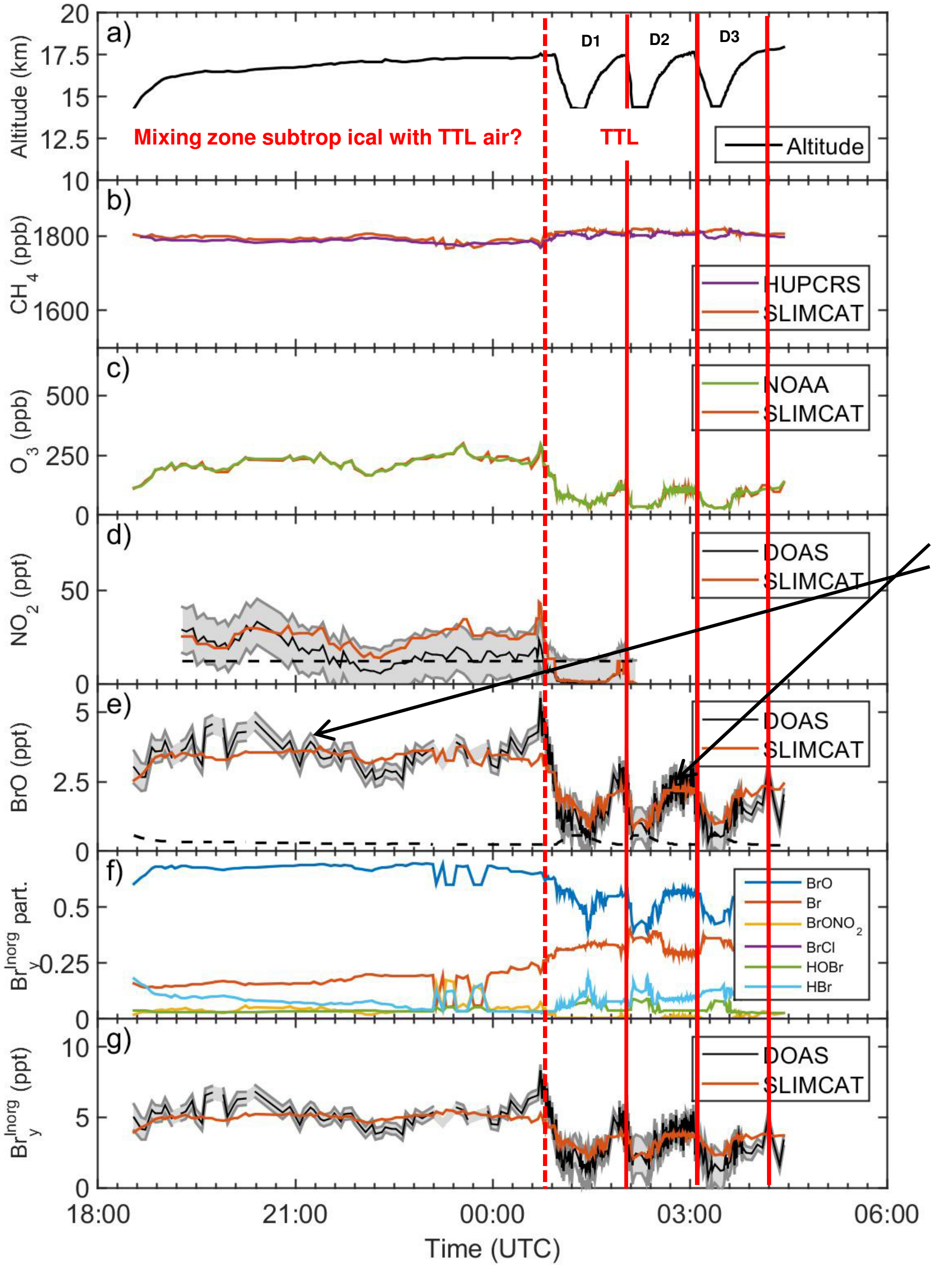
Measurement vs run with k_{Br+O3} increased (SF3 on Feb. 14/15, 2013)



