Inorganic and organic bromine measurements around the extra-tropical tropopause in fall: Insights into the transport of bromine into the stratosphere

Meike Rotermund[1], B. Schreiner[1], F. Kluge[1], T. Hüneke[1], A. Engel[2], T. Schuck[2], T. Keber[2], J.-U. Grooß[3], A. Zahn[4], K. Pfeilsticker[1]

[1]IUP, Universität Heidelberg, Germany
[2]IAU, Goethe University Frankfurt, Germany
[3]IEK-7, Forschungszentrum Jülich GmbH, Germany
[4]IMK-ASF, Karlsruhe Institute of Technology, Germany

Contents

Institut für Umweltphysik
University of Heidelberg

Objectives

Our objectives for the research campaign are to:

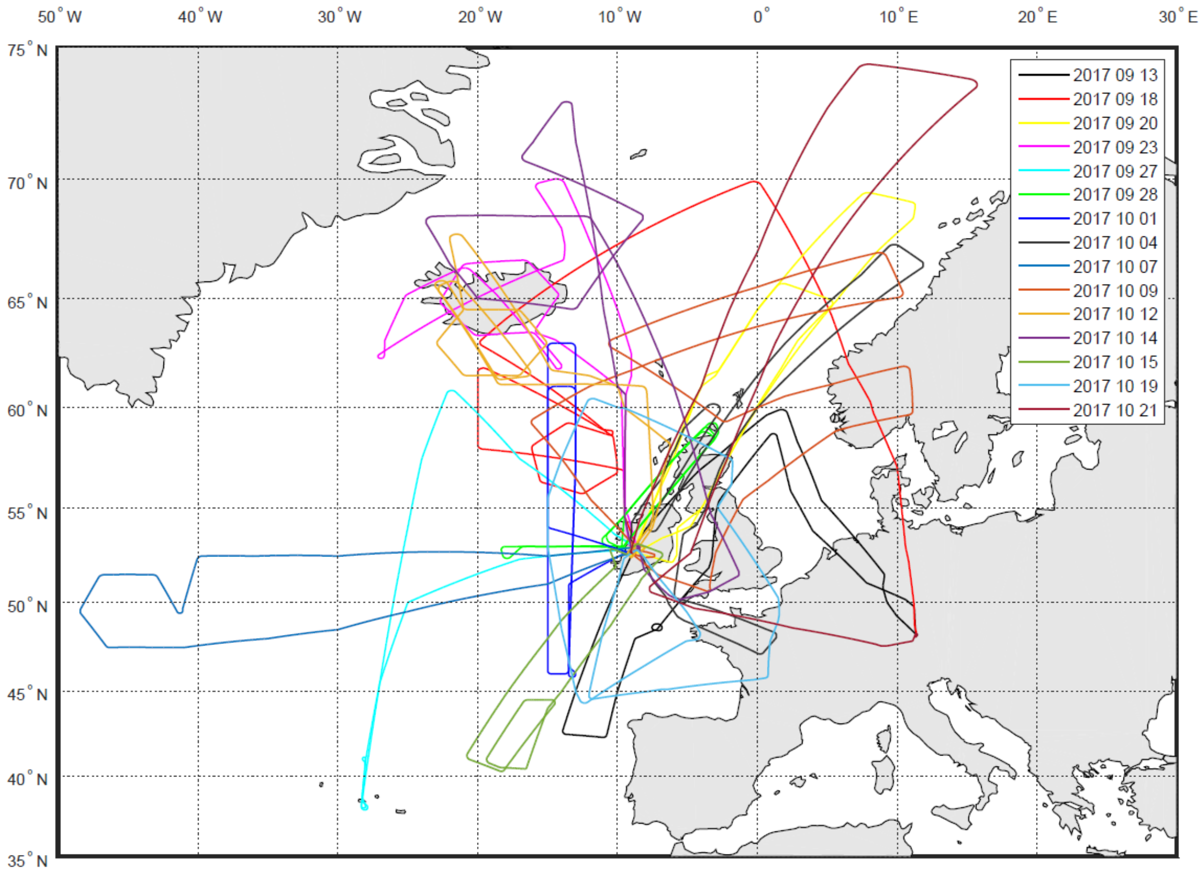
- **Measure halogenated trace gases (ozone depleting substances) around the Extratropical Upper Troposphere/Lower Stratosphere (ExUT/LS)**
  - **We measure trace gases such as: BrO, O_3, NO_2, OClO and IO around the UT/LS from air-borne data**

- **Compute the BrO to Br_y^{inorg} partitioning using CLaMS (Chemical LAgrangian Model of the Stratosphere) data provided by Forschungszentrum Jülich**
  - **Trace gas curtains are modelled along each flight trajectory allowing for direct comparisons**

- **Infer the total bromine, i.e. organic (measured by University of Frankfurt) and inorganic (us!) bromine (and eventually iodine and chlorine) around the UTLS**
  - **Determine a consistent climatology and trend of total bromine around the ExUT/LS**

Institut für Umweltphysik
University of Heidelberg

Research Campaign: WISE
(Wave Driven ISentropic Exchange)



Details:

[Adopted from: http://www.gulfstream.com/special-missions/recent-programs]

- **Airborne research from the HALO (High Altitude and Long range) aircraft**
- **Time: Sept./Oct. 2017**
- **Based from Shannon, Ireland**
- **Flight altitudes >15km: mainly along the ExUT/LS**

