Observed distribution of halocarbons in the Southern Hemispheric UTLS and Implications for the bromine and chlorine budget of the lowermost stratosphere

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Scientific motivation: halocarbons

- The total ozone abundance decreased since about 1980, which can be linked to chlorine and bromine containing substances such as chlorofluorocarbons (CFCs) (*Solomon, 1999*).
- Introduction of the Montreal Protocol 1987 and its amendments lead to a slow recovery or stabilization of stratospheric ozone, especially in relation to the Antarctic ozone hole and the polar regions (*WMO, 2018*).
- Next to regulated long-lived substances, substances containing chlorine and bromine with a lifetime of less than 6 months, also known as "very short-lived" substances (VSLS) can reach the lower stratosphere.
- Bromine VSLS are produced mainly naturally, whereas chlorine VSLS originate primally anthropogenic.
- Due to their short atmospheric lifetime, VSLS can release reactive bromine and chlorine to the lower stratosphere (see Fig. 1). This region reacts sensitively to changes in ozone (*Hossaini et al., 2015*).
- The relative contribution of some VSLS to stratospheric chlorine loading appears to increase, while that of long-lived substances appears to decrease (*Hossaini et al., 2019*).

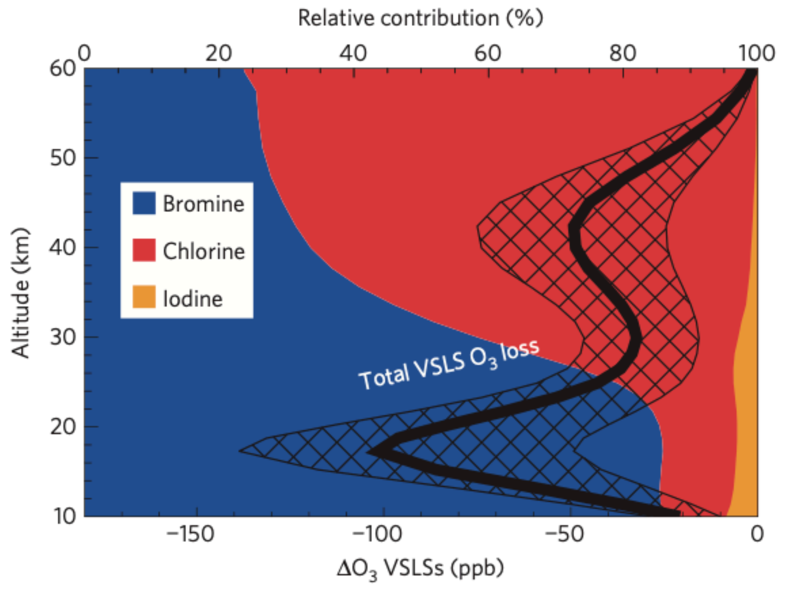

Figure 1: Annual global mean (2011) change in stratospheric ozone (O3) volume mixing ratio (ppb) due to VSLS (bottom x-axis). Grated area shows the range due to uncertainty in VSLS loading. Shaded regions represent the contribution of each halogen to the total O3 loss due to VSLS (%; top x-axis) (*Hossaini 2015*)

GC/MS-system operated during SOUTHTRAC

- Data presented here have been measured with the in-situ **G**as **Ch**romatograph for **O**bservational **S**tudies using **T**racers (GhOST-MS), installed on board the HALO (High Altitude and Long Range Research Aircraft) aircraft.
- GhOST-MS is a two-channel gas chromatograph (GC) combining an Electron Capture Detector (ECD, GC isotherm) and a Quadrupole Mass Spectrometer (MS, GC temperature-programmed and cryogenic preconcentration System) in a newly used electron ionization (EI) mode (*Keber et al., 2019; Obersteiner et al., 2016*).
- Using EI, samples were taken in a time resolution of around 6 minutes.

	Substances
CFCs	CFC-11, CFC-12, CFC-113 CFC-114, CFC-115
HCFCs	HCFC-141b, HCFC-142b HCFC-22
HFCs	HFC-125, HFC-134a HFC-142a
Halons	Halon-1211, Halon-1301 Halon-2402
Chlorocarbons	CH_3Cl, CCl_4, CH_3CCl_3
Bromocarbons	CH_3Br
VSLS	CH_2Cl_2, CH_2Br_2, $CHCl_3$, $CHBr_3$, $CHBr_2Cl$, CH_3I, C_2Cl_4

Table 1: List of the substances, which are measured with the GhOST-MS during the SOUTHTRAC Campaign.