Mixing of TTL air
into the subtropics

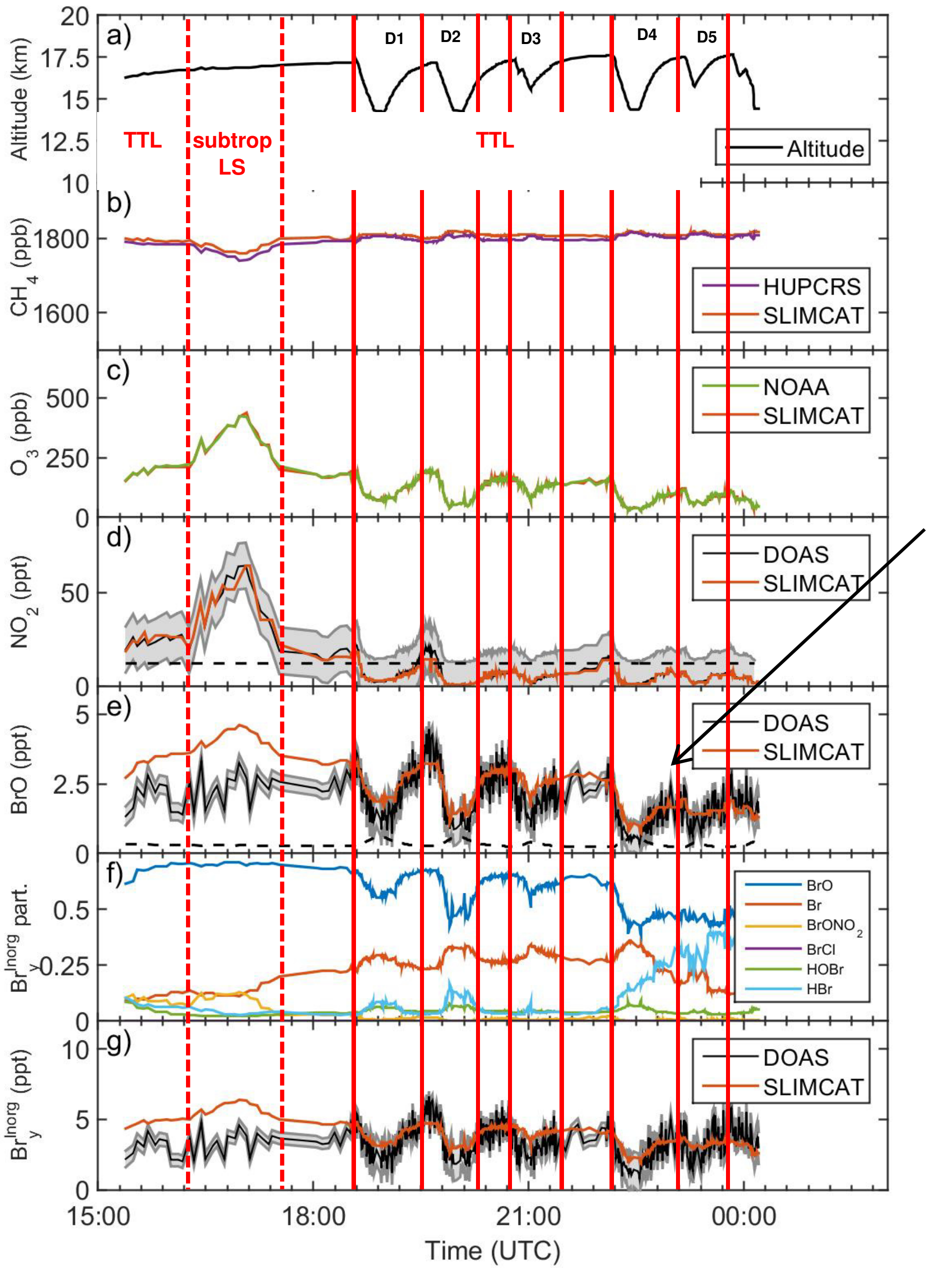
Reduced under-prediction
(< 0.5 ppt) of measured
BrO within the TTL

Measurement vs control run #583 (SF5 on Feb. 26/27, 2013)