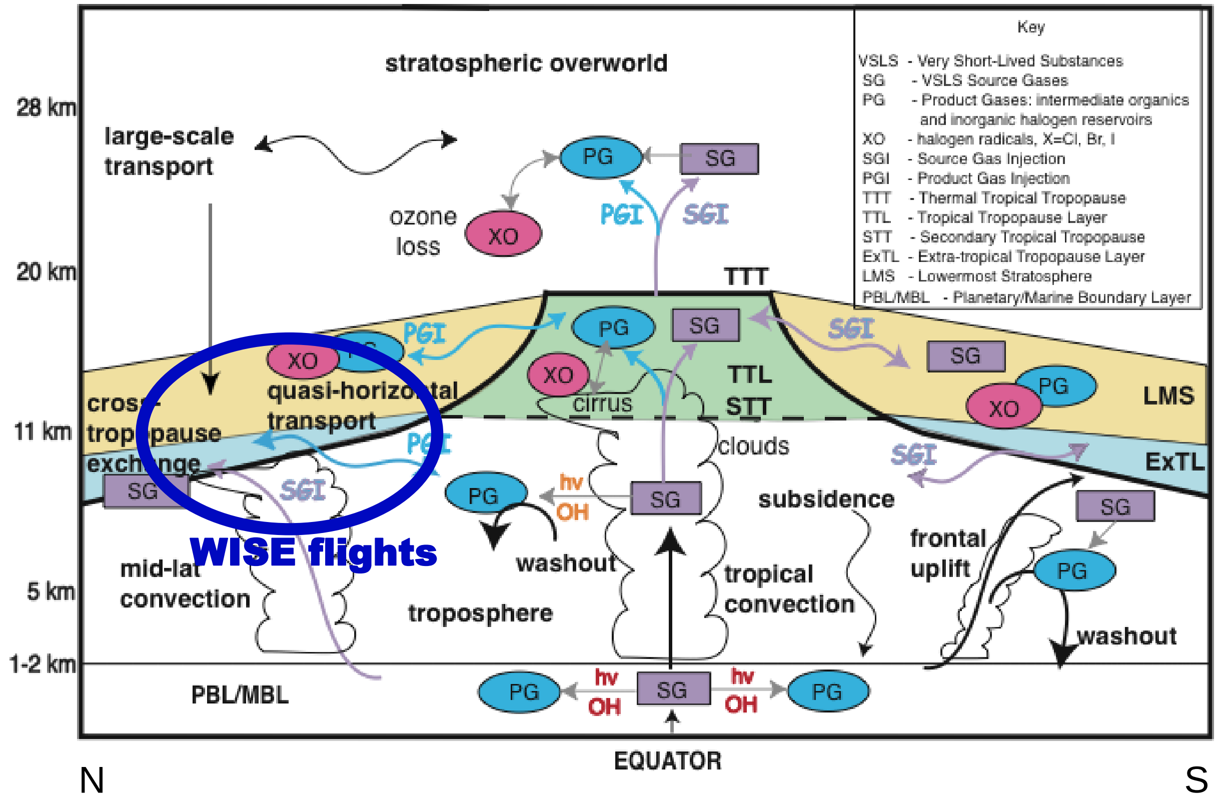
Institut für Umweltphysik
University of Heidelberg

The Role of Halogens in the Stratospheric Circulation

A more modern view of the stratospheric circulation was suggested by Holton et al., 1995. Thereby, beside the action of diabatic processes, the action of breaking (mostly planetary) waves has been more recognized.

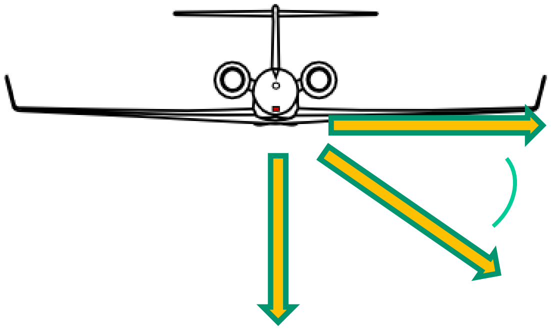
- **Mid-latitude large scale waves drive a pump that sucks air out of the tropical pipe and pushes it to more polar latitudes.**
- **Diabatic processes adjust the air masses to the ambient radiation conditions.**
- **The Lowermost Stratosphere-LS with Θ < 380 K, is relatively isolated from the above stratosphere and is separated from the troposphere and stratosphere by different Θ and PV values.**
- **Bromine in the LS has two origins (1) isentropic transport from the tropics or (2) transport through the extratropical tropopause.**

Chemical and Dynamical Processes Affecting VSLS



[Fig. 2-1, WMO-2006]

mini-DOAS: Some Basic Features and Analysis Method



Measurement principle:

- Remote sensing of UV/vis/nearIR skylight in limb scanning and nadir geometry

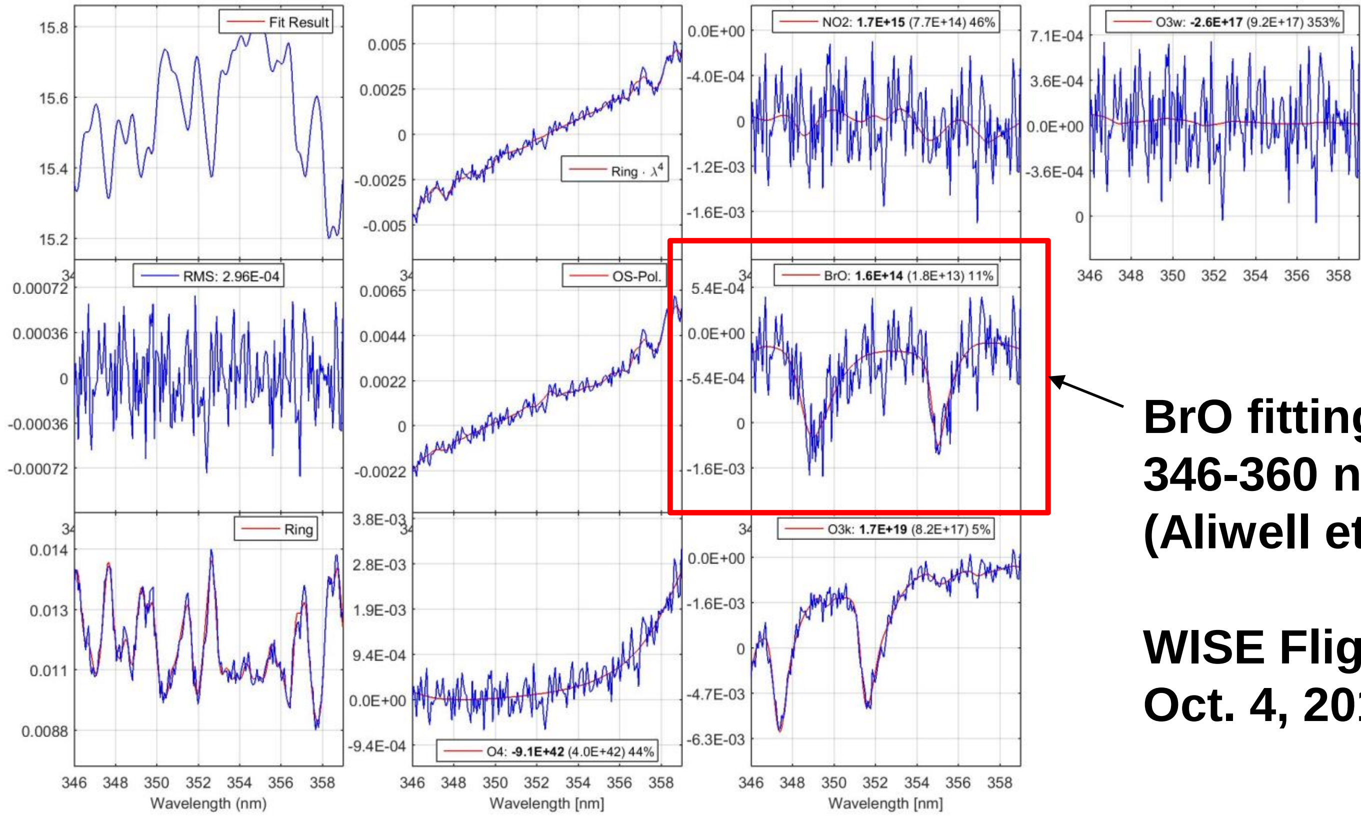
Data Evaluation includes 3 steps:

