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Contribution of VLSL  
to stratospheric  
chlorine and bromine

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# Contribution of very short-lived organic substances to stratospheric chlorine and bromine in the tropics – a case study

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## Abstract

The total stratospheric organic chlorine and bromine burden was derived from balloon-borne measurements in the tropics (Teresina, Brazil, 5°04'S, 42°52'W) in 2005. Whole air samples were collected cryogenically at altitudes between 15 and 34 km. For the first time, we report measurements of a set of 28 chlorinated and brominated substances in the tropical upper troposphere and stratosphere including ten substances with an atmospheric lifetime of less than half a year. The substances were quantified using pre-concentration techniques followed by Gas Chromatography with Mass Spectrometric detection. In the tropical tropopause layer at an altitude of 15.2 km we found 1.4% of the chlorine and 8% of the bromine to be present in the form of very short-lived compounds. By combining the data with tropospheric reference data and age of air observations the abundances of inorganic chlorine and bromine ( $Cl_y$  and  $Br_y$ ) were derived. At an altitude of 34 km we calculated 3062 ppt of  $Cl_y$  and 17.5 ppt of  $Br_y$  from organic source gases. Furthermore we present indications for the presence of additional organic brominated substances in the tropical upper troposphere and stratosphere.

## 1 Introduction

The potential of chlorinated and brominated organic substances to enhance the catalytic destruction of ozone in the stratosphere is well known. Once in the stratosphere, the substances are destroyed by photolysis and reactions with active oxygen ( $O^1D$ ) and OH radicals. Inorganic bromine is present in the form of BrO, Br, HOBr and HBr. These species and the corresponding chlorine species are responsible for the catalytic destruction of ozone. Although the abundance of the summed-up chlorine and bromine from longer-lived organic gases in the stratosphere has decreased since the late 1990s (e.g. Engel et al., 2002; Montzka and Fraser, 2003) the impact of very short-lived substances (VLSL) on that total remains unsure. Bromine has, on average and on a per

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atom basis, a 60 times higher efficiency to destroy ozone than chlorine. Thus, even very low mixing ratios of brominated substances of less than 0.1 part per trillion (ppt) are of importance for stratospheric ozone depletion. Especially the brominated VSLs are suspected “to make a significant contribution to total stratospheric bromine and its effect on stratospheric ozone” (Law and Sturges, 2007).

The uncertainty in the amounts of VSLs reaching the stratosphere is due to the short atmospheric lifetimes of these substances (less than half a year) compared to atmospheric transport times which leads to a highly variable tropospheric distribution in time and space (Law and Sturges, 2007). Additionally there have been very few measurements of VSLs in the main stratospheric entrance region, the tropical tropopause layer (TTL) or above in the tropical lower stratosphere. Published observations of VSLs in the inner tropics above 15 km are presented in Schauffler et al. (1998 and 1999), Sinnhuber and Folkins (2006) and Law and Sturges (2007). Schauffler et al. (1998) performed measurements of nine brominated substances up to about 21 km while Sinnhuber and Folkins only used bromoform data from three campaigns in 1996, 1999 and 2004 for comparison with models. Law and Sturges (2007) used data at altitudes between 10 and 17.5 km originating from six measurement campaigns that were carried out within a period of eight years (1996–2004) to estimate the amount of chlorine and bromine from VSLs that is present in the tropical upper troposphere. Also several model studies were performed to quantify in particular the influence of brominated VSLs to ozone depletion (Dvortsov et al., 1999; Nielsen et al., 2001; Levine et al., 2007). Current estimates of the World Meteorological Organisation for the upper tropical troposphere range from 52 to 60 ppt for chlorine and 3.1 to 4.0 ppt for bromine from VSLs, but measurements show a much higher variability and uncertainty (Law and Sturges, 2007).

We present results from the flight BII 42 of the whole-air-sampler BONBON launched from Teresina, Brazil (5°04'S, 42°52'W) inside the inter tropical convergence zone on 8 June 2005 with a balloon operated by the French space agency CNES (Centre National d'Etudes Spatiales). This flight was part of a campaign for the validation of the

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ENVISAT satellite. Between 15.2 and 34 km altitude 15 samples were collected by pumping air cryogenically into electropolished stainless steel cylinders (for details see Schmidt et al., 1987; Engel et al., 1997). Three samples could not be analysed due to technical failure during sampling and one sample showed contamination from the balloon exhaust. No samples are available below 15 km for technical reasons.

## 2 Analytical procedure

The whole air samples were analysed in December 2005 using Gas Chromatography with Electron Impact Mass Spectrometric detection (GC-EI-MS; Siemens Si1 GC with Agilent 5975 MS) at the University of Frankfurt and in February 2006 with GC-Negative Ion Chemical Ionisation-MS (GC-NICI-MS; Agilent 6890/5973) at the University of East Anglia (UEA). Trace gases in the air samples were enriched cryogenically by cooling the sample loop with liquid nitrogen and using about 300 ml of air (UEA: 2 litres pre-concentrated on two bed adsorbent trap containing Carbograph-TD and Carboxen-1000 at  $-10^{\circ}\text{C}$  using a Peltier cooler). Separation took place on a micro-packed PorasilC/n-octane column (UEA: Restek 502.2 capillary column). The MS was operated in EI-SIM (Selected Ion Monitoring) mode measuring three ions at a time (UEA: NICI-SIM monitoring ions with  $m/z$  35, 37, 79 and 81 throughout the chromatogram). The Frankfurt analytical system provides high precisions and detection limits in the lower and sub-ppt range. In EI mode the substances are broken into characteristic cations using a high energy electron beam. This often allows quantification even if several substances elute at the same time. The UEA system uses NICI – a very sensitive and substance-specific method to detect amounts of a few parts per quadrillion (ppq) of especially brominated organic substances (Buser, 1986). Bromine anions are formed via dissociative electron capture from thermal electrons provided by an ionised reactant gas (here: methane). The masses 79 and 81 in a ratio of 1:1 are typical for bromine in the atmosphere, consisting of a nearly 50:50 mixture of these two isotopes. Chlorine can also be detected in a similar way by measuring on the relevant

