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Very short-lived bromomethanes measured by the CARIBIC observatory over the North Atlantic, Africa and Southeast Asia during 2009–2013

A. Wisher[1], D. E. Oram[2], J. C. Laube[1], G. P. Mills[1], P. van Velthoven[3], A. Zahn[4], and C. A. M. Brenninkmeijer[5]

[1]Centre for Ocean and Atmospheric Sciences (COAS), School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
[2]National Center for Atmospheric Science (NCAS), Centre for Ocean and Atmospheric Sciences (COAS), School of Environmental Sciences, University of East Anglia, Norwich, NR4 7TJ, UK
[3]Royal Netherlands Meteorological Institute (KNMI), P.O. Box 201, 3730 AE, de Bilt, the Netherlands
[4]Karlsruhe Institute of Technology-Atmospheric Trace Gases and Remote Sensing (IMK-ASF), Postfach 36 40, 76021, Karlsruhe, Germany
[5]Max Planck Institute for Chemistry, Air Chemistry Division, Hahn-Meitner Weg 1, 55128, Mainz, Germany

Correspondence to: A. Wisher (a.wisher@uea.ac.uk)

Abstract. Short-lived organic brominated compounds make up a significant part of the organic bromine budget in the atmosphere. Emissions of these compounds are highly variable and there are limited measurements, particularly in the extra-tropical upper troposphere/lower stratosphere and tropical troposphere. Measurements of five very short-lived bromomethanes (VSLB) were made in air samples collected on the CARIBIC project aircraft over three flight routes; Germany to Venezuela/Columbia during 2009–2011, Germany to South Africa during 2010 and 2011 and Germany to Thailand/Kuala Lumpur, Malaysia during 2012 and 2013.

In the tropical troposphere, as the most important entrance region to the stratosphere, we observe a total mean organic bromine derived from these compounds across all flights at 10–12 km altitude of 3.4 ± 1.5 ppt. Individual mean tropical tropospheric mixing ratios across all flights were 0.43, 0.74, 0.14, 0.23 and 0.11 ppt for $CHBr_3$, CH_2Br_2, $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl respectively. The highest levels of VSLB-derived bromine (4.20 ± 0.56 ppt) were observed in flights between Bangkok and Kuala Lumpur indicating that the South China Sea is an important source region for these compounds. Across all routes, $CHBr_3$ and CH_2Br_2 accounted for 34 % (4.7–71) and 48 % (14–73) respectively

of total bromine derived from the analysed VSLB in the tropical mid-upper troposphere totalling 82 % (54–89).

In samples collected between Germany and Venezuela/Columbia, we find decreasing mean mixing ratios with increasing potential temperature in the extra-tropics. Tropical mean mixing ratios are higher than extra-tropical values between 340–350 K indicating that rapid uplift is important in determining mixing ratios in the lower tropical tropopause layer in the West Atlantic tropics.

O_3 was used as a tracer for stratospherically influenced air and we detect rapidly decreasing mixing ratios for all VSLB above ~ 100 ppb O_3 corresponding to the extra-tropical tropopause layer.

1 Introduction

Chlorinated and brominated organic compounds have the potential to catalytically destroy ozone in the stratosphere via processes involving the inorganic products of photochemical decomposition. The influence of long-lived anthropogenic species such as chlorofluorocarbons (CFCs), bromochlorofluorocarbons and bromofluorocarbons (halons) is well documented. However, short-lived

compounds with lifetimes of less than ~ 6 months, termed very short-lived substances (VSLS), can also transport significant quantities of reactive halogens to the stratosphere. The most significant biogenic brominated VSLS are bromoform ($CH Br_3$), dibromomethane ($CH_2 Br_2$), dibromochloromethane ($CH Br_2 Cl$), bromodichloromethane ($CH Br Cl_2$) and bromochloromethane ($CH_2 Br Cl$). These very short-lived brominated compounds (VSLB) are emitted predominantly from natural sources namely macroalgae in coastal regions and oceanic phytoplankton (e.g. Leedham et al., 2013; Brinckmann et al., 2012; Carpenter et al., 2009; Montzka and Reimann, 2011). There are also minor contributions of trihalomethanes from drinking water chlorination and power plant cooling water (Quack and Wallace, 2003).