1. Retrieval of trace gas slant column densities (SCDs) using the DOAS method (Platt & Stutz, 2008)
2. Forward radiative transfer modelling for each measurement (Deutschmann et al., 2011)
3. Concentration retrieval using the novel scaling method for UV/vis data (Stutz et al., 2017, Hüneke et al., 2017; Werner et al., 2017).

	Wavelength Region [nm]	Resolution FWHM [nm]	Field of View [deg]	Targeted Trace Gases
UV	310 – 440	0.72	0.4	O_4, O_3, BrO, OClO, HONO, SO_2, CH_2O
VIS	420 – 550	0.76	0.4	O_4, O_3, NO_2, $C_2H_2O_2$, $C_3H_4O_2$, H_2O(g), OBrO, IO, IO_2, I_2
NIR	1100 - 1680	4-7	0.52	H_2O: vapour, liquid, ice CO_2, CH_4

Institut für Umweltphysik
University of Heidelberg

Sample DOAS Fit for BrO



BrO fitting window:
346-360 nm
(Aliwell et al. 2002)

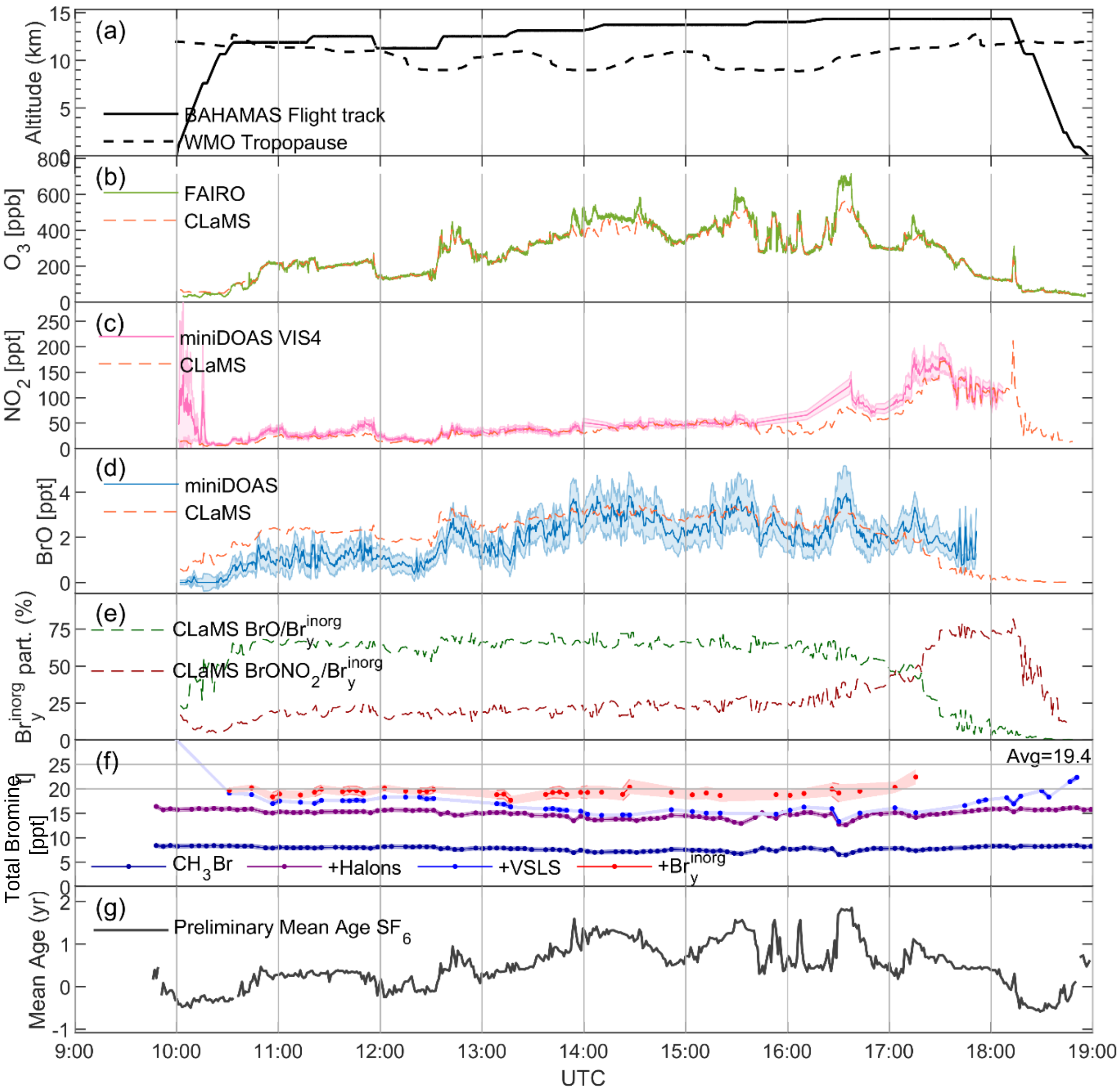
WISE Flight:
Oct. 4, 2017

S/N

BrO-Fit | MeasSpec: M000302 | RefSpec: 450 | Recording Time: 10:26:52 -- 10:29:06 UTC | Lat./Long.: 58.2184/-5.7449 | Alt: 12.5068 km
NScans: 500 | ExpTime: 305.27 ms | Temp: 1.21 °C | EA: 0° | SZA: 66.1089° | SRAA: 56.927°
S/N: 9.20 | χ^2: 1.64E-05 | DOAS-Polynom. deg: 2 | OffSet-Polynom. deg: 1
RefRingShift: 0.00081248 (0.00011807) | RefRingSqueeze: 1 (1.4024e-05)
GasShift: 0.024539 (0.015192) | GasSqueeze: 0.99336 (0.0030382)

Institut für Umweltphysik
University of Heidelberg

WISE Example Flight on Oct. 12, 2017



(a) HALO flight track and the WMO tropopause.