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chlorine masses. However, if substances co-elute no quantification is possible with this method. The NICI detection also allows no certain identification of the detected compounds in the chromatogram and is based on the compounds retention times which must be known.

### 3 Results and discussion

#### 3.1 Quality assurance and air mass origin

A list of the quantified compounds, their source of calibration and detection limits can be found in Table 1. To assure the quality of the data, three cylinders were measured again in August 2007 at the University of Frankfurt. The chlorofluorocarbons (CFCs), hydro-chlorofluorocarbons (HCFCs) and halons proved to be stable, whereas the  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$  and  $\text{CCl}_4$  mixing ratios had drifted systematically in the cylinders. A wall reaction follows the first-order rate law and can be approximated as a linear process with respect to time if it is slow. Assuming that such a process is responsible for the observed drift we calculated an increase of 0.73% per month for  $\text{CH}_3\text{Cl}$ , of 2.90% for  $\text{CH}_2\text{ClCH}_2\text{Cl}$  and a decrease of 1.57% per month for  $\text{CCl}_4$  relative to their initially measured values. The mixing ratios of both substances in the air samples were corrected by linear extrapolation of the calculated trends to the flight date. Five other substances –  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{C}_2\text{Cl}_4$  and  $\text{CH}_3\text{Br}$  – showed changes but these were non-systematic and/or did not occur in all reanalysed samples. For these substances the maximum extrapolated difference (at most  $\pm 0.6\%$  per month) was added to the error bars as a systematic error. The substances measured at the UEA could not be rechecked except for the  $\text{CH}_2\text{Br}_2$  content of one sample which was the same within the measurement uncertainties.

Most of the longer-lived compounds are measured regularly at remote sampling locations by the Global Monitoring Division (GMD) which belongs to the Earth System Research Laboratory (ESRL) of the National Oceanic Atmospheric Administra-

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tion (NOAA), USA. Longer-lived trace gases show rather uniform concentrations in the global background troposphere because their atmospheric lifetimes are high compared with the atmospheric transport times. In order to check the quality of our measurements we compared the mixing ratios in the sample collected at 15.2 km with the globally averaged mixing ratios derived from NOAA-ESRL ground-based observations in June 2005. The measurements of F12, F11, F113, F22, F142b, F141b, CCl<sub>4</sub>, CH<sub>3</sub>CCl<sub>3</sub> and H1211 agreed within 3%. This indicates that we sampled a well mixed air mass with little influence from local convection. However, three of the longer-lived substances showed higher differences. The first is H1301 which we found to be 8.8% higher than the NOAA-ESRL reference but still within the 2 $\sigma$  measurement uncertainties. The second is CH<sub>3</sub>Br which was 14.7% (1.14 ppt) lower than the NOAA-ESRL reference. This discrepancy could be caused by a decrease of mixing ratio with altitude in the troposphere as reported by Blake et al. (1997) but also by a decrease due to instability within this particular sample cylinder. The third substance showing a difference to NOAA-ESRL values was CH<sub>3</sub>Cl. We found 601 ppt of CH<sub>3</sub>Cl at 15 km while the globally averaged mixing ratio at ground levels in June 2005 was 538 ppt. One possible explanation could be that our correction of the drift in the cylinders was insufficient. However, the South American tropical rainforest is reported to be a source region of CH<sub>3</sub>Cl. Gebhardt et al. (2008) found levels around 600 ppt for CH<sub>3</sub>Cl in air samples taken at altitudes around 10 km above Surinam in October 2005. As CH<sub>3</sub>Cl is longer-lived in the atmosphere the observed elevated mixing ratio could originate from the rainforest without being influenced from local convection. Trajectories were calculated by the Free University Berlin (FUB) using a model (Langematz et al., 1987; Reimer and Kaupp, 1997) with a resolution of 1.25° × 1.25° and 59 potential temperature levels and operational ECMWF fields as meteorological input. In Fig. 1 ten-day backward trajectories are shown. They were initialised at 5.28° S and 44.99° W which is the mean geographical location of the samples taken at 15.2 and 16.4 km altitude. The trajectories show, that the air around 15 km was most probably coming from North-West while the air around 16.5 km travelled over South-West South America. Other backward tra-

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jectories were initialised 2.5° north, east, south and west from this place and showed similar results. We conclude that the air sampled in the TTL has most probably been influenced from continental air masses originating from both hemispheres.