Recent WMO reports (Law and Sturges, 2007; Montzka and Reimann, 2011) indicate that natural halocarbon emissions are associated with significant stratospheric O_3 depletion. Bromine has an ~ 60 times higher efficiency, on average and on a per atom basis, to destroy ozone than chlorine (Sinnhuber et al., 2009). This, combined with the highly variable spatial and temporal distribution of VSLS in the troposphere, indicates that even at low mixing ratios, brominated VSLS species could contribute significantly to stratospheric ozone depletion. Hossaini et al. (2012a) suggest that VSLS source gas injection into the stratosphere is likely to increase in response to future climate change. Furthermore, as levels of anthropogenic halogenated source gases are predicted to decrease (e.g. Montzka and Reimann, 2011), as a result of the Montreal Protocol, biogenic halocarbons including bromomethanes will become proportionally more significant in the future. Additionally, there is a relative paucity of measurements in the region of the upper troposphere/lower stratosphere (UTLS); an important region when considering the transport of compounds into the stratosphere.

Currently, the best estimate of the contribution of brominated VSLS to inorganic bromine in the stratosphere, as inferred from measurements of inorganic decomposition products such as BrO, is 6 (range 3–8) ppt (Montzka and Reimann, 2011) which represents ~ 27 % (13–36) of total stratospheric bromine. Uncertainties in this estimate include the high degree of variability in source emissions, limited understanding of transport pathways to the upper tropical tropopause, differences in calibration scales between measurements, limited spatial and temporal data coverage and uncertainties in kinetic parameters used to calculate decomposition rates.

Within the tropics, the region between the level of maximum convective outflow (345 K potential temperature, ~ 12 km) and the cold point tropopause (380 K potential temperature, ~ 17 km) is termed the tropical tropopause layer (TTL) (Law and Sturges, 2007). The TTL acts as a source region for the stratospheric overworld and the extra-tropical lowermost stratosphere. Therefore, mixing ratios of halogenated compounds (including VSLB) in this region are crucial for understanding stratospheric ozone depletion in the lower and upper stratosphere.

Although it is not as significant for upper stratospheric ozone depletion, the extra-tropical UTLS is of interest as bidirectional transport influences the chemistry of the upper troposphere (UT) and lower stratosphere (LS). This region is also of significance due to its strong influence on surface climate, climate feedbacks and tropospheric weather regimes (e.g. Gettelman et al., 2011). The chemical, radiative and dynamical properties of this region are coupled. Therefore, changes in chemistry in the UTLS may have consequences for tropospheric chemistry (Anderson et al., 2012) and climate (Riese et al., 2012). Additionally, it is possible that future climate change may impact on VSLB transport into the UTLS through changes in oceanic emissions as ocean temperature and acidity change and also through atmospheric processes such as increased convection and large-scale vertical transport (Dessens et al., 2009) or sea surface temperature, wind speed and marine boundary layer height (Hepach et al., 2014). These factors might increase the quantity of VSLB transported to the UTLS and hence, impact on stratospheric ozone.

The CARIBIC project (Containerised Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container, www.caribic-atmospheric.com) has, since 2005, made regular deployments of a fully automated container-based atmospheric laboratory aboard a Lufthansa Airlines Airbus A340–600 (Brenninkmeijer et al., 2007). Flights originate in Frankfurt (Germany) with routes to North America, Asia, Africa and South America. At cruising altitudes (approximately 10–12 km), the aircraft typically intersects air masses representative of the free troposphere in the tropics, and both the upper troposphere and lowermost stratosphere (UT/LMS) at mid- to high latitudes. The UT/LMS is of particular interest as this is a complex region of the atmosphere with a limited number of measurements made within it. During each flight, real-time trace-gas and aerosol measurements are made alongside the collection of whole-air samples. A subset of whole-air samples have been analysed for VSLB ($CH Br_3$, $CH_2 Br_2$, $CH Br_2 Cl$, $CH Br Cl_2$ and $CH_2 Br Cl$) (Sect. 2). Here we provide a description of the analysis of VSLB in CARIBIC and the results obtained.