(b-d) Comparison to CLaMS model results for O_3, NO_2, and BrO VMR.

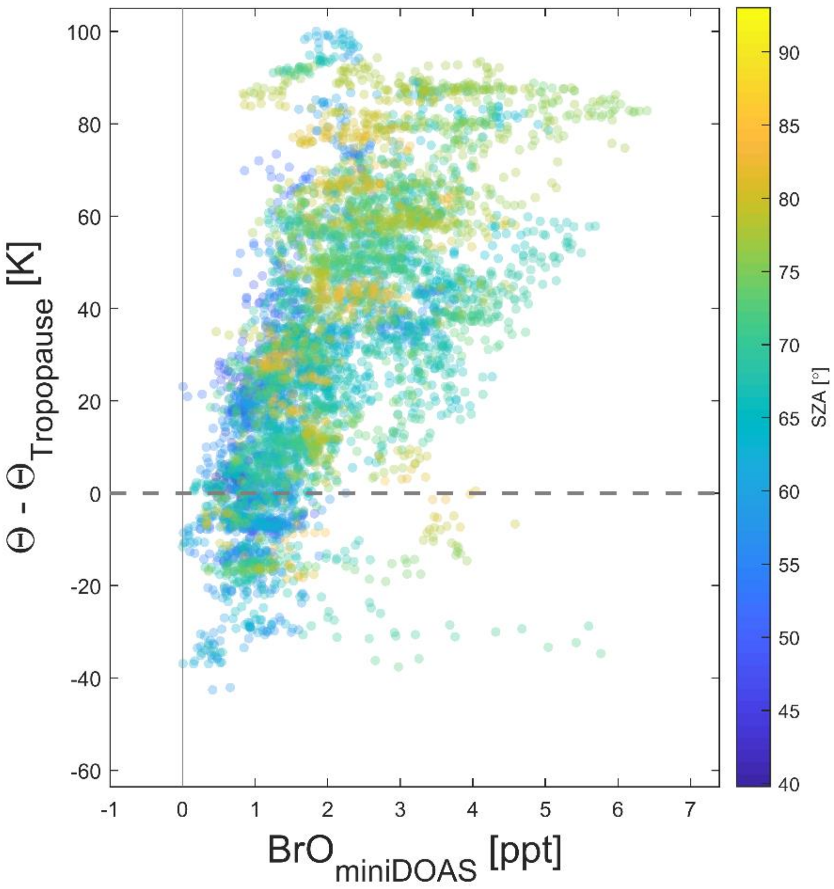
(e) Modelled BrO/Br_y^{inorg} partitioning coefficient to infer the inorganic bromine contribution as measured by miniDOAS.

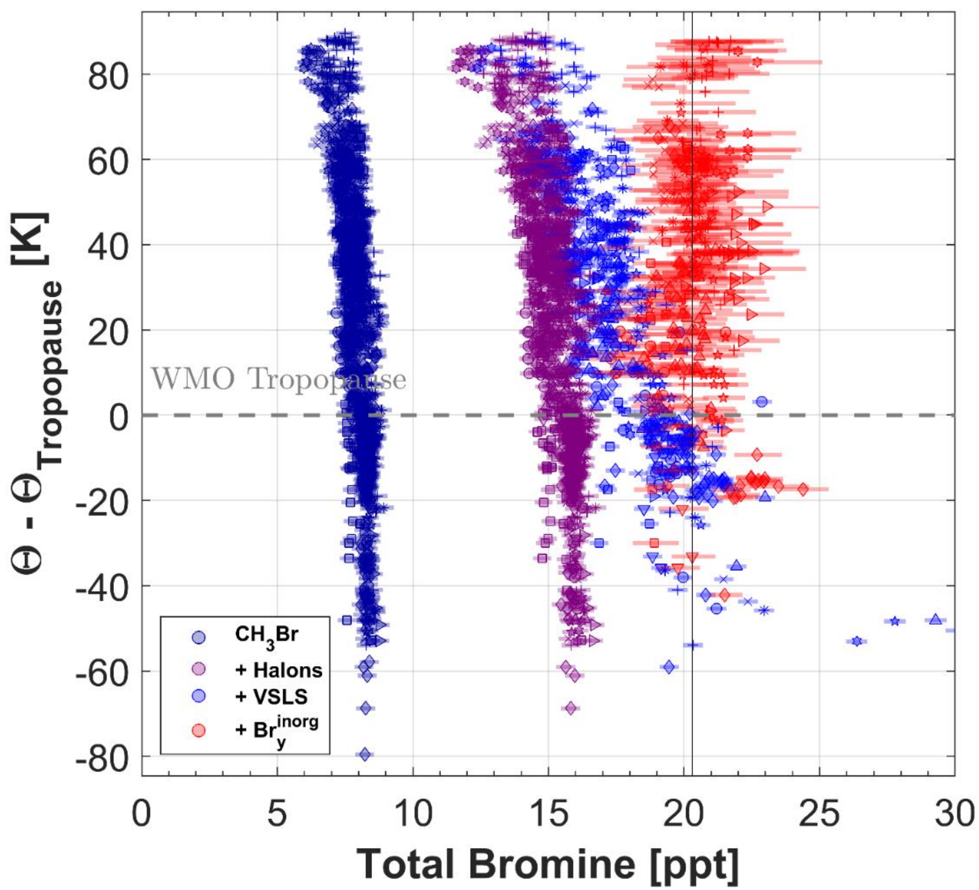
(f) Total bromine budget: organic bromine (CH_3Br, Halons, VSLS) and inorganic bromine (BrO).

(g) Preliminary mean age of the measured air masses.

