Atmos. Chem. Phys., 8, 7325–7334, 2008
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Atmospheric Chemistry and Physics

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

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Received: 17 March 2008 – Published in Atmos. Chem. Phys. Discuss.: 7 May 2008
Revised: 15 September 2008 – Accepted: 30 October 2008 – Published: 11 December 2008

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 altitudes between 15 and 17 km we found 1.1–1.4% of the chlorine and 6–8% of the bromine to be present in the form of very short-lived organic 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 the decomposition of both long- and short-lived 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 mainly present in the form of BrO, Br, HOBr, $BrONO_2$ and HBr. These species and the corresponding chlorine species (including BrCl and Cl_2O_2) are responsible for the catalytic destruction of ozone (e.g. Solomon, 1999). 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 (VSLS) on that total remains unsure. Bromine has, on average and on a per atom basis, a 60 times higher efficiency to destroy ozone than chlorine (WMO, 2007). 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 are very few measurements in the main stratospheric entrance region, the tropical tropopause layer (TTL) or above in the tropical lower stratosphere. Published observations of organic VSLS in the inner tropics above 15 km are presented in Schauffler et al. (1998, 1999), Sinnhuber and Folkins (2006) and Law and Sturges (2007). Schauffler et al. 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 available data at altitudes between 10 and 17.5 km from six measurement campaigns that were carried out within a period of eight years (1996–2004) to

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assess 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 (see e.g. the data set presented in Law and Sturges, 2007).

2 Analytical procedures

2.1 Sampling techniques

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 ENVISAT satellite. Between 15.2 and 34 km altitude 15 samples were collected by pumping air cryogenically into electropolished stainless steel containers (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.

2.2 Measurement techniques

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, see also Worton et al. (2008) for further analytical details) 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°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; Worton et al., 2008). 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 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.

2.3 Air mass origin

Quasi-isentropic trajectories were calculated by the Free University Berlin (FUB) using a model (Langematz et al., 1987; Reimer and Kaupp, 1997) with a resolution of $1.25° \times 1.25°$ and 59 potential temperature levels and operational ECMWF fields as meteorological input. Above 380 K heating rates were calculated using the radiative transfer scheme of the SLIMCAT 3-D chemical transport model (Chipperfield, 1999). SLIMCAT heating rates are not available below 380 K. Therefore, diabatic motions below 380 K were derived based on climatological heating rates and a Newtonian cooling approach. This yields to an ascent of the air masses from +0.3 K/day around 356 K of up to 0.8 K/day around 400 K. 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 trajectories 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 air masses originating from both hemispheres.

3 Quality assurance

3.1 Concentration drift and blank correction

It is a known problem that many organic trace gases drift in concentrations if stored in metal containers for longer time periods. These changes depend e.g. on the nature, past use, and pre-treatment of the container surface, the compound, the container pressure, the storage temperature, the ozone content and the water vapour content (Finlayson-Pitts and Pitts, 2000). They can be caused by adsorption or chemical reactions e.g. on active spots of the container walls (Pate et al., 1992; Apel et al., 1994). Surface passivations via fluorination or electro-polishing are common techniques to avoid wall reactions (e.g. Blake et al., 1994) but this is not sufficient