2　Methods

The CARIBIC container instrumentation carries out a number of in situ measurements during each flight (Brenninkmeijer et al., 2007). In addition, whole-air samples are collected for later laboratory analysis. A detailed description of CARIBIC sample collection can be found in Baker et al. (2011a). The whole-air sampler unit consists of a pumping unit and two TRAC (Triggered Retrospective Air Collector) sampling units. Each TRAC contains 14 2.7 L glass sampling flasks with a normal flight consisting of 14 samples taken on
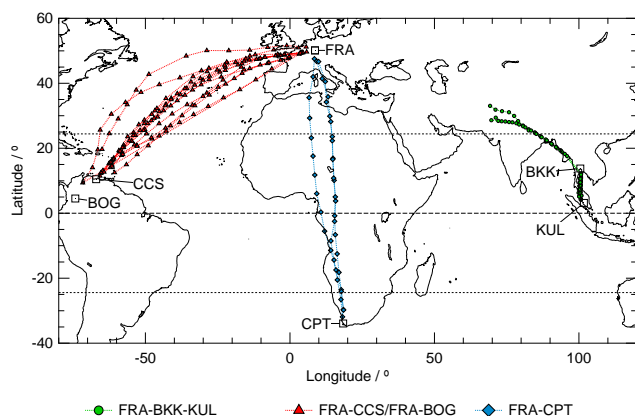
Fig. 1. Collection locations of whole air samples for CARIBIC flight routes FRA-CCS/BOG, FRA-CPT and FRA-BKK-KUL. For the latter, air sample collection north of approximately 30° N were not analysed at UEA.

the outbound and 14 on the return flight, making a total of 28 samples per round-trip flight. Samples are collected along the flight route at predetermined, evenly spaced sampling intervals of ~ 35 min, or ~ 480 km between samples. Filling times are on average 45 s (30–90 s) corresponding to a spatial coverage of 7–21 km. TRACs are routinely analysed after the flight at different laboratories for non-methane hydrocarbons (Baker et al., 2010), non-halogenated and halogenated greenhouse gases, e.g. N_2O, CH_4, SF_6 and CO_2 (Schuck et al., 2010) and a variety of short- and long-lived halocarbons at the University of East Anglia (e.g. Laube et al., 2010, 2012; Baker et al., 2011b; Lai et al., 2011; Oram et al., 2012; Sturges et al., 2012).

Between June 2009 and May 2011 the container was installed on flights between Frankfurt, Germany (FRA) and Caracas, Venezuela (CCS); between Frankfurt and Bogotá, Columbia (BOG), and between Frankfurt and Cape Town, South Africa (CPT). During November and December 2012 and February 2013 the container was installed on flights between Frankfurt and Bangkok, Thailand (BKK) and between Bangkok and Kuala Lumpur, Malaysia (KUL). Figure 1 shows the sampling locations for all Central American flights (FRA-CCS/BOG), South African flights (FRA-CPT) and Southeast Asian flights (FRA-BKK and BKK-KUL). CARIBIC flights are at civil aircraft cruising altitudes and those included in this study were between 6.9 and 12 km and on average at ~ 11 km (~ 220 hPa).