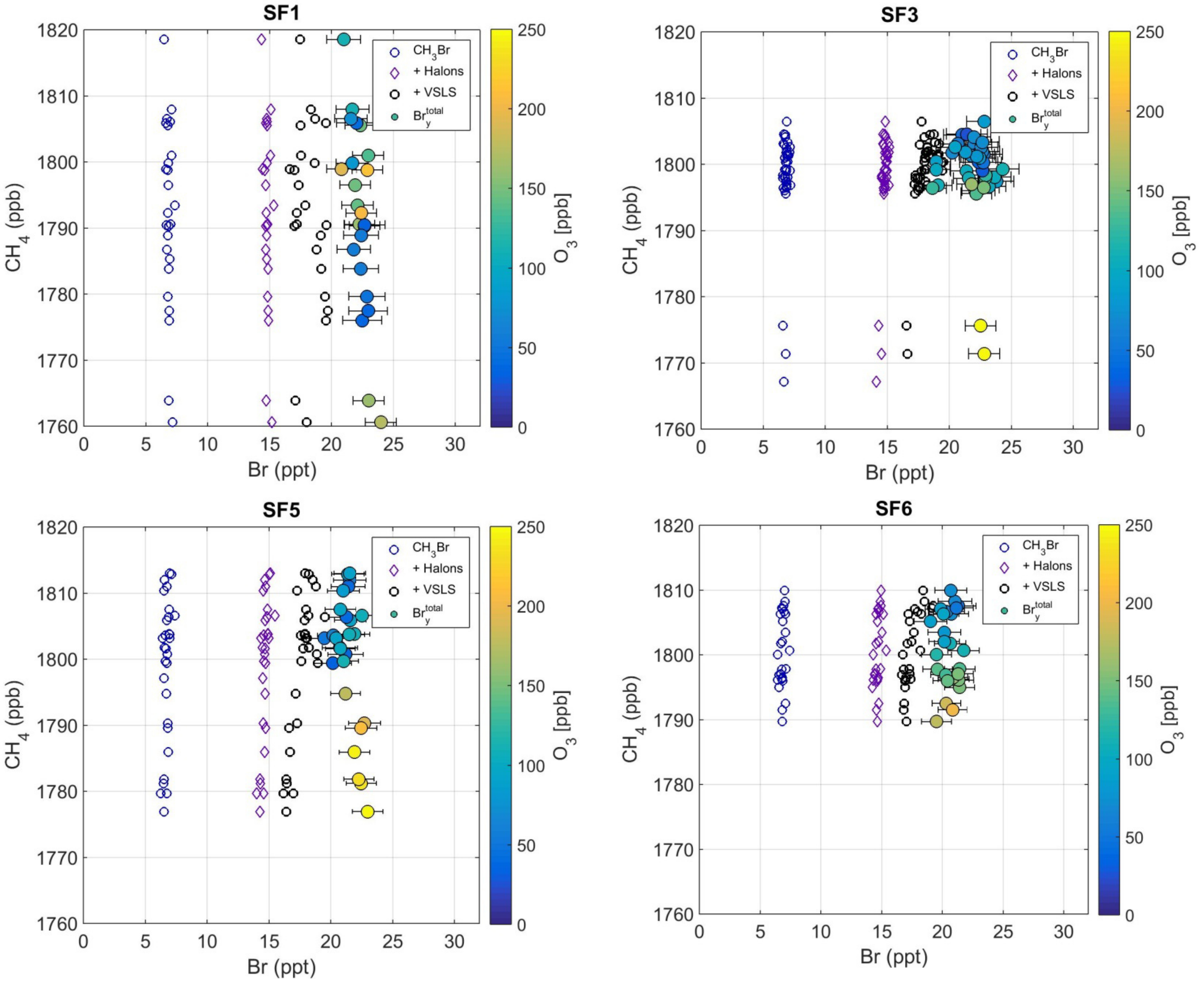
Small (if any) under-prediction (< 0.5 ppt) of measured BrO within the TTL

Measurement vs control run #583 (SF6 on March 1/2, 2013)