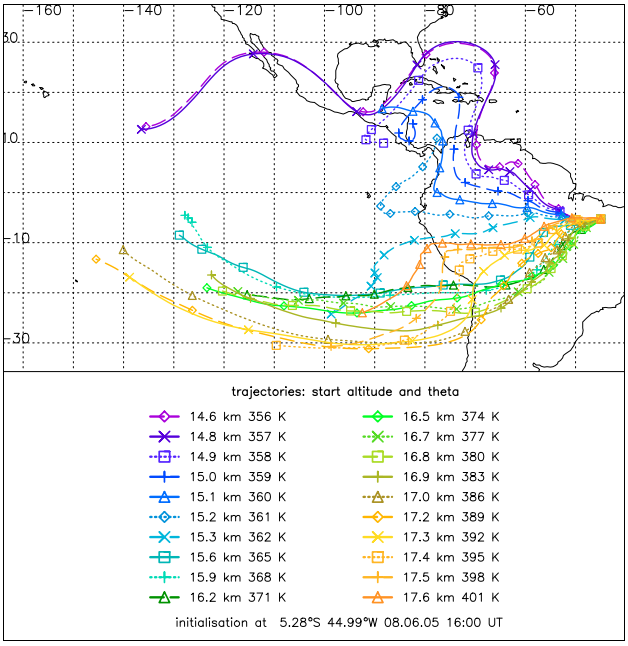

Fig. 1. Quasi-isentropic ten-day backward trajectories calculated with a resolution of 1.25°×1.254° on 59 potential temperature levels. They were initialised at 5.28° S and 44.99° W within the TTL on 8 June 2005. The trajectories show, that the sampled air was coming from both hemispheres.

in all cases. Positive changes with time have also been observed in containers. They can originate from uptake into a film of water on the container surface which can be reversed if pressure is reduced as samples are removed from the container (Finlayson-Pitts and Pitts, 2000).

To assure the quality of the data, three of the sample containers were measured again in August 2007 at the University of Frankfurt. A list of the quantified compounds, their source of calibration and detection limits can be found in Table 1. The chlorofluorocarbons (CFCs), hydro-chlorofluorocarbons (HCFCs) and halons proved to be stable, whereas the CH_3Cl, $CH_2Cl{-}CH_2Cl$ and CCl_4 mixing ratios had drifted systematically in the containers. If changes occurred in all containers that contained the substance they were assumed to be systematic if the mean percentage change exceeded the percentage 1σ standard deviation of the samples concentration changes. This means that the variability of the concentration changes did not exceed the changes itself. 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% (22.4 ppt) per month for CH_3Cl, of 2.90% (0.01 ppt) for CH_2ClCH_2Cl and a decrease of 1.57% (4.06 ppt) per month for CCl_4 relative to their initially measured values. The mixing ratios of these substances in the air samples were corrected by linear extrapolation of the calculated trends to the flight date. Five other substances – CH_2Cl_2, $CHCl_3$, CH_3CCl_3, C_2Cl_4 and CH_3Br – 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 ±0.6% per month) was added to the error bars as a systematic error (see below). The substances measured at the UEA could not be rechecked except for the CH_2Br_2 content of one sample which was the same within the measurement uncertainties. Moreover, low mixing ratios of up to 2.7 ppt of CH_2Cl_2 were detected in some samples collected above 19 km. As CH_2Cl_2 should be completely depleted at these altitudes we suggest non-systematic processes in the containers (such as out gassing from container valves or production reactions) as an explanation and included these blank values in our error calculation. For the other VSLS we found rather uniform container and system blanks, which were below 0.02 ppt for all species and corrected for them.

3.2 Intercomparison with ground-based observations

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 Administration (NOAA), USA. Longer-lived trace gases show rather uniform concentrations in the global background and upper troposphere because their atmospheric lifetimes are high compared with the corresponding 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. These mixing ratios are publicly available and can be accessed as anonymous ftp data under http://www.esrl.noaa.gov/gmd/. The measurements of F12, F11, F113, F22, F142b, F141b, CCl_4, CH_3CCl_3 and H1211 agreed within 3%. In combination with the observed low VSLS mixing ratios (see below) this indicates that a well mixed air mass with little influence from local deep convection was sampled (VSLS would be super-elevated in the case of convective influence). Moreover it provides evidence, that the samples were not contaminated e.g. by balloon exhaust. 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 2σ measurement uncertainties. The second is CH_3Br 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), by its latitudinal gradient or by a decrease due to instability within this particular sample container. The third substance showing a difference to NOAA-ESRL values was CH_3Cl. We found 601 ppt of CH_3Cl at 15 km while the globally averaged mixing ratio at ground levels in June 2005 was 538 ppt (source: http://www.esrl.noaa.gov/gmd/). One possible explanation