Routine analysis of whole-air samples for halocarbons is normally carried out by conventional gas chromatography mass spectrometry (GC-MS) in electron ionisation mode (EI-GCMS). However, the analysis of VSLB reported here was performed on a subset of CARIBIC samples using a quadrupole GC-MS running in negative ion chemical ionisation (NICI) mode. NICI has been shown to give much improved response for organic compounds containing bromine

and iodine atoms (Worton et al., 2008). The GC-MS (Agilent Technologies GC 6890/MS 5973N) was coupled to a thermal desorption pre-concentrator (UNITY2™ and Online Air Server; Markes International Ltd.) as described in Worton et al. (2008). Accurately measured air samples (~ 500 mL, flow rate ~ 40 mL min^{-1}) were dried with a counterflow nafion drier (Permapure™, 100 mL min^{-1} counterflow of dry nitrogen) prior to pre-concentration on a packed capillary cold trap at -30 °C and thermally desorbed at a rate > 60 °C s^{-1} to a maximum of 310 °C for 6 min. Chromatographic separation was achieved using an RTX-502.2 capillary column (105 m $\times$ 320 μm OD, 1.8 μm film, Restek™ Corporation) using research grade helium (≥ 99.9995 % purity) as the carrier gas and by temperature-programmed gas chromatography (30 °C hold 2 min, 8 °C min^{-1} to 150 °C hold 16 min, 20 °C min^{-1}, to 220 °C hold 5 min). The column effluent was subjected to negative ion chemical ionisation in the presence of methane reagent gas (research grade, ≥ 99.9995 %) prior to detection by a quadrupole mass selective detector operating in selective ion mode (SIM) and monitoring the Br ion (m/z 79, 81) for brominated compounds. CARIBIC measurements of VSLB are reported as dry-air mole fractions, pmol mol^{-1} (dry air), abbreviated here to ppt (parts per trillion).

Analytical uncertainties were calculated on a per-run basis and are the 1σ standard deviation of the working standard on the respective measurement day. Estimated limits of detection in parts per trillion (ppt), average compound-dependent analytical precisions and the mixing ratios of the working standard at which the measurements where made for the compounds in this study are shown in Table 1. For more details on the working standard see Sect. 2.1.

A number of trace gases are continuously measured through the same inlet line as used for collection of TRAC samples. For each TRAC sample, values for continuously measured trace gases are determined by integration over the sampling period. Ozone (O_3) measurements used in this study were measured using a custom-made dual-beam UV-photometer, developed and maintained by the Institute for Meteorology and Climate Research, Karlsruhe, Germany with a time resolution of 4 s and a precision of 0.5 ppb or 0.5 % (whichever is the larger) and a total uncertainty of 1.5 % (Brenninkmeijer et al., 2007; Zahn et al., 2012). Ozone mixing ratios are reported in this study as wet-air mole fractions, nmol mol^{-1} (air), abbreviated here to ppb (parts per billion).

Meteorological analyses and backward trajectory calculations are performed along the flight track using the TRAJKS model, of the Royal Netherlands Meteorological Institute (KNMI; Scheele et al. (2007), see also http://www.knmi.nl/samenw/campaign_support/CARIBIC/). The trajectory model uses as input 6 hourly wind fields at 1° × 1° resolution derived from archived analysis fields from the European Centre for Medium range Weather Forecasting (ECMWF). 5 day back trajectories are calculated along the

Table 1. Estimated limits of detection (LOD), compound dependant analytical precisions and mixing ratios at which the precision measurement was made for short-lived bromomethane species considered in this study (see Sect. 2.1 for further discussion of the working standard).

Species	Estimated Limit of Detection (LOD) [ppt]	Mean Analytical Precision [%]	Mixing Ratio [ppt]
Bromoform	0.001*	5.3	1.57–2.23
Dibromomethane	0.001*	5.1	1.23
Dibromochloromethane	0.001*	4.3	1.17
Bromodichloromethane	0.0008*	4.3	1.60
Bromochloromethane	0.005	6.1	0.29

All LODs given in parts per trillion (ppt) rounded to one significant figure.