### 3.2 Organic chlorine and bromine

5 During the balloon flight the cold-point tropopause was located at 16.8 km (385 K potential temperature). The two lowest samples were collected at 15.2 km (359 K) and 16.36 km (371 K) within the TTL. For all further discussions, we will use the TTL definition given by Gettelman and Forster (2002). According to this definition the TTL extends from the minimum potential temperature lapse rate to the cold point. Air parcels  
10 reaching the level of zero radiative heating, which is located at 15±0.5 km and 360 K, are expected to be transported to the stratosphere (Gettelman et al., 2004). We will assume that the signatures of both samples originating from the TTL are very likely to be injected into the stratosphere. However, since many processes influence the composition of the tropical region around 15 km (see e.g. Tuck et al., 2004) we do not claim  
15 global significance for the lowest altitude sample. On the other hand the air sampled at 16.4 km was located very close to the upper limit of the TTL and thus its chemical composition should be representative for the inner tropics (Gettelman and Forster, 2002).

The total halogen mixing ratios and the contribution of the source gas subgroups at the different altitudes are shown in Fig. 2a for chlorine and 2b for bromine. The error bars  $\chi_{\text{org}}$  include the 1 $\sigma$  measurement uncertainties and the sample instability errors as calculated using Eq. (1) and weighting with the number of chlorine or bromine atoms contained in the respective substance.

$$\chi_{\text{org}} = \pm \left[ \sum_i e_{si,i} + \sqrt{\sum_i (\sigma_{sm,i}^2 + \sigma_{ct,i}^2)} \right] \quad (1)$$

25 The sample instability errors  $e_{si}$  (if observed) are systematic errors. For that reason

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they were summed up separately. Due to the limited amount the samples were measured only twice. Thus  $\sigma_{sm}$  is the standard deviation of the calibration standard on the measuring day. As we used a secondary standard for the measurements  $\sigma_{ct}$  is the standard deviation from the calibration of that standard. As  $\sigma_{sm}$  and  $\sigma_{ct}$  are statistic errors the square root of the sum of the squares can be taken. Calibration uncertainties are not included in the error bars. Please note, that the samples at 28 and 32 km altitude could not be measured at the UEA due to insufficient amount of air remaining in the canisters. Thus, the values for total organic bromine and chlorine in these samples do not include the mixing ratios of H1202, CH<sub>2</sub>BrCl, CHBrCl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub>, CHBr<sub>2</sub>Cl and CHBr<sub>3</sub>. Table 2 shows the total halogen mixing ratios corresponding to the values shown in Fig. 2a and b and the altitude range, over which the air has been sampled into each canister during the slow descent of the balloon. Longer-lived halocarbon data from the flight are shown in Table 3 while in Table 4 the mixing ratios of the VSLS for the four lowest altitude samples can be found. C<sub>2</sub>Cl<sub>4</sub> (1.02 ppt) and CHBr<sub>3</sub> (0.016 ppt) could only be detected in the sample collected at 15.2 km and are therefore not listed. CHClBr<sub>2</sub> and C<sub>2</sub>HCl<sub>3</sub> were below detection limit (see Table 1) for all samples. Also not shown are low mixing ratios of up to 2.7 ppt of CH<sub>2</sub>Cl<sub>2</sub> which we detected in some samples collected at higher altitudes. As CH<sub>2</sub>Cl<sub>2</sub> should be completely depleted at these altitudes we suggest non-systematic processes in the canisters as an explanation and included these blank values in our error calculation. For the other VSLS we found rather uniform canister and system blanks, which were below 0.02 ppt for all species and corrected for them.

In the TTL at 15.2 km we found 3431±30 ppt of chlorine from organic substances. About 62.1% of the chlorine is present in the form of CFCs, while HCFCs contributed 6.3%, longer-lived non-fluorinated chlorocarbons 30.1% and H1211 0.1%. Only 1.4% (47.1±5.7 ppt) of chlorine came from VSLS, whereby the main contribution was from CH<sub>2</sub>Cl<sub>2</sub> (22.4±1.8 ppt). The estimated tropical upper tropospheric mixing ratio in Table 2-2 of Law and Sturges (2007) is 55 ppt (range: 52–60 ppt) for total chlorine from VSLS including 1.5 ppt from chloroethane which is the only source gas mentioned by Law and

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Sturges (2007) that was not quantified in our study. Taking this into account, Law and Sturges (2007) derived an average of 53.5 ppt (range: ~51–58 ppt) for the remaining chlorinated VLSL in the tropical upper troposphere. This agrees with our findings within the given error bars. At 16.4 km we found  $3377 \pm 30$  ppt of organic chlorine with 1.1% (36.6  $\pm$  5.1 ppt) from VLSL. As described above the air mass sampled is very likely to have been transported into the stratosphere because of its location above the level of zero radiative heating. Above the tropopause the total organic chlorine decreases with altitude due to conversion into inorganic species. At the highest flight altitude (34 km) all short lived source gases were depleted to values below our detection limits and the remaining organic chlorine was  $452 \pm 10$  ppt. This corresponds to about 13% of the amount observed in the TTL.