Table 1. Measured compounds grouped by substance classes with source of calibration and detection limits. All NOAA calibrations originate from a calibrated container obtained from NOAA-ESRL and were transferred to an internal secondary calibration container used for sample measurements. The years indicate the revision of the calibration scale. The University of East Anglia (UEA), UK calibrations originate from a direct cross-comparison of that secondary container with an internal secondary UEA calibration container for C_2HCl_3 and C_2Cl_4. Four substances were calibrated using air samples from UEA which were measured twice at both institutes: F115, F114, F114a and H2402. The remaining substances – 1,2-dichloroethane and F124 – were quantified via a cross-comparison with a container calibrated by E. Atlas of the University of Miami, USA which is owned by the Max-Planck-Institute for Chemistry in Mainz, GER.

Substance group	Formula (name)	Calibration source	Detection limit [ppt]
CFCs	CF_2ClCF_3 (F115)	UEA	0.4
	CF_2Cl_2 (F12)	NOAA-2001	0.3
	CF_2ClCF_2Cl (F114)	UEA	0.2
	$CFCl_2CF_3$ (F114a)	UEA	0.1
	$CFCl_3$ (F11)	NOAA-1993	0.1
	$CFCl_2CF_2Cl$ (F113)	NOAA-2002	0.1
Halons	CF_3Br (H1301)	NOAA-2006	0.4
	CF_2ClBr (H1211)	NOAA-2006	0.6
	CF_2BrCF_2Br (H2402)	UEA	0.2
	CF_2Br_2 (H1202)*	UEA	0.002
HCFCs	CHF_2Cl (F22)	NOAA-2006	0.5
	$CHFClCF_3$ (F124)	U. Miami	0.4
	CH_3CF_2Cl (F142b)	NOAA-1994	0.3
	CH_3CFCl_2 (F141b)	NOAA-1994	0.3
Longer-lived chloro- and bromocarbons	CH_3Cl	NOAA-2003	19
	CCl_4	NOAA-2002	0.2
	CH_3CCl_3	NOAA-2003	0.3
	CH_3Br	NOAA-2003	0.4
VSLS	CH_2Cl_2	NOAA-1992	0.8
	$CHCl_3$	NOAA-1992	0.4
	CH_2ClCH_2Cl	U. Miami	0.1
	C_2HCl_3	UEA	1.8
	C_2Cl_4	UEA	0.7
	CH_2BrCl*	UEA	0.01
	$CHBrCl_2$*	UEA	0.0008
	$CHBr_2Cl$*	UEA	0.001
	CH_2Br_2*	UEA	0.001
	$CHBr_3$*	UEA	0.001

* measured at the University of East Anglia (UEA)

could be that our correction of the drift in the containers was insufficient. However, the tropics are a source region of CH_3Cl. For instance Khalil and Rasmussen (1999) reported elevated surface mixing ratios in tropical regions and Gebhardt et al. (2008) found levels around 600 ppt for CH_3Cl in air samples taken at altitudes around 10 km above Surinam in October 2005. As CH_3Cl is longer-lived in the atmosphere the observed elevated mixing ratio could e.g. originate from the rainforest without being influenced from local convection.

3.3 Error bar calculations

The error bars of the measured organic chlorine and bromine χ_{org} (see Sect. 4.1) include the 1σ 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.