* Values from Worton et al. (2008).

flight track at 3 min intervals. Additionally, at 6 s time steps, 8 day back trajectories are calculated during the sampling interval of each whole air sample. Additional meteorological parameters, such as potential vorticity (PV), were interpolated along the flight tracks at time intervals of 1 min by linear interpolation in space and time from the archived ECMWF analyses.

2.1 Calibration of short-lived halocarbons

Mixing-ratios of short-lived halocarbons are known to drift when stored for long periods in certain types of metal container (e.g. Laube et al., 2008; Hall et al., 2013; Butler et al., 2007, supplemental). Regular comparisons to known standards are necessary to ensure a consistent dataset. Calibration of the bromocarbons is based on individual compound response factors determined by comparison to a working standard with known mixing ratios. The working standard was an aluminium cylinder containing dry ambient air at high pressure. The mixing ratios of halocarbons in the working standard were determined by repeat comparison to calibrated gas standards supplied by the Global Monitoring Division of NOAA-ESRL in 34 L electropolished stainless steel canisters (Essex Cryogenics, St. Louis, MO, US). Mixing ratios in these standards are known to be stable over a period of years (e.g. Hall et al., 2013; Butler et al., 2007, supplemental). These comparisons are performed periodically and allow an assessment of any potential changes in the absolute mixing ratio of halocarbons in our working standard over time.

From comparisons with 3 separate NOAA standards: SX-3546 (comparison performed in 2008); SX-3570 (2010); and SX-3568 (twice in 2012) we estimate that the mixing ratio of CHBr$_3$ in the working standard has declined by 38 % over the period October 2008–September 2012, whilst that of CH$_2$Br$_2$ has remained unchanged (1.23 ± 0.07 ppt, or 5.6 %, 1σ). NOAA calibration data for the 3 mixed bromochloromethanes were only available for the 2010 and 2012 comparisons and our analysis shows that the concentrations of CH$_2$BrCl and CHBr$_2$Cl in the working standard have remained approximately constant (0.28 ± 0.004 ppt, or

1.5 %; and 1.18 ± 0.04 ppt, 3.4 % respectively) whilst that of CHBrCl$_2$ may have increased by 16 %. Calibration factors applied to the CARIBIC data for CHBr$_3$ have been time-corrected using a quadratic fit to the inter-comparison values. A calibration factor was applied to CH$_2$Br$_2$ based on mean values from 2008–2012 comparisons. Calibration factors for CHBr$_2$Cl, CHBrCl$_2$ and CH$_2$BrCl are based on the mean values of the 2010 and 2012 comparison. Again, note that the differences in calibration scales for these compounds limit this comparison.

The mixing ratios reported here are therefore based on the latest NOAA-ESRL scales for CH$_2$Br$_2$ (2004) and CHBr$_3$ (2003), and on a preliminary NOAA scale for CHBr$_2$Cl, CHBrCl$_2$ and CH$_2$BrCl (Brad Hall, personal communication). The accuracy of the absolute mixing ratio in the working standard, based on combined uncertainties associated with the standard comparisons and NOAA's stated uncertainties was ± 6.0 % for CHBr$_3$, ± 7.8 % for CH$_2$Br$_2$, ± 6.7 % for CHBr$_2$Cl, ± 9.9 % for CHBrCl$_2$ and ± 9.0 % for CH$_2$BrCl.
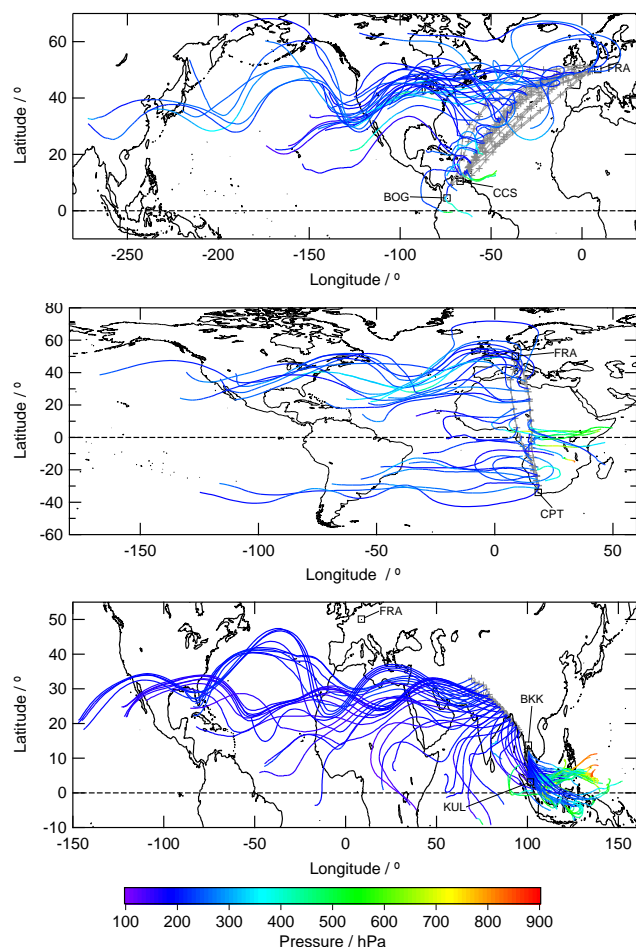
3 Results and discussion