Organic bromine at 15.2 km was  $16.2 \pm 1.1$  ppt with 51% present in the form of halons, 41% in the form of  $\text{CH}_3\text{Br}$  and 8% ( $1.25 \pm 0.08$  ppt) originating from the five brominated VLSL listed in Table 4. In 16.4 km we found a fraction of bromine from VLSL of about 6% ( $0.98 \pm 0.08$  ppt). Both VLSL contributions are substantially lower than the global tropical upper tropospheric mixing ratio of 3.5 ppt (range: 3.1–4.0 ppt) estimated by Law and Sturges (2007). In particular we found  $\text{CH}_2\text{Br}_2$  with a mixing ratio of  $0.55 \pm 0.001$  ppt at 15.2 km to be the dominant very short-lived source gas while the  $\text{CHBr}_3$  mixing ratio was very low ( $0.016 \pm 0.005$  ppt) in this sample. Sinnhuber and Folkins (2006) presented higher  $\text{CHBr}_3$  mixing ratios of up to about 0.2 ppt above 15 km in the tropics. This is not in contrast with our findings as the VLSL have a high atmospheric variability. Moreover the mixing ratios agree with previous observations of Schauffler et al. (1998), who found about 0.5 ppt of  $\text{CH}_2\text{Br}_2$  in the inner tropics at 15 km altitude while  $\text{CHBr}_3$  was near or below detection limit. Also in agreement with Schauffler et al. (1998) we observed  $\text{CH}_2\text{Br}_2$  up to 18.7 km. In common with chlorine, the organic bromine mixing ratio decreased with altitude in the stratosphere, but in contrast to chlorine no brominated organic substances were detected in both samples collected above 30 km.

### 3.3 Inorganic chlorine and bromine

Inorganic chlorine ( $\text{Cl}_y$ ) and bromine ( $\text{Br}_y$ ) can be calculated as the difference between the total amount of halogen which initially entered the stratosphere and the total measured halogen amount from organic substances. The stratospheric entry mixing ratio for each substance must be known for this calculation. As the air is ascending very slowly in the TTL and above the entry mixing ratio needs to be corrected for tropospheric time trends and how the air masses are mixed on their transport upwards. We use a procedure for the calculation of the mean stratospheric entry mixing ratios described by Engel et al. (2002). First for every sample the mean age of air was derived from measured  $\text{SF}_6$  mixing ratios. The mean age of air is a measure of the stratospheric residence time of an air parcel. According to Hall and Plumb, 1994 every stratospheric air parcel consists of a large number of irreversibly mixed parcels and its age can be described with a distribution function. The mean age of air is the centre of this function. As we can only calculate the mean age from our measurements we used a width parameterisation according to Engel et al. (2002) to derive the distribution function. Using this function and global tropospheric time trends we calculated the amount of trace gas that would be present without chemical degradation i.e. the mean entrance mixing ratio. Global tropospheric trend data was taken from NOAA-ESRL. For substances without these trend functions available a simplified procedure was applied. First we assumed that our sample at 15.2 km is reflecting the mean stratospheric entrance mixing ratio. For  $\text{CH}_3\text{Cl}$ , H2402 and the VSLs which show no systematic or significant global trend we took the observed mixing ratio in that sample as the stratospheric entry mixing ratio for all other samples. We assumed the same for F115, F114, F114a, F124 and H1202 but additionally corrected for their tropospheric trend to reconstruct the tropospheric time series backwards (extrapolated linear trend between 2003 and 2004 as reported in Table 1–2 of Clerbaux and Cunnold, 2007). The derived  $\text{Cl}_y$  and  $\text{Br}_y$  and the corresponding total chlorine and bromine from the entrance mixing ratios are depicted in Fig. 3. Please note, that the contribution from a product gas injection

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tion as derived by Law and Sturges, 2007 (40–50 ppt of chlorine) was not considered in our  $Cl_y$  calculation. For comparison with the measurements  $Cl_y$  and  $Br_y$  are also shown in Table 2.

The error of the estimated total chlorine/bromine  $\chi_{total}$  was derived as the sum of the measurement uncertainties of  $CH_3Cl$ , F115, F114, F114a, F124, H1202, H2402 and the VLSL according to Eq. (1) and  $\chi_{NOAA}$  – the standard deviations of the global mixing ratios for all other substances averaged over 2001 as provided by NOAA-ESRL. Both errors were calculated with respect to the number of chlorine/bromine atoms. The error of the inorganic chlorine/bromine  $\chi_y$  is the sum of  $\chi_{org}$  and  $\chi_{NOAA}$ . Please note that the influence of our measurements on  $Cl_y$ ,  $Br_y$  and the corresponding error bars decreases with altitude. Changes in  $Cl_y/Br_y$  due to mean age of air calculations carried out with  $SF_6$  mixing ratios  $\pm 2\sigma$  of the measured values were also calculated and ranged from  $-6$  to  $+2$  ppt for  $Cl_y$  and from  $-0.03$  to  $+0.03$  ppt for  $Br_y$ . We also estimated  $Cl_y/Br_y$  changes derived from different width parameterisations of the age distribution function. The  $Cl_y$  changes ranged from  $-8$  to  $+7$  ppt while  $Br_y$  varied between  $-0.04$  and  $+0.12$  ppt. We conclude that both uncertainties have little influence on the derived  $Cl_y/Br_y$ .

The derived  $Cl_y$  at 15.2 km is zero within the error bars ( $-0.1 \pm 31$  ppt) and proves the good agreement with most global tropospheric mixing ratio observations by NOAA-ESRL. Notable is the sharp increase to  $340 \pm 24$  ppt just above the tropopause, which is mostly caused by the rapid decomposition of the non-fluorinated chlorocarbons.