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

The sample instability errors e_{si} (if observed) are systematic errors. For that reason they were summed up separately. Due

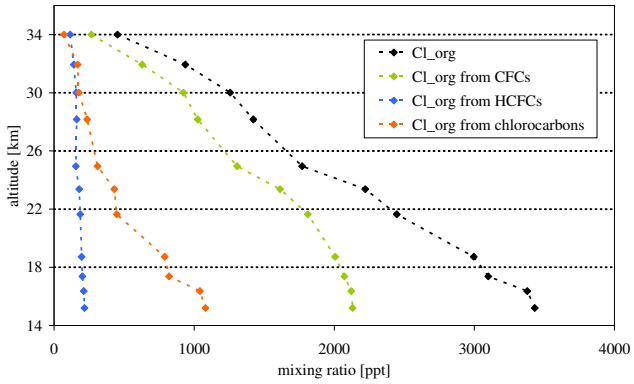

Fig. 2a. Total mixing ratios of chlorine from organic source gases (Cl_{org}) and contributions of substance subgroups to that total in the different altitudes. The data for chlorocarbons include VSLS and non-fluorinated longer-lived chlorocarbons (see Tables). Chlorine from H1211 is only included in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

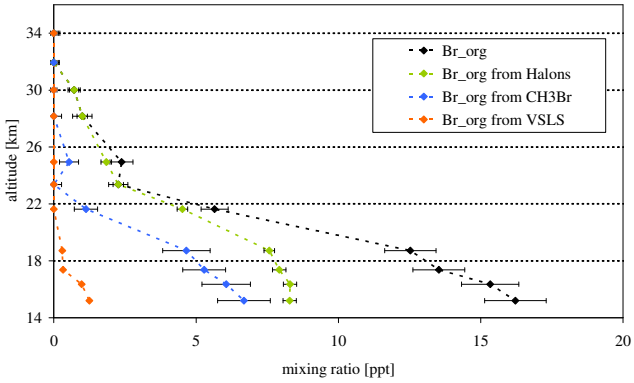

Fig. 2b. The same as Fig. 2a but for bromine.

to the limited amount of air available from the containers the samples where measured only twice. Thus σ_{sm} is the standard deviation of the calibration standard on the measuring day. We used a secondary standard for the measurements. Therefore σ_{ct} is the standard deviation from the calibration of that standard. As σ_{sm} and σ_{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.

The error of the estimated total chlorine/bromine χ_{total} (see Sect. 4.2) was derived as the sum of the measurement uncertainties of CH_3Cl, F115, F114, F114a, F124, H1202, H2402 and the VSLS according to Eq. (1) and χ_{NOAA} – the standard deviations of the global mixing ratios for all other substances averaged over 2001 as provided by NOAA-ESRL (source: http://www.esrl.noaa.gov/gmd/). Both errors were calculated with respect to the number of chlorine/bromine atoms. The error of the inorganic chlorine/bromine χ_y is the sum of χ_{org} and χ_{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. Uncertainties which could originate from hemispheric mixing ratio gradients were not estimated.

4 Results and discussion

4.1 Organic chlorine and bromine

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 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, due to the high variability of VSLS in the troposphere and since many processes influence the composition of the tropical region around 15 km (see e.g. Tuck et al., 2004) we do not claim global significance for the mixing ratios found in 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 more 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. 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 containers. Thus, the values for total organic bromine and chlorine in these samples do not include the mixing ratios of H1202, CH_2BrCl, $CHBrCl_2$, CH_2Br_2, $CHBr_2Cl$ and $CHBr_3$ (see Tables 3 and 4). 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 container 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

Table 2. The measured total organic halogen mixing ratios with 1σ measurement and sample instability uncertainties in ppt. All samples where taken during balloon descent and represent altitude ranges, while Θ 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]	Θ [K]	Cl_{org}	Cl_{org} error	Br_{org}	Br_{org} error	Cl_y	Cl_y error	Br_y	Br_y 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	55.6	30	1.8	1.2
15.20	0.5	359.2	3431	30	16.2	1.1	−0.2	31	0.9	1.2

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

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_3Cl and CCl_4 were shifted due to drifts in the sample containers.