Figure 2: GhOST-MS installed in the HALO aircraft

SouthTRAC Campaign

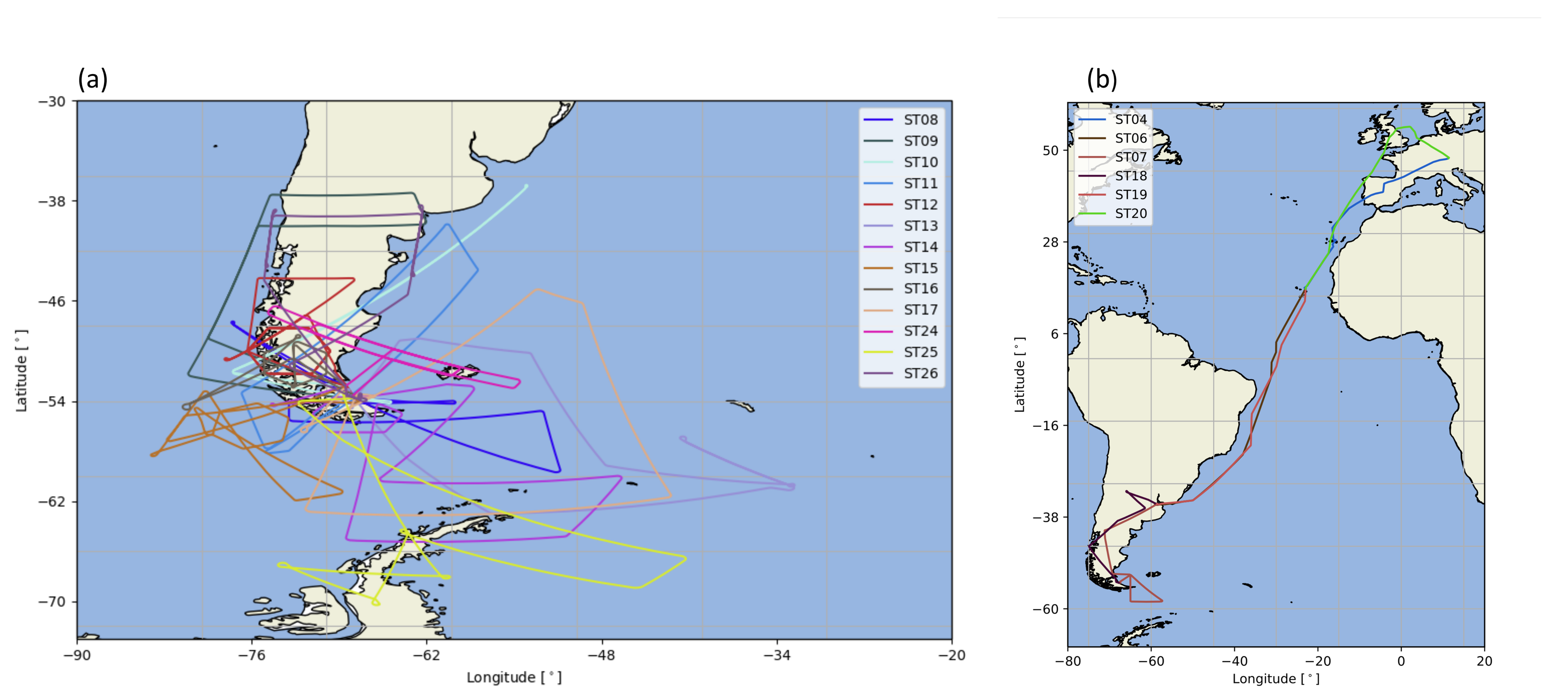

Figure 3: Flight tracks of HALO for (a) the local flights and (b) the transfer flights where the MS channel of GhOST-MS was activated. Basis of the local flights during SOUTHTRAC was Rio Grande (Argentina). The transfer flights started and ended in Oberpfaffenhofen (near Munich, Germany) via Sal and Buenos Aires.

- The campaign started early September 2019 and ended in late November 2019, covering winter and spring season of the mid to high latitude southern hemisphere upper troposphere and lower stratosphere (UTLS).
- In total 23 measurement flights took place, including 9 transfer flights starting from Oberpfaffenhofen (Germany) via Sal and Buenos Aires to Rio Grande (Argentina).
- The MS channel of GhOST-MS was active during 6 transfer flights and 13 local flights, resulting in 1349 in-situ measurements mostly between -35° and -70° latitude.

Results I: Upper tropospheric latitudinal cross sections

- First investigation and comparison to northern hemispheric variability of the upper tropospheric input region of the southern hemisphere for bromine VSLS by using binned values of the substances according to latitude and ozone difference to the chemical tropopause (*Zahn et al*., 2004) (see Fig. 4).
- Data in an range of 20 ppb below the chemical tropopause have been averaged to characterize the upper tropospheric input region.
- For the comparison, data from the campaign PGS* are used, which took place from December 2015 to March 2016 in the northern hemisphere, mainly in the Arctic.