For  $Br_y$  low mixing ratios of  $1.8 \pm 1.2$  ppt at 16.4 km and  $3.6 \pm 1.1$  ppt at 17.4 km were inferred. At 34 km, where all organic bromine is destroyed we derived  $17.5 \pm 0.4$  ppt of  $Br_y$  based on the organic bromine from ground-based NOAA observations and our measurements in the TTL. During another balloon flight on the 17 June 2005 BrO was measured by the University of Heidelberg using Differential Optical Absorption Spectroscopy (DOAS). By using a photochemical model and correcting for the BrO/ $Br_y$  ratio they derived  $21.5 \pm 2.5$  ppt of  $Br_y$  at 33 km (Dorf, 2005). Thus, both calculations differ by 4.0 ppt but the significant uncertainty range of  $\pm 2.9$  ppt should be noted. A difference

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was also found in earlier studies (e.g. Salawitch et al., 2005; Feng et al., 2006, Law and Sturges, 2007) and a number of causes could account for it. Our observations and calculations are mainly based on the NOAA calibration scale. For instance the other large global monitoring network AGAGE found 0.72 ppt higher bromine from H1211 and H1301 in 2004 (see Table 1–2 in Clerbaux and Cunnold, 2007) probably reflecting differences in absolute calibration scales. This could explain a part of the difference in the derived  $Br_y$  values. Another possibility is that the observed TTL region did not represent global VSLS mean entrance mixing ratios to the stratosphere. An injection of higher amounts of source gases at different seasons, latitudes or longitudes due to the local influence of convection might have lead to higher  $Br_y$  (see e.g. Levine et al., 2007). Especially bromoform was found to be higher in other studies (Sinnhuber and Folkins, 2006; Law and Sturges, 2007). We could assume that the 3.5 ppt of bromine from VSLS in the upper tropical troposphere as estimated by Law and Sturges (2007) are more representative for air entering the stratosphere. If we calculate  $Br_y$  using this VSLS amount we find 19.75 ppt of  $Br_y$  which agrees with the  $21.5 \pm 2.5$  ppt derived from BrO (Dorf, 2005) even without deriving error bars.

A direct product gas injection as proposed by Ko et al. (1997) could also cause the difference in  $Br_y$  by bringing inorganic bromine species contained in the upper tropospheric aerosol (Murphy and Thompson, 2000) or in gaseous form into the stratosphere. Another option is the presence of additional brominated organic substances. As shown in Fig. 4 we have found substances showing signals at ions with  $m/z$  79 and 81 (the two stable isotopes of bromine) in the NICl chromatogram of the sample taken at 15.2 km altitude. We suggest four of these signals to belong to  $C_2H_5Br$  (bromoethane),  $CF_3CHClBr$  (halothane),  $C_3H_7Br$  (n-propyl bromide) and  $CH_2BrCH_2Br$  (1,2-dibromoethane) but at least four further unidentified signals remain. Please note, that in NICl mode the size of a peak is not indicative for its concentration. For instance, in Fig. 4  $CH_3Br$  appears as a small peak, but is more abundant than H1211. Some of the peaks were also present in samples taken at higher altitudes. These are strong indications for a further contribution from organic source gases to stratospheric

bromine.

## 4 Conclusions

Our study adds to the very few data available on VSLs in the tropical upper troposphere and lower stratosphere. From our measurements of 28 chloro- and bromo-carbons including ten very short-lived substances we derived a VSLs contribution of 6–8% (0.98–1.25 ppt) to total organic bromine and 1.1–1.4% (36.6–47.1 ppt) to total organic chlorine entering the stratosphere above Brazil in June 2005. In addition we have found strong indications for the presence of additional bromine source gases in this region. Identification and quantification of these substances is crucial for future estimates of stratospheric bromine. We derived  $Cl_y$  and  $Br_y$  values based on ground-based observations from NOAA-ESRL and our measurements.  $Br_y$  was calculated to be  $17.5 \pm 0.4$  ppt in 34 km altitude which is in disagreement with  $Br_y$  derived from quasi-simultaneous observations of BrO (Dorf, 2005). An additional source of stratospheric bromine is a likely explanation in order to reconcile  $Br_y$  derived from organic substances with  $Br_y$  derived from the measurements of BrO. However, if calibration uncertainties and the atmospheric variability of VSLs are taken into account the derived  $Br_y$  values could agree within their error bars. Further studies with higher spatial and temporal coverage and also a wider range of substances are needed to quantify the global influence of very short-lived brominated and chlorinated organic substances on stratospheric ozone. Differences in absolute calibration scales need to be resolved.

*Acknowledgements.* We would like to thank the European Space Agency, the Deutsches Zentrum fuer Luft- und Raumfahrt (project 50EE0016), the European Union (SCOUT-O3 project GOCE-CT-2003-505390) as well as the Deutsche Forschungsgesellschaft (CAWSES project EN 367/4) for funding and Elliot Atlas (University of Miami) for calibration. Furthermore we appreciate the work of the CNES balloon team who organised the campaign and of the NOAA-ESRL GMD teams who provided global tropospheric data.

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**Table 1.** Measured compounds grouped by substance classes with source of calibration and detection limits.