	Altitude [km]/Mixing ratio [ppt]										
Substance	15.20	16.36	17.37	18.72	21.64	23.37	24.95	28.17	30.01	31.94	34.00
CF_2Cl_2 (F12)	538.7	537.8	530.4	523.8	492.8	465.8	435.5	375.0	353.4	252.1	103.9
$CFCl_3$ (F11)	254.8	252.1	243.9	233.7	187.9	143.6	87.54	28.04	14.32	1.55	n.d.
$CF_2ClCFCl_2$ (F113)	80.90	80.89	78.05	70.76	72.49	68.90	43.57	49.87	43.85	27.21	7.84
CF_2ClCF_2Cl (F114)	16.65	16.66	16.58	16.36	16.39	16.12	15.06	15.5	15.35	14.92	13.28
C_2F_5Cl (F115)	8.82	8.97	8.76	8.94	8.73	8.48	8.48	8.38	8.29	8.14	7.82
CF_3CFCl_2 (F114a)	2.05	2.01	1.94	1.69	1.70	1.58	1.48	1.25	1.19	n.d.	n.d.
CHF_2Cl (F22)	164.0	160.3	152.6	151.1	142.2	138.6	125.1	130.5	130.8	121.2	102.9
CH_3CFCl_2 (F141b)	18.05	17.35	16.65	15.01	14.62	13.17	8.76	8.73	7.45	3.98	0.87
CH_3CF_2Cl (F142b)	15.27	15.04	14.39	14.31	13.66	13.18	11.69	12.14	12.02	11.26	9.65
$CHFClCF_3$ (F124)	1.68	1.64	1.55	1.40	1.38	1.13	0.69	0.73	0.69	0.72	0.43
CH_3Cl	600.9	570.8	459.8	427.3	182.9	254.6	241.4	224.0	171.0	164.8	71.84
CCl_4	93.50	93.70	75.52	77.47	58.54	37.58	12.51	1.63	n.d.	n.d.	n.d.
CH_3CCl_3	19.22	19.50	18.08	16.11	9.96	7.98	4.82	n.d.	0.61	n.d.	n.d.
CH_3Br	6.68	6.05	5.28	4.66	1.13	n.d.	0.54	n.d.	n.d.	n.d.	n.d.
CF_2ClBr (H1211)	4.17	4.13	3.9	3.89	1.93	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CF_3Br (H1301)	3.19	3.18	3.25	3.01	2.55	2.24	1.84	1.00	0.71	n.d.	n.d.
CF_2BrCF_2Br (H2402)	0.43	0.46	0.35	0.30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
CF_2Br_2 (H1202)	0.034	0.035	0.029	0.031	0.018	0.010	0.002	n.m.	n.d.	n.m.	n.d.

four lowest altitude samples can be found. C_2Cl_4 (1.02 ppt) and $CHBr_3$ (0.016 ppt) could only be detected in the sample collected at 15.2 km and are therefore not listed. $CHClBr_2$ and C_2HCl_3 were below detection limit (see Table 1) for all samples.

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_2Cl_2(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 Sturges (2007) that

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 containers.

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

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 VSLS in the tropical upper troposphere. This agrees with our findings within the given error bars. At 16.4 km we found 3377±30 ppt of organic chlorine with 1.1% (36.6±5.1 ppt) from VSLS. 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±10 ppt. This corresponds to about 13% of the amount observed in the TTL.

Organic bromine at 15.2 km was 16.2±1.1 ppt with 51% present in the form of halons, 41% in the form of CH_3Br and 8% (1.25±0.08 ppt) originating from the five brominated VSLS listed in Table 4. In 16.4 km we found a mixing ratio of bromine from VSLS of about 0.98±0.08 ppt (6%). Both VSLS 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 CH_2Br_2 with a mixing ratio of 0.55±0.001 ppt at 15.2 km to be the dominant very short-lived source gas while the $CHBr_3$ mixing ratio was very low (0.016±0.005 ppt) in this sample. Sinnhuber and Folkins (2006) presented higher $CHBr_3$ 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 VSLS 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 CH_2Br_2 in the inner tropics at 15 km altitude while $CHBr_3$ was near or below detection limit. Also in agreement with Schauffler et al. (1998) we observed CH_2Br_2 and CH_2Cl_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.