Institut für Umweltphysik
University of Heidelberg

All 15 WISE Flights: Relative Distance to Tropopause

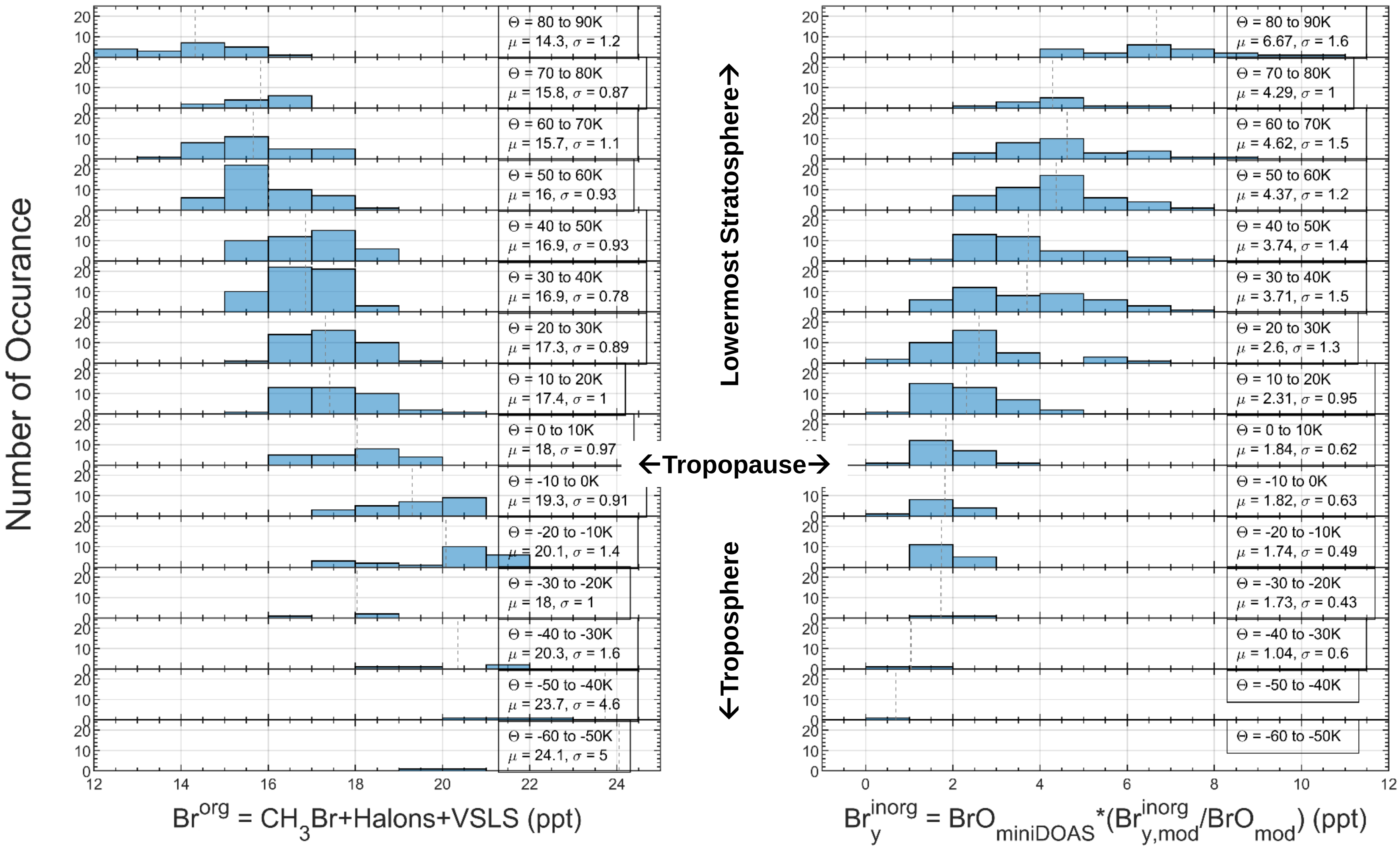




- ➢ Daytime BrO VMR in ExUT/LS.
- ➢ Br_y^{inorg} increases further into stratosphere (+ΔΘ).
- ➢ Organic bromine is compensated by inorganic bromine.
- ➢ Total bromine is 20.3 ± 1.2 ppt

Institut für Umweltphysik
University of Heidelberg

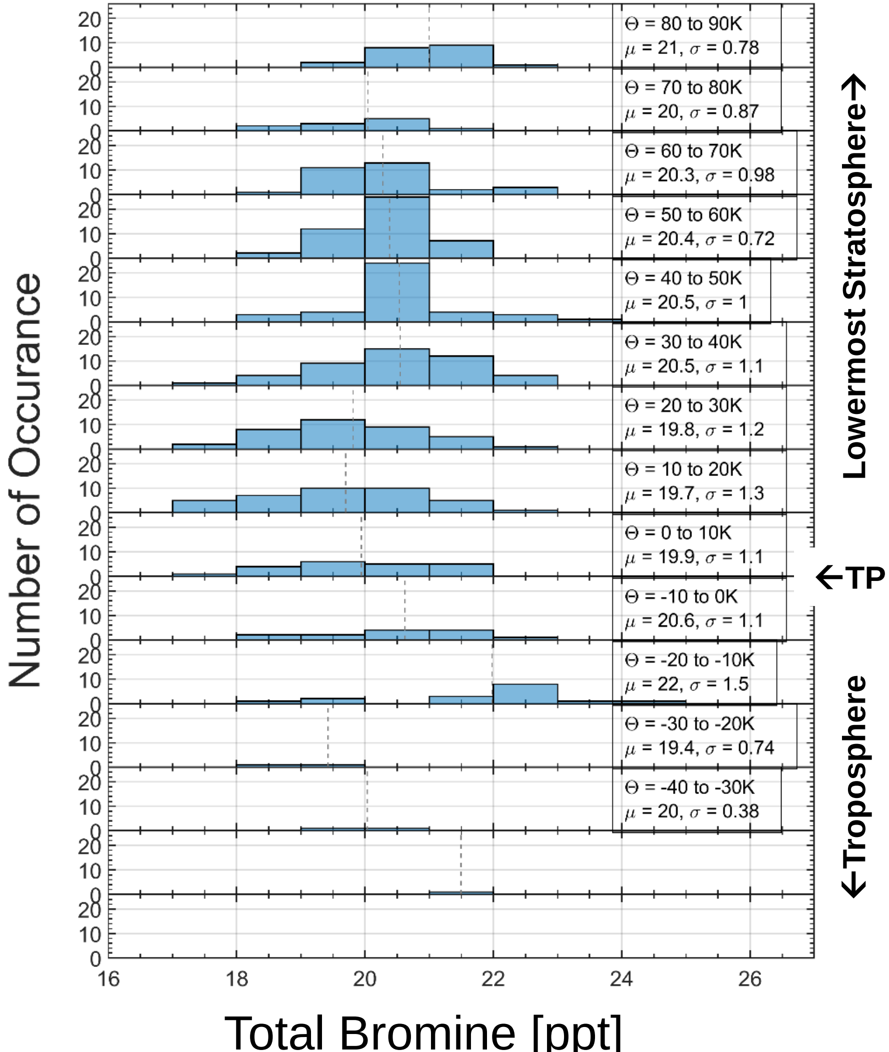
Probability Distribution of Organic & Inorganic Bromine