Substance group	Formula (name)	Calibration source	Detection limit [ppt]
CFCs	CF <sub>2</sub> CICF <sub>3</sub> (F115)	UEA	0.4
	CF <sub>2</sub> Cl <sub>2</sub> (F12)	NOAA-2001	0.3
	CF <sub>2</sub> CICF <sub>2</sub> Cl (F114)	UEA	0.2
	CFCl <sub>2</sub> CF <sub>3</sub> (F114a)	UEA	0.1
	CFCl <sub>3</sub> (F11)	NOAA-1993	0.1
	CFCl <sub>2</sub> CF <sub>2</sub> Cl (F113)	NOAA-2002	0.1
Halons	CF <sub>3</sub> Br (H1301)	NOAA-2006	0.4
	CF <sub>2</sub> ClBr (H1211)	NOAA-2006	0.6
	CF <sub>2</sub> BrCF <sub>2</sub> Br (H2402)	UEA	0.2
	CF <sub>2</sub> Br <sub>2</sub> (H1202)*	UEA	0.001
HCFCs	CHF <sub>2</sub> Cl (F22)	NOAA-2006	0.5
	CHFClCF <sub>3</sub> (F124)	U. Miami	0.4
	CH <sub>3</sub> CF <sub>2</sub> Cl (F142b)	NOAA-1994	0.3
	CH <sub>3</sub> CFCl <sub>2</sub> (F141b)	NOAA-1994	0.3
Longer-lived chloro- and bromocarbons	CH <sub>3</sub> Cl	NOAA-2003	19
	CCl <sub>4</sub>	NOAA-2002	0.2
	CH <sub>3</sub> CCl <sub>3</sub>	NOAA-2003	0.3
VSLS	CH <sub>3</sub> Br	NOAA-2003	0.4
	CH <sub>2</sub> Cl <sub>2</sub>	NOAA-1992	0.8
	CHCl <sub>3</sub>	NOAA-1992	0.4
	CH <sub>2</sub> ClCH <sub>2</sub> Cl	U. Miami	0.1
	C <sub>2</sub> HCl <sub>3</sub>	UEA	1.8
	C <sub>2</sub> Cl <sub>4</sub>	UEA	0.7
	CH <sub>2</sub> BrCl*	UEA	0.01
	CHBrCl <sub>2</sub> *	UEA	0.006
	CHBr <sub>2</sub> Cl*	UEA	0.003
	CH <sub>2</sub> Br <sub>2</sub> *	UEA	0.004
CHBr <sub>3</sub> *	UEA	0.007	

\*measured at the University of East Anglia.

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**Table 2.** The measured total organic halogen mixing ratios with  $1\sigma$  measurement and sample instability uncertainties in ppt. All samples were taken during balloon descent and represent altitude ranges, while  $\Theta$  is the potential temperature. Also shown are the derived inorganic mixing ratios in ppt. Their errors include our measurement uncertainties as well as the uncertainties from NOAA-ESRL ground-based measurements.

Altitude [km]	Range [km]	$\Theta$ [K]	Cl <sub>org</sub>	Cl <sub>org</sub> error	Br <sub>org</sub>	Br <sub>org</sub> error	Cl <sub>y</sub>	Cl <sub>y</sub> error	Br <sub>y</sub>	Br <sub>y</sub> error
34.00	1.5	1036.7	452	10	0.0	0.2	3062	11	17.5	0.4
31.94*	1.1	907.8	937	12	0.0	0.2	2558	13	17.5	0.4
30.01	0.7	819.7	1257	12	0.7	0.2	2228	13	16.7	0.4
28.17*	0.5	751.1	1422	12	1.0	0.3	2063	14	16.4	0.5
24.95	0.7	636.5	1771	14	2.4	0.4	1703	15	15.0	0.6
23.37	0.9	577.8	2221	16	2.3	0.3	1244	18	15.0	0.5
21.64	0.6	521.2	2447	18	5.7	0.5	1008	19	11.6	0.6
18.72	0.4	437.7	2996	24	12.5	0.9	444	26	4.6	1.1
17.37	0.3	402.5	3099	22	13.5	0.9	340	24	3.6	1.1
16.36	0.6	371.1	3377	29	15.3	1.0	55.7	30	1.8	1.2
15.20	0.5	359.2	3431	30	16.2	1.1	-0.1	31	0.9	1.2

\* Not measured at the University of East Anglia – several substances are not included (see Table 1).

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**Table 3.** Observed mixing ratios of CFCs, HCFCs and longer-lived non-fluorinated chloro- and bromocarbons in ppt (n. d. – not detected; n. m. – not measured). The mixing ratios of CH<sub>3</sub>Cl and CCl<sub>4</sub> were shifted due to drifts in the sample canisters.

Substance	Altitude [km] / Mixing ratio [ppt]											
	15.20	16.36	17.37	18.72	21.64	23.37	24.95	28.17	30.01	31.94	34.00	
CF <sub>2</sub> Cl <sub>2</sub> (F12)	538.7	537.8	530.4	523.8	492.8	465.8	435.5	375.0	353.4	252.1	103.9	
CFCl <sub>3</sub> (F11)	254.8	252.1	243.9	233.7	187.9	143.6	87.54	28.04	14.32	1.55	n. d.	
CF <sub>2</sub> CICFCI <sub>2</sub> (F113)	80.90	80.89	78.05	70.76	72.49	68.90	43.57	49.87	43.85	27.21	7.84	
CF <sub>2</sub> CICF <sub>2</sub> Cl (F114)	16.65	16.66	16.58	16.36	16.39	16.12	15.06	15.5	15.35	14.92	13.28	
C <sub>2</sub> F <sub>5</sub> Cl (F115)	8.82	8.97	8.76	8.94	8.73	8.48	8.48	8.38	8.29	8.14	7.82	
CF <sub>3</sub> CFCl <sub>2</sub> (F114a)	2.05	2.01	1.94	1.69	1.70	1.58	1.48	1.25	1.19	n. d.	n. d.	
CHF <sub>2</sub> Cl (F22)	164.0	160.3	152.6	151.1	142.2	138.6	125.1	130.5	130.8	121.2	102.9	
CH <sub>3</sub> CFCl <sub>2</sub> (F141b)	18.05	17.35	16.65	15.01	14.62	13.17	8.76	8.73	7.45	3.98	0.87	
CH <sub>3</sub> CF <sub>2</sub> Cl (F142b)	15.27	15.04	14.39	14.31	13.66	13.18	11.69	12.14	12.02	11.26	9.65	
CHFClCF <sub>3</sub> (F124)	1.61	1.56	1.48	1.33	1.32	1.08	0.66	0.69	0.66	0.69	0.41	
CH <sub>3</sub> Cl	600.9	570.8	459.8	427.3	182.9	254.6	241.4	224.0	171.0	164.8	71.84	
CCl <sub>4</sub>	93.50	93.70	75.52	77.47	58.54	37.58	12.51	1.63	n. d.	n. d.	n. d.	
CH <sub>3</sub> CCl <sub>3</sub>	19.22	19.50	18.08	16.11	9.96	7.98	4.82	n. d.	0.61	n. d.	n. d.	
CH <sub>3</sub> Br	6.68	6.05	5.28	4.66	1.13	n. d.	0.54	n. d.	n. d.	n. d.	n. d.	
CF <sub>2</sub> ClBr (H1211)	4.17	4.13	3.9	3.89	1.93	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	
CF <sub>3</sub> Br (H1301)	3.19	3.18	3.25	3.01	2.55	2.24	1.84	1.00	0.71	n. d.	n. d.	
CF <sub>2</sub> BrCF <sub>2</sub> Br (H2402)	0.43	0.46	0.35	0.30	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	n. d.	
CF <sub>2</sub> Br <sub>2</sub> (H1202)	0.034	0.035	0.029	0.031	0.018	0.010	0.002	n. m.	n. d.	n. m.	n. d.	