4.2 Inorganic chlorine and bromine

Inorganic chlorine (Cl_y) and bromine (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 used 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 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 CH_3Cl, 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 Cl_y and 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 as derived by Law and

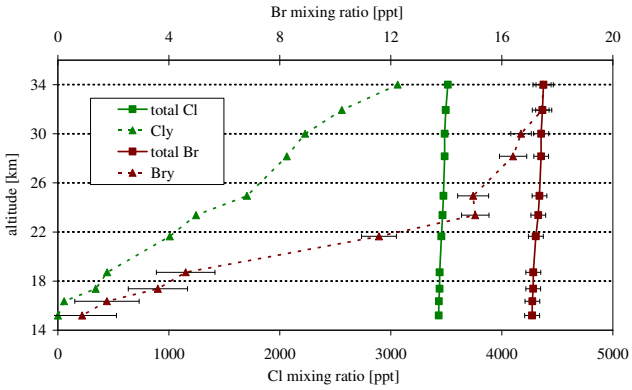

Fig. 3. The derived inorganic chlorine (Cl_y) and bromine (Br_y) and the corresponding total Cl and Br for the different altitudes. The error bars are the same as in Table 2 and less than the size of the symbols for chlorine.

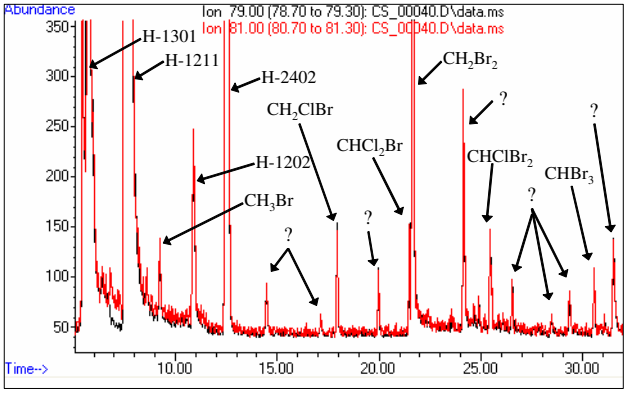

Fig. 4. The chromatogram of the air sample collected at 15.2 km altitude as analysed with GC-NICI-MS at the University of East Anglia. The displayed ions with a mass/charge ratio of 79 and 81 in a ratio of 1:1 are specific for bromine containing species which indicates that at least eight additional 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.

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 derived Cl_y at 15.2 km is zero within the error bars (-0.2 ± 31 ppt) and proves the good agreement with most global tropospheric mixing ratio observations by NOAA-ESRL. Notable is the sharp increase to 340 ± 24 ppt just above the tropopause, which is mostly due to the rapid decomposition of CH_3Cl and CCl_4.

For Br_y low mixing ratios of 1.8 ± 1.2 ppt at 16.4 km and 3.6 ± 1.1 ppt at 17.4 km were inferred. At 34 km, where all organic bromine is destroyed we derived 17.5 ± 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 ± 2.5 ppt of Br_y at 33 km (Dorf, 2005; Dorf et al., 2008). Thus, both calculations differ by 4.0 ppt but the significant uncertainty range of ±2.9 ppt should be noted. A difference 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 http://agage.eas.gatech.edu/ or 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 ± 2.5 ppt derived from BrO (Dorf, 2005; Dorf et al., 2008) 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 NICI 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 NICI 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.

5 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 bromocarbons 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±0.4 ppt in 34 km altitude which is in disagreement with Br_y derived from quasi-simultaneous observations of BrO (Dorf, 2005; Dorf et al., 2008). 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, Elliot Atlas (University of Miami) in combination with Sarah Gebhardt (Max-Planck-Institute for Chemistry in Mainz) for calibration and Martyn Chipperfield for providing heating rates. Furthermore we appreciate the contribution of the anonymous referees, the work of the CNES balloon team who organised the campaign and of the NOAA-ESRL GMD teams who provided global tropospheric data.

Edited by: M. V. Roozendael

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