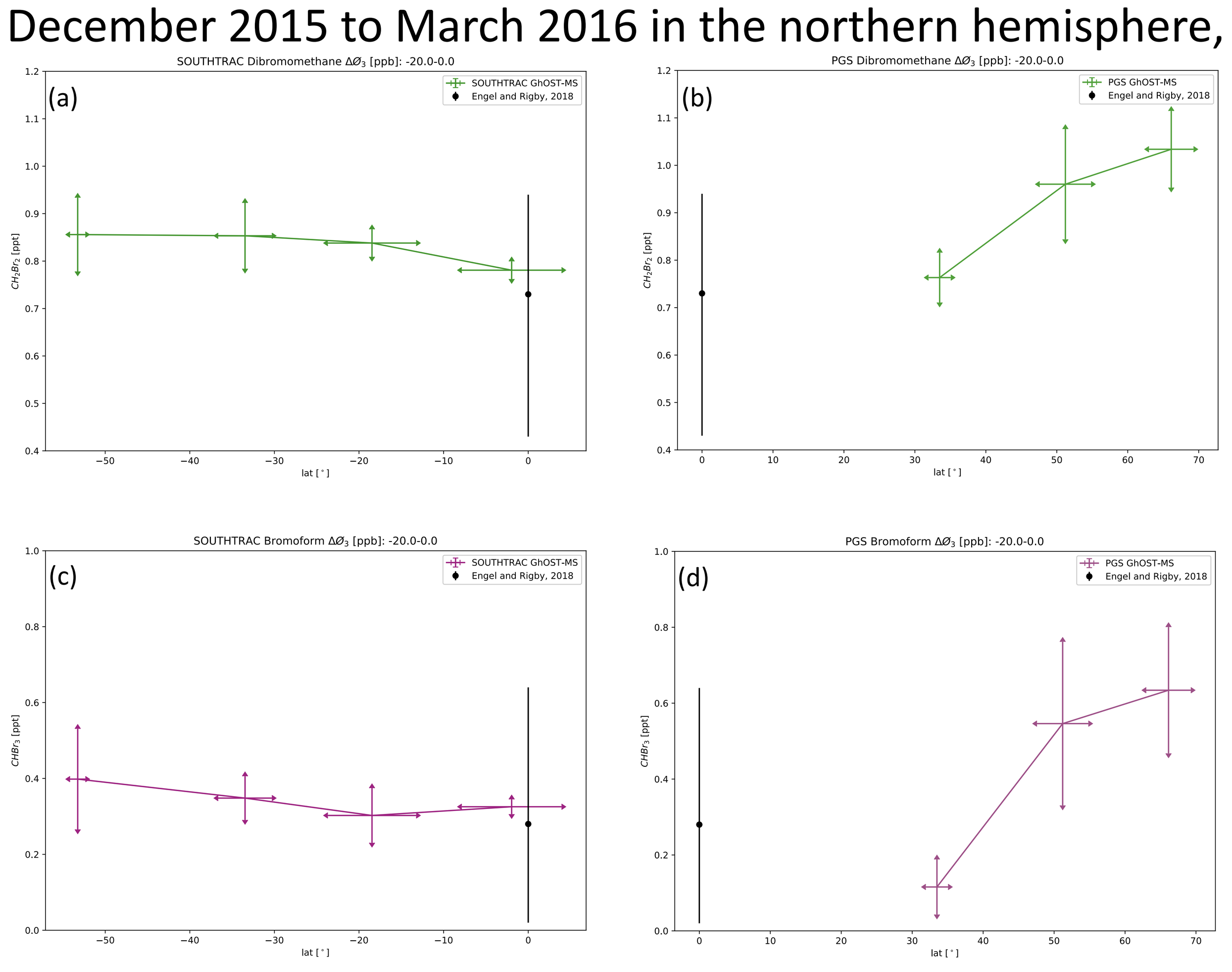

Figure 4: Latitudinal cross section of CH_2Br_2 (a) for SouthTRAC and (b) for PGS as well as $CHBr_3$ (c) for SouthTRAC and (d) for PGS, binned by latitude and averaged within 20 ppb below the chemical tropopause ozone values. Also included are the reference mixing ratios for the upper tropical tropopause (Engel and Rigby, 2018)

Results II: Biomass Burning Events

- Biomass burning (BB) in Australia and Brazil occurred during the SouthTRAC campaign (see Fig. 6).
- Usage of chloromethane (CH_3Cl) as a biomass burning tracer and dichloromethane (CH_2Cl_2) as a non biomass burning tracer (Engel & Rigby et al, 2018; Lawson et al, 2015).
- Distinction between stratosphere and troposphere via chemical tropopause using the empirical formula by Zahn et al. (2004).
- BB event still visible when considering stratosphere data only (see Fig. 5 red box) during three flights (ST06, ST19 and ST25) of which two flight may show biomass burning from Brazil (ST06 and ST19) and one flight from Australia (ST25).