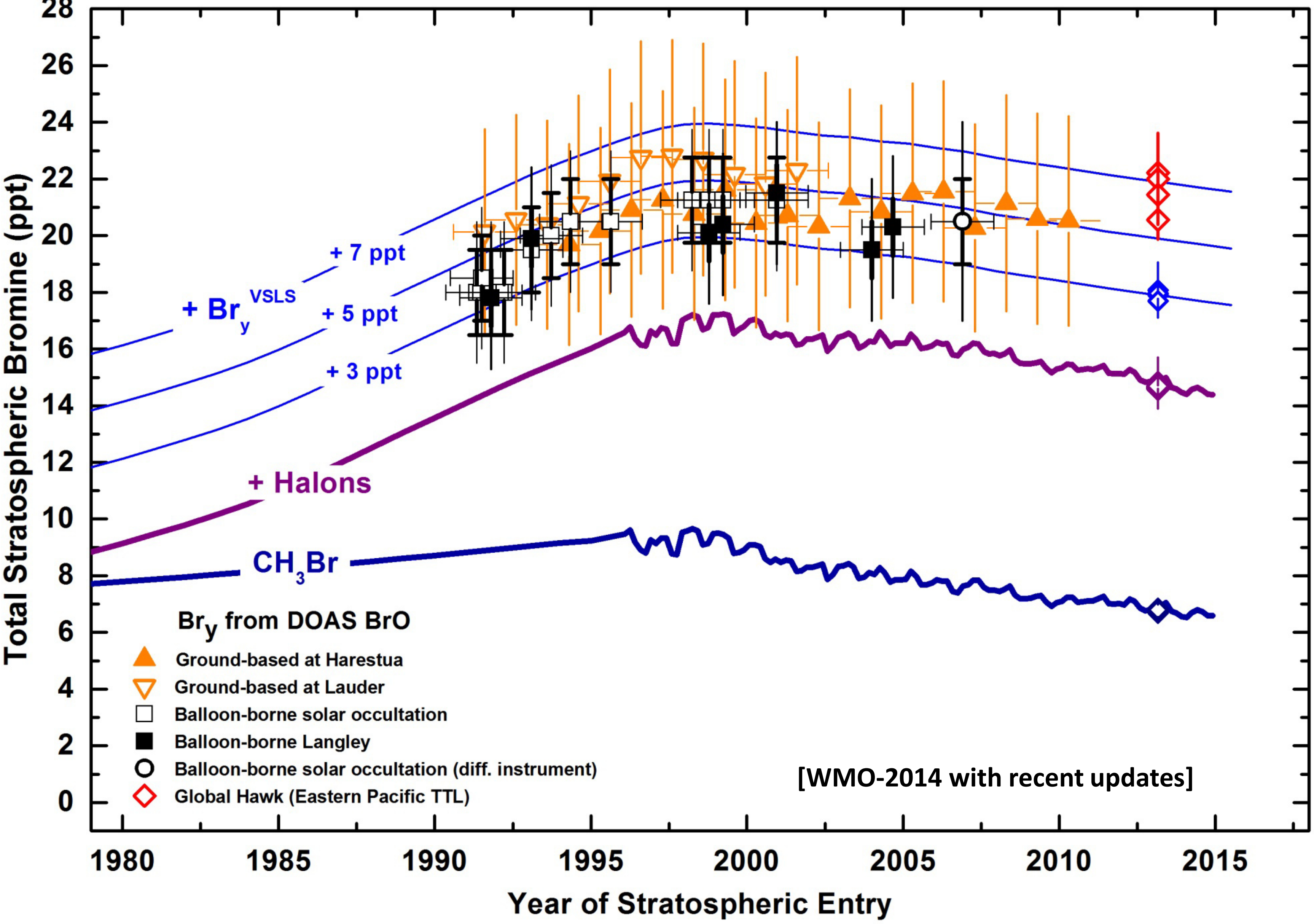


Small (if any) under-prediction (< 0.5 ppt) of measured BrO within the TTL

Total bromine Br_y ($=Br_y^{org} + Br_y^{inorg}$) as function of CH_4



Budget of total stratospheric bromine



[WMO-2014 with recent updates]

Lists of (preliminary) findings

1. **GH ATTREX flights mostly probed 3 regimes in 2013**
   - **subtropical lowermost stratosphere (LS_{extrop})**
   - **TTL**
   - **Mixing across the subtropical jet**

2. Measured CH_4, O_3, and NO_2 compares excellently with SLIMCAT simulations

3. In the TTL measured Br_y^{inorg} (1 – 5 ppt) increases in overall agreement with observed and modelled Br_y^{inorg} destruction