Samples for the following analysis were categorised into tropospheric samples and those with stratospheric influence. Samples with stratospheric influences were defined as having an O$_3$ mixing ratio exceeding the seasonally-dependent ozone threshold value determined by Eq. (1) (Zahn and Brenninkmeijer (2003), confirmed by Thouret et al., 2006). This excludes the influence of stratospheric air on samples and is independent of seasonal variations in the thermal tropopause (see Sect. 3.1.3).

$$O_3 = 97 + \sin\left(\frac{2\pi\,(\text{Day of Year} - 30)}{365}\right) \text{ (in ppb)} \quad (1)$$

3.1 Central American flights
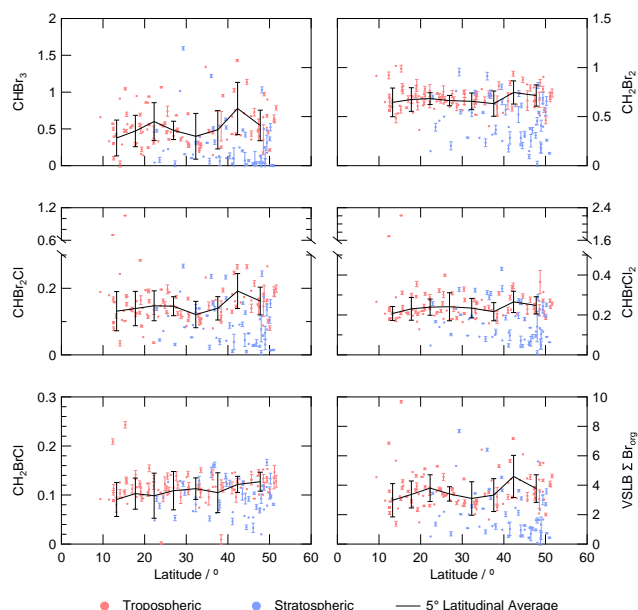
3.1.1 Latitudinal distribution and averages

Back trajectories from a typical Central American flight are shown in Fig. 2. On this route (FRA-CCS/BOG), the

Fig. 3. Northern-hemispheric latitudinal distributions in Central American flights of VSLB and total VSLB-derived bromine (VSLB Σ Br$_{org}$) for tropospheric samples, samples classified as having some stratospheric influence (following the definition in Sect. 3) and 5° latitudinal means of tropospheric samples above 10 km altitude with 1 σ error bars representing variability. Error bars on individual samples represent analytical uncertainties. All VSLB values on the vertical axes are given in ppt.

CARIBIC aircraft samples air mainly originating from the west with some air uplifted from the surface at the northern and southern ends of the flight track.