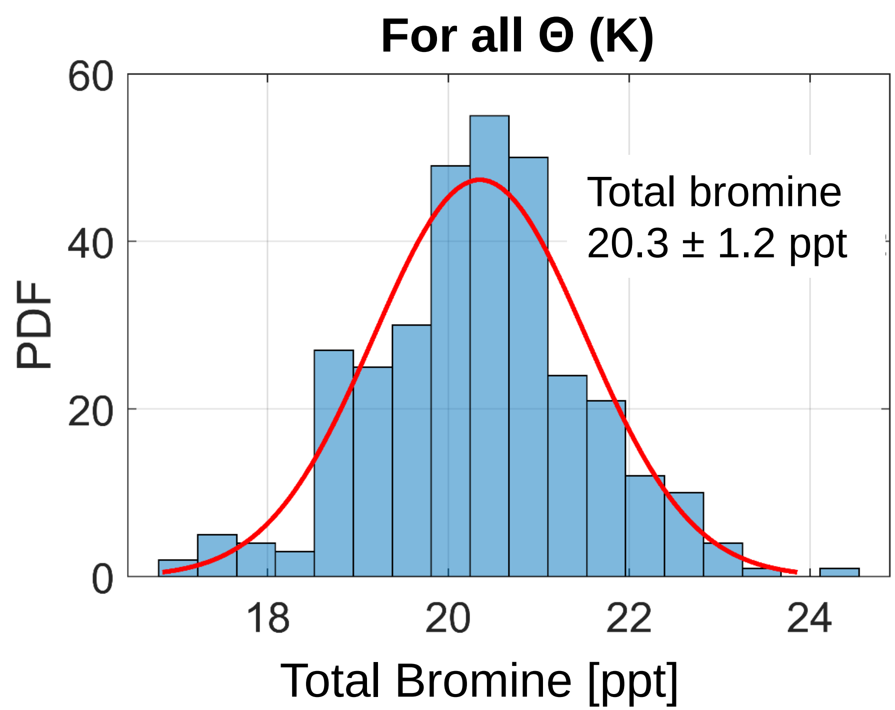


EGU Online Conference: May 5, 2020
Session: AS3.5

Institut für Umweltphysik
University of Heidelberg

Probability Distribution of Total Bromine





EGU Online Conference: May 5, 2020
Session: AS3.5

Institut für Umweltphysik
University of Heidelberg

Summary & Conclusion

- The WISE flights (Sept./Oct. 2017) have a total bromine = 20.3 ± 1.2 ppt
  - Variability is mostly due to mixing of air masses of the 'lower branch' and those across the ExUT/LS
- With complimentary measured data (UFRA) and CLaMS modelling (FZJ)
  - We compared miniDOAS measured BrO (and NO_2) data to the CLaMS predictions ... for photochemical ozone loss
  - We investigated the ExUT/LS climatology of BrO and total bromine (using the partitioning of inorganic bromine)
- As compared to total bromine expected for the deep stratosphere (~19.6 ppt), the ExUT/LS total bromine is ~0.7 ppt larger. A possible reason is heterogeneous uptake of inorganic bromine (HBr, $BrONO_2$…) on precipitating aerosol/cirrus cloud particles.
- Individual air contributions from the tropics and extra tropics leads to variable total bromine in the LS with a tendency of larger variability near the tropopause
  - Details in Keber et al (2020) and CLaMS simulations are needed to understand the cause of the variability.

Institut für Umweltphysik
University of Heidelberg

Outlook

1. **Continue analysis for the other campaigns (TACTS/ESMVal-2012, POLSTRACC-2016, Southtrac-2019 etc.)**

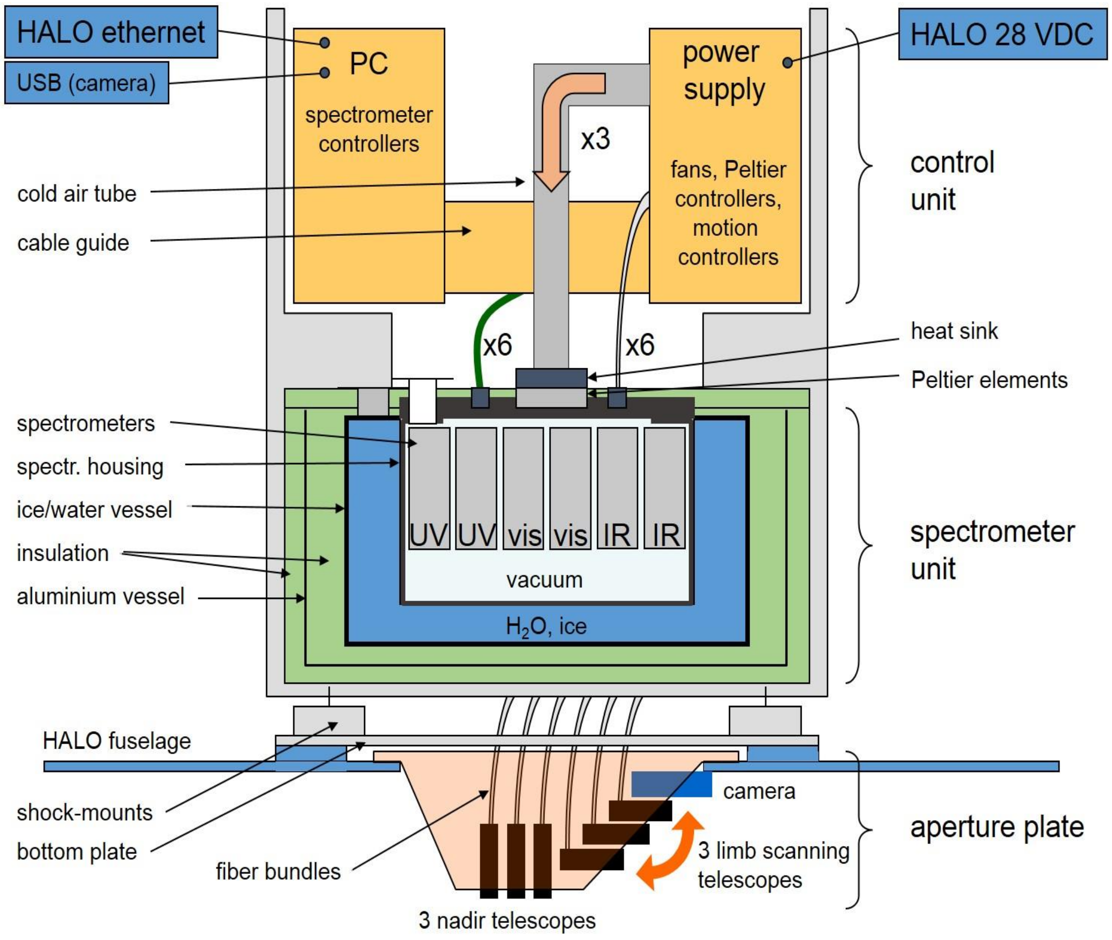
2. **Search for additional potential gases: OClO?, IO, O_4, H_2O (g,l,s)**
   - **to test the CLaMS prediction of the measured O_x, NO_x/NO_y, ClO_x/BrO_x, .. for photochemical ozone loss, the NO_x/NO_y partitioning,…..**