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**Table 4.** Observed mixing ratios of VSLS in ppt.  $C_2Cl_4$  (1.0 ppt) and  $CHBr_3$  (0.016 ppt) were only detected at 15.2 km and are not listed.  $CHClBr_2$  and  $C_2HCl_3$  were below detection limit (n. d. - not detected). The mixing ratios of  $CH_2ClCH_2Cl$  were shifted due to drifts in the sample canisters.

Altitude [km]	$CH_2Cl_2$ [ppt]	$CHCl_3$ [ppt]	$CH_2ClCH_2Cl$ [ppt]	$CH_2BrCl$ [ppt]	$CHBrCl_2$ [ppt]	$CH_2Br_2$ [ppt]
18.72	1.9	n. d.	n. d.	0.020	n. d.	0.139
17.37	2.3	n. d.	n. d.	0.030	n. d.	0.147
16.36	9.8	1.9	5.6	0.090	0.010	0.439
15.20	11.2	2.7	6.2	0.087	0.017	0.549

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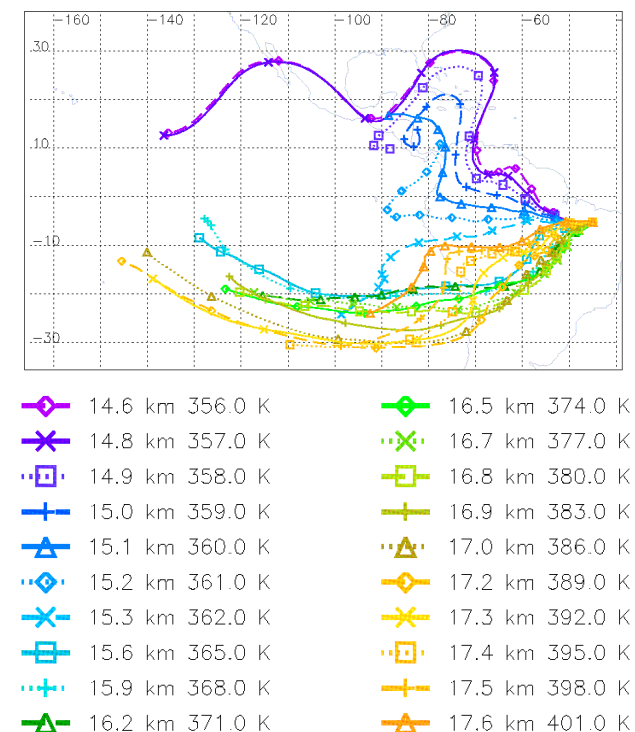
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**Fig. 1.** Ten-day backward trajectories calculated with a resolution of  $1.25^\circ \times 1.25^\circ$  on 59 potential temperature levels. They were initialised at  $5.28^\circ \text{S}$  and  $44.99^\circ \text{W}$  within the TTL on 8 June 2005. The trajectories show, that the air around 15 km was coming from North-West while the air around 16.5 km was coming from South-West both travelling over the South American continent.