Figure 3 shows the latitudinal distributions of VSLB during the Central American flights. There is little latitudinal variation over the range covered with larger mixing ratios in only a small number of samples in the tropics compared to higher latitudes. Notably, there are two samples with higher mixing ratios of CHBr$_2$Cl, CHBrCl$_2$ and CH$_2$BrCl at 10–20° N with no enhancement in CHBr$_3$ and negligible enhancement in CH$_2$Br$_2$ (see Sect. 4). CHBr$_3$, and to a lesser extent CHBr$_2$Cl, have lower mean mixing ratios in the region of 20–40° N though this is not significant within the uncertainties. CHBr$_3$ and CHBr$_2$Cl have the shortest local lifetimes of the five VSLB (24 days and 59 days, respectively, Montzka and Reimann, 2011). This indicates that there has been a higher degree of photochemical processing and mix-

ing in these air-masses due to longer range transport from high altitudes in these regions as in the example flight in Fig. 2. It is possible that source emission variations could also contribute to lower mixing ratios in this region.

The CARIBIC data can be compared to other recent aircraft studies in the region including CR-AVE, Costa Rica AVE (e.g. Kroon et al., 2008; Aschmann et al., 2009; Hossaini et al., 2010; Ashfold et al., 2012) and HIPPO-1, HIAPER Pole-to-Pole Observations (Wofsy, 2011; Hossaini et al., 2012b, 2013). CR-AVE took place January and February 2006 over the Eastern Pacific and HIPPO-1 took place during January 2009 with some measurements in the region of Central America. HIPPO-1 mixing ratios are on the NOAA scale and are directly comparable to CARIBIC. HIPPO values are based on a regionally relevant subset of all measurements made during the campaign available from the HIPPO data archive (Wofsy et al., 2012). The calibration scale used in CR-AVE has mixing ratios that are $\sim$ 10 % higher for CHBr$_3$ and $\sim$ 20 % higher for CH$_2$Br$_2$ than the NOAA-ESRL scale (Elliot Atlas, personal communication). Additionally, CARIBIC results can be compared to WMO 2010 (Montzka and Reimann, 2011). WMO 2010 values referred to in this study are 10–12 km upper tropospheric values from Tables 1–7 of WMO 2010. These values are mean values of DC-8 observations made during the TC4,

PEM-West A and PEM-West B campaigns (Toon et al., 2010; Hoell et al., 1999, 1997; Schauffler et al., 1999). The minimum and maximum values given in WMO 2010 are based on the smallest mean minus one standard deviation and the largest mean plus one standard deviation respectively, across all campaigns. Again, note that the differences in calibration scales for these compounds limit this comparison.

A summary of the tropical and extra-tropical 10–12.3 km means and medians for the Central American flights with comparison to literature values is shown in Table 2. Mean values for the tropical region show good agreement with WMO 2010. $CHBrCl_2$ has a larger mean and range in CARIBIC than in WMO 2010.

HIPPO-1 mean mixing ratios agree within the uncertainties given. However, CH_2Br_2 is notably higher (0.88 ppt) than in CARIBIC (0.72 ppt) and total VSLB-derived organic bromine (VSLB Σ Br_{org}) is similar to CARIBIC (3.2 ppt for HIPPO-1 compared to 3.7 ppt for CARIBIC) without the addition of $CHBrCl_2$ and CH_2BrCl, both of which were unavailable for HIPPO-1. HIPPO-1 samples used in this study were collected further west than the CARIBIC Central American flights which may account for some of the differences in mean mixing ratios. Additionally, his might reflect some seasonality in VSLB, especially CH_2Br_2, as HIPPO-1 took place in January whereas CARIBIC Central American flights took place during March–September.