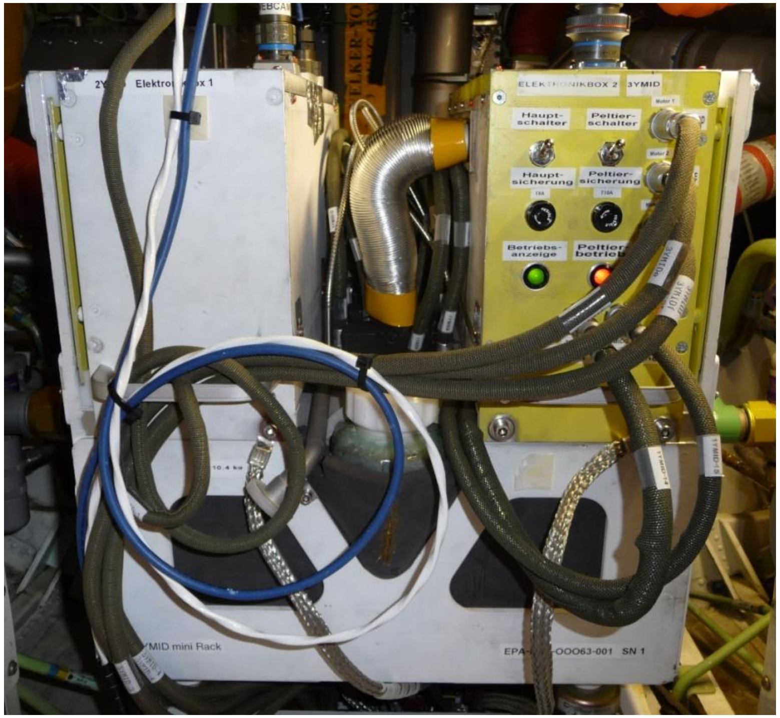
1. **If OClO is detected at twilight:**
   - **the inter-halogen reactions of ClO_x and BrO_x, in particular the formation of OClO, as by-product of the reaction ClO + BrO (branching ratio of ClO + BrO → BrCl + O_2 (43%), or Br + ClOO (20%), or Br + OClO (39%), but reaction rates and branching ratio are uncertain by 41% (Frieler et al., 2006)!**

Institut für Umweltphysik
University of Heidelberg

Thank you!

mini-DOAS Instrument





Weight: 58 kg including aperture plate
Power consumption: ~200 W at 28 DC
Location: HALO boiler room (back of the aircraft underside)

Institut für Umweltphysik
University of Heidelberg

Concentration retrieval using the novel scaling method

The concentration of the targeted gas X is inferred from the knowledge of concentration of a reference gas

- **Use the differential absorption (dSCD) measured adjacent to an O_3 (or O_4) absorption band**
- **Scale concentration of X to the in-situ measured [O_3] (or [O_4], ..) concentration, via**

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

$$SCD = dSCD_{meas} + dSCD_{ref,solar}$$

RT Model calculations (α)