4. Measured and simulated BrO (or Br_y^{inorg}) largely agree, but comparing the data on a flight-to-flight basis indicates some variability that the model does not yet capture, due to

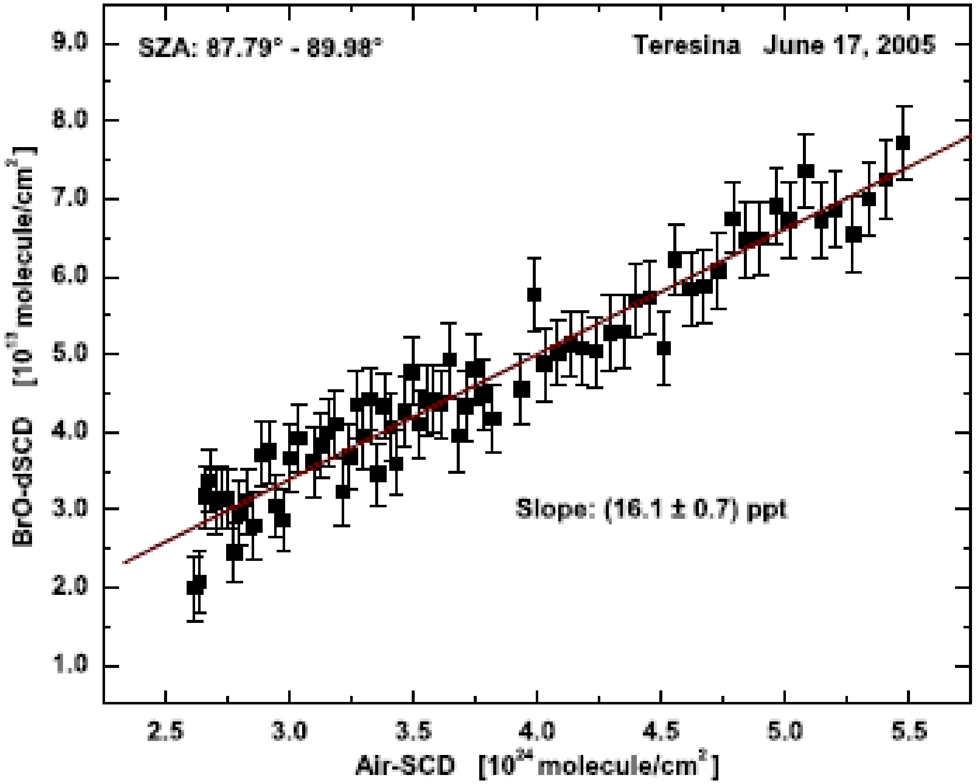
- ➢ **variable emissions of the brominated source gases (see the poster Navarro et al.,)**
- ➢ **uncertainties/discrepancies kinetic constants**
  - **for $k_{BrO+NO2}$ i.e. $J/k|_{BrO+NO2} = 1.7+0.4/-0.2$ for $BrONO_2$ destruction and formation (Kreycy et al., 2013) (important for the LS_{extrop} Br_y^{inorg} partitioning)**
  - **for $Br + O_3$, which is ± 30% uncertain at low T_s (important for the TTL Br_y^{inorg})**

5. Our BrO detection limit of < 1ppt prevents to yet firmly conclude on the amount of Br_y^{inorg} influx (c.f. Wang et al., 2015), and the Br_y^{inorg} partitioning around the LZRH (Fernandez et al., 2015)

6. $\sum Br_y^{org} + Br_y^{inorg}$ inferred for LS_{extrop} and at the highest TTL level point to $[Br_y] = 19.5$ to 23 ppt in 2013, which is somewhat larger (0 – 3 ppt) than what is presently measured within the stratosphere.

➢ **Is some Br_y^{inorg} removed by heterogeneous processing of HBr, HOBr, … on cirrus particles within TTL (e.g., Aschmann et al., 2011)?**

Measurement of BrO mixing ratio above 33 km tropics



- The BrO measurement implied [Bry] = 21.5 ± 2.5 ppt for 4.5 year old air
- Simultaneous brominated SG measurements indicated [Bry] = 17.5 ± 0.4 ppt