Seasonality has been observed for $CHBr_3$ in the boundary layer (e.g. Carpenter et al., 2005). However, it is uncertain as to whether a seasonal cycle in $CHBr_3$, or other VSLB, would be present in the upper troposphere or the regions sampled in this study. Due to the limited temporal coverage of CARIBIC, seasonal cycles cannot be identified or ruled out. Transport processes and the high degree of variability in source emissions of VSLB could also account for these differences.

CR-AVE mean mixing ratios for $CHBr_3$ (0.69 ppt) and CH_2Br_2 (0.96 ppt) are higher than in CARIBIC. However, when differences in calibration scales are taken into account, the CR-AVE means are more similar, i.e. ~ 0.62 ppt and ~ 0.77 ppt for $CHBr_3$ and CH_2Br_2 respectively. CR-AVE measurements were made further west than CARIBIC and may be more influenced by Pacific and Gulf of Mexico. Significant differences between standards and calibration methodologies for these compounds are known (e.g. Jones et al., 2011) therefore caution should be exercised when drawing conclusions based on these inter-campaign comparisons. This also applies to South African and Southeast Asian routes (see Sects. 3.2 and 3.3).

3.1.2 Potential temperature

The tropical tropopause layer (TTL) (between 345 K and 380 K potential temperature, approximately 12–17 km altitude) acts as a source region for the stratospheric overworld and for the extra-tropical lowermost stratosphere (Law and

Sturges, 2007). Figure 4 shows plots of bromocarbons vs. potential temperature (Θ). Also plotted are 5 K binned means $\pm 1\sigma$ vs. Θ. In the tropics, the five VSLB show little change in mean mixing ratio, within the natural variability, with increasing Θ. VSLB Σ Br_{org} has a maximum mean mixing ratio of 3.74 ppt at 340–345 K. From 340 K to 355 K (disregarding the points at lower Θ as the means are based on only one or two points), the tropical means are higher than in the extra-tropics. This is a possible indication that vertical transport mechanisms in the tropics are a significant factor in supplying VSLB to the stratosphere although this difference is not significant or very small when the natural variability is taken into account. Back trajectory analysis indicates that enhanced mixing ratios in the tropics are due to uplift from the Gulf of Mexico or Eastern Pacific region. The CARIBIC aircraft has a maximum altitude of ~ 12 km and reaches potential temperatures of ~ 360 K, i.e. just at the entrance to the TTL. Therefore, mixing ratios obtained from CARIBIC in the tropics do not directly represent the quantity of VSLB available for transport from within the TTL into the tropical stratosphere. Rather, they represent an upper limit on organic bromine derived from VSLB available for transport into the stratospheric overworld with the proviso that further photochemical processing and physical transport processes will reduce mixing ratios entering the tropical stratosphere.

In the extra-tropics, there is a seasonal variation in the height of the thermal tropopause (e.g. Gettelman et al., 2011). Therefore, binned means $\pm 1\sigma$ in Fig. 4 are separated, for the extra-tropics, into the two seasonal periods covered by the Central American flights analysed in this study; March, April, May (MAM) and June, July, August and September (JJAS). All five VSLB show an overall decrease in extra-tropical mean mixing ratio during MAM with increasing Θ; VSLB Σ Br_{org} decreases from ~ 3.7 ppt at 320–325 K to ~ 1.5 ppt at 340–345 K. No data for MAM are available above 345 K. During JJAS, mean mixing ratios are constant, within the uncertainties, up to 340–345 K after which there is a decrease to 355–360 K beyond which there is no data available. VSLB Σ Br_{org} decreases from ~ 3.2 ppt to ~ 0.8 ppt over this range of Θ. This decrease in mixing ratios above ~ 345 K corresponds to the extra-tropical tropopause layer (ExTL). There are a number of samples with enhanced mixing ratios in the extra-tropics. However, back trajectories do not indicate a consistent origin for the air in these samples.

3.1.3 Ozone and height above the tropopause

O_3 is measured in situ on CARIBIC flights and provides an alternative tracer when considering UTLS structure and chemistry. Figure 5 shows plots of the five VSLB and VSLB Σ