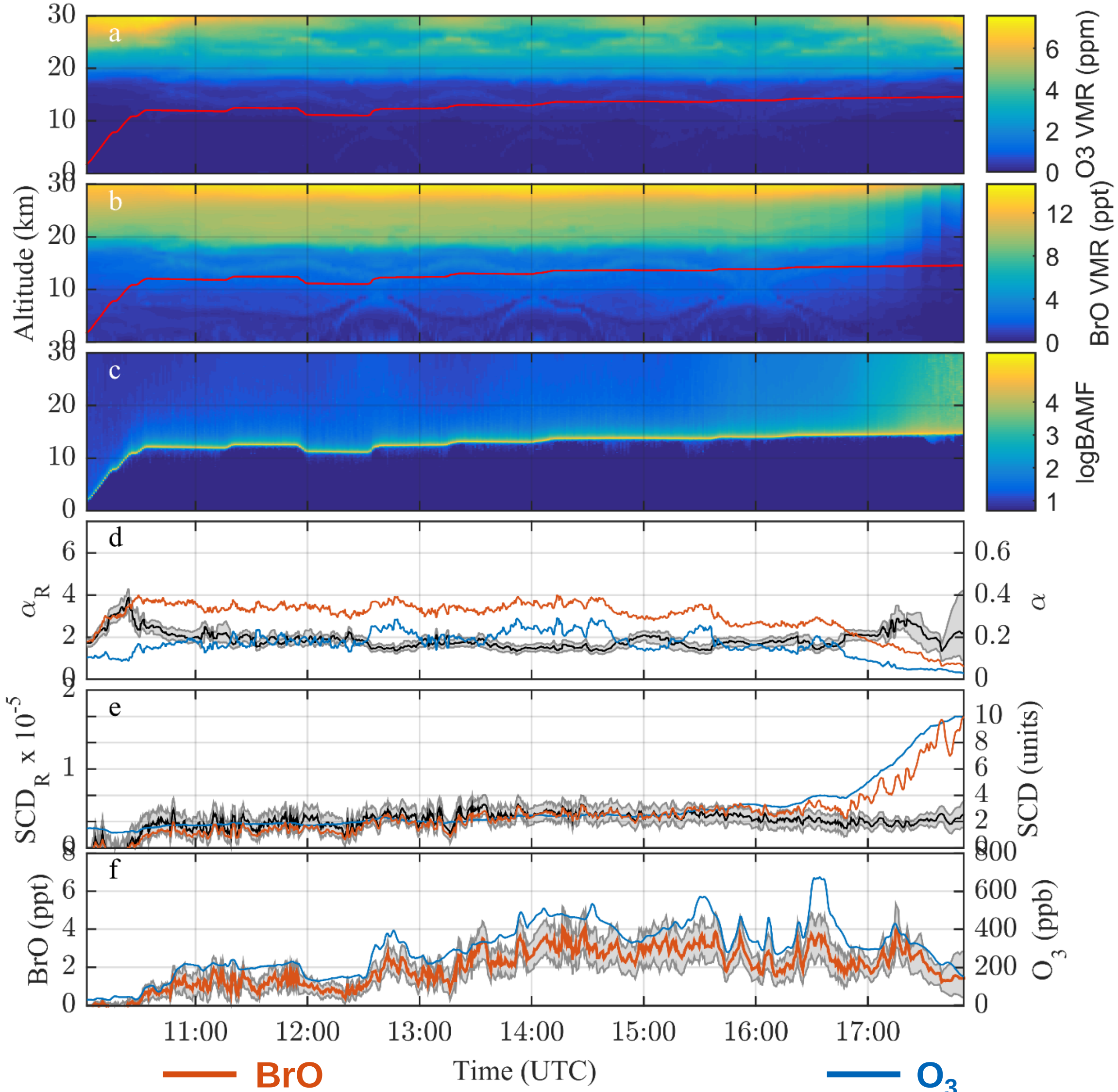
DOAS ($dSCD_{meas}$)

SLIMCAT, EMAC, CLAMS, .. ($dSCD_{ref,solar}$)

Fairo Instrument ($[O_3]_{in-situ}$)

Stutz et al., (2017), Werner et al., (2017), Hüneke et al., (2017)

WISE Example Flight on Oct. 12, 2017



(a-b) CLaMS model curtains are used to constrain RT for O_3 and BrO VMR.

(c) BoxAirMass Factor BAMF, is the weighting factor for how sensitive the instrument is to incoming light at any altitude.

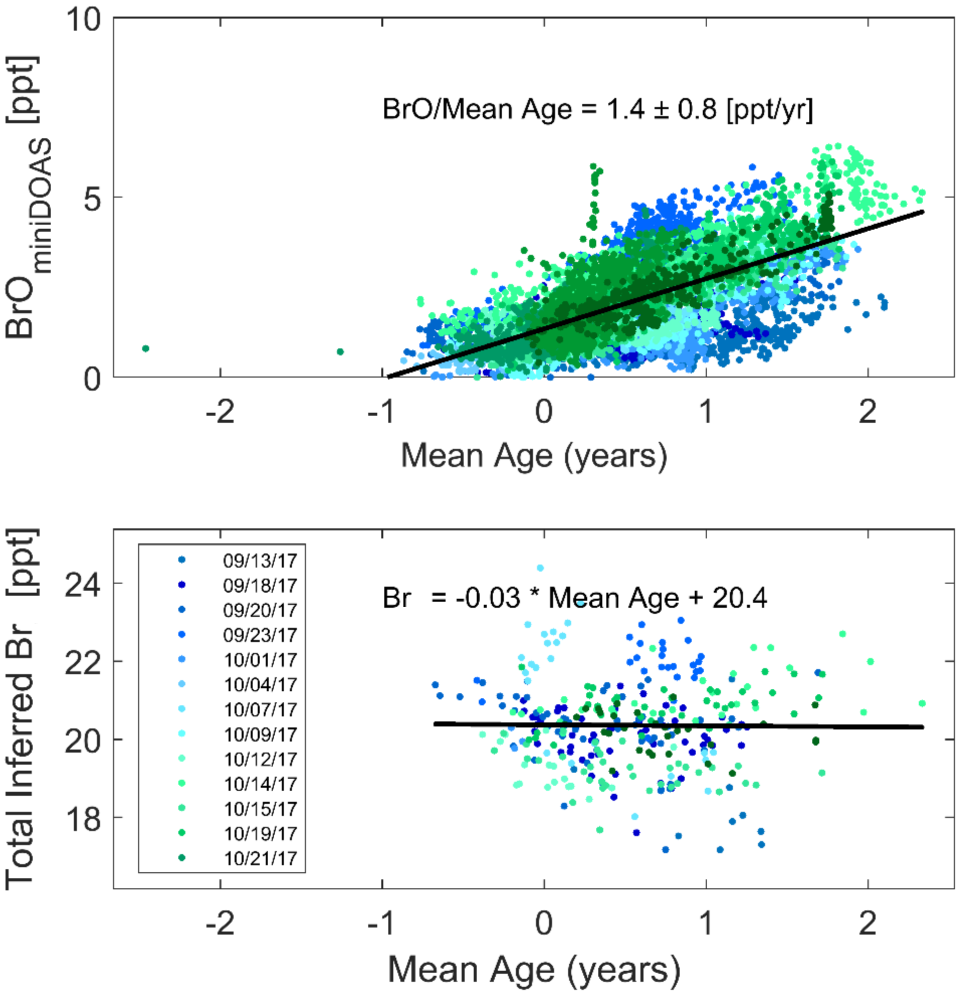
(d) The α-factor, dependent on BAMF, is the absorption of the target gas in the field of view in relation to the total measured absorption.

(e) The SCDs, slant column density, show the trace gas amount along the line of sight (impacted by SZA).

(f) VMR result of the target gas (BrO, NO_2) with in-situ measured scaling gas (O_3).

Institut für Umweltphysik
University of Heidelberg

All WISE flights vs. Mean Age



Institut für Umweltphysik
University of Heidelberg