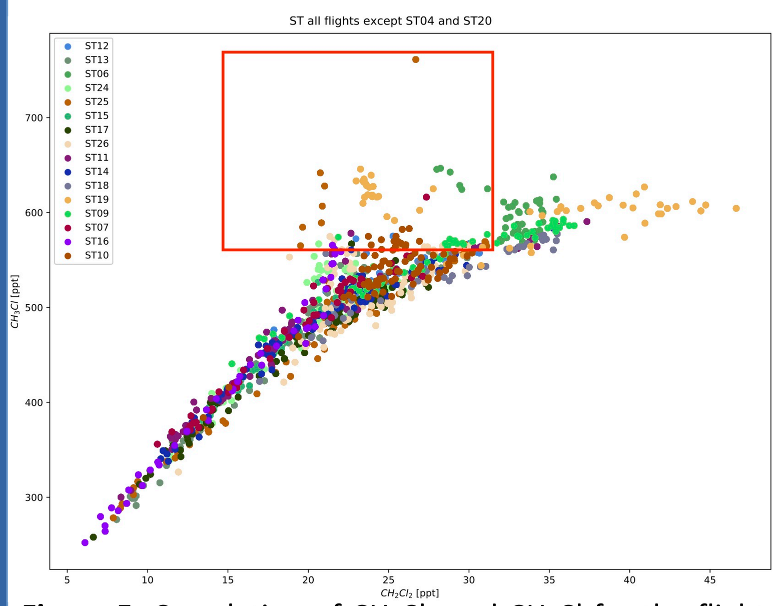

Figure 5: Correlation of CH_2Cl_2 and CH_3Cl for the flights ST06 (08.09.2019), ST19 (07.10.2019), and ST25 (12.11.2019), where biomass burning events are suggested

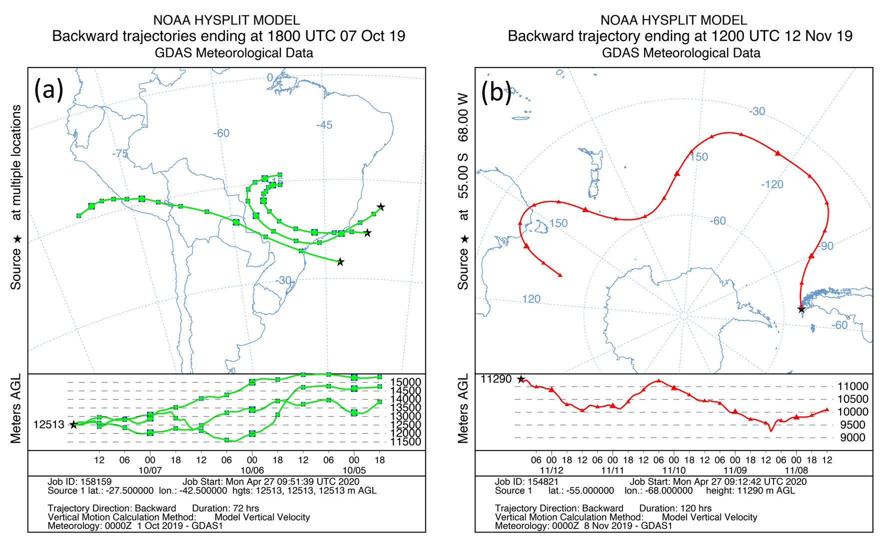

Figure 6: HYSPLIT Backward Trajectory Model results for (a) ST19 with three starting points along the flightpath where CH_3Cl is elevated and for (b) ST25 with one starting point for the short period for the increased mixing ratio of CH_3Cl

CONCLUSIONS & OUTLOOK

- Good quality of the SouthTRAC campaign data for the chlorine and bromine VSLS.
- First results of the southern upper tropospheric latitudinal cross section for the two major bromine VSLS indicate similar behaviour to that in the northern hemisphere, but with a much weaker increase for higher latitudes.
- Good agreement with the input mixing ratios for the tropical tropopause from various measurements campaigns, given by Engel and Rigby (2018).
- CH_3Cl has been found to be a good tracer for biomass burning, revealing three events during SouthTRAC connected to biomass burning in Brazil and Australia.

- Finalise calibration and data from SouthTARC as well as integrating further data sources.
- Comparison not only with PGS but also with other airborne measurement campaigns.
- Comparison with emission scenarios and models.

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* PGS: POLSTRACC (Polar Strato- sphere in a Changing Climate), GW-LCYCLE (Investiga- tion of the Life cycle of gravity waves) and SALSA (Sea- sonality of Air mass transport and origin in the Lowermost Stratosphere)