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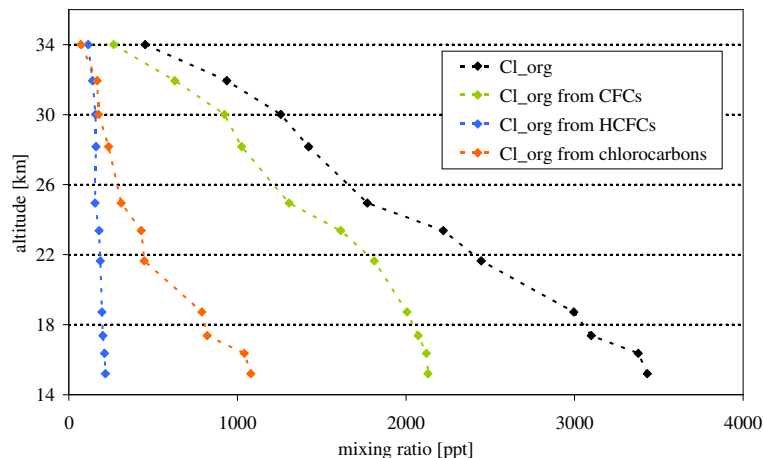
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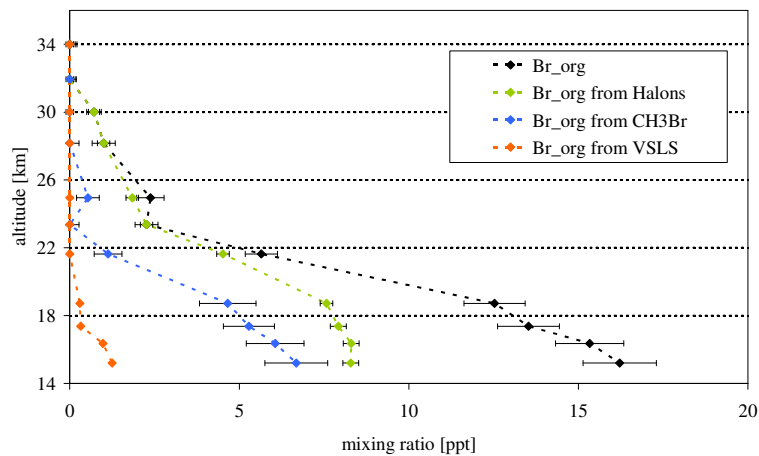


**Fig. 2a.** Total mixing ratios of chlorine from organic source gases ( $\text{Cl}_{\text{org}}$ ) and contributions of substance subgroups to that total in the different altitudes. The data for chlorocarbons include VSLs and non-fluorinated longer-lived chlorocarbons (see Tables). Chlorine from H1211 is only included in the  $\text{Cl}_{\text{org}}$ . The error bars are less than the size of the symbols and include the  $1\sigma$  uncertainties of the measurements and the sample instability errors if observed.

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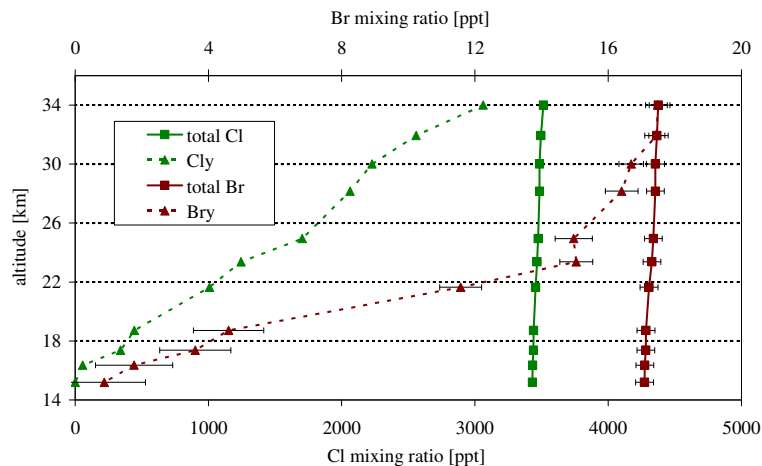
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**Fig. 2b.** The same as Fig. 2a but for bromine.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



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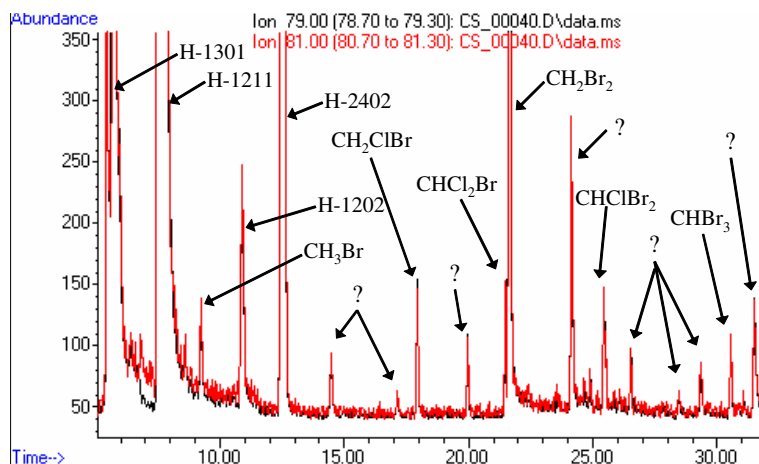


**Fig. 3.** The derived inorganic chlorine ( $Cl_y$ ) and bromine ( $Br_y$ ) and the corresponding total Cl and Br for the different altitudes. The error bars are the same as in Table 2 and less than the size of the symbols for chlorine.

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## Contribution of VSLS to stratospheric chlorine and bromine

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**Fig. 4.** The chromatogram of the air sample collected at 15.2 km altitude as analysed with GC-NICI-MS at the University of East Anglia. The displayed ions with a mass/charge ratio of 79 and 81 in a ratio of 1:1 are specific for bromine containing species which indicates that at least eight additional brominated substances are present in the tropical tropopause region. The peaks at about 14.5, 17, 20 and 26.5 min retention time are suggested to belong to  $C_2H_5Br$  (bromoethane),  $CF_3CHClBr$  (halothane),  $C_3H_7Br$  (n-propyl bromide) and  $CH_2BrCH_2Br$  (1,2-dibromoethane) but four further unidentified brominated compounds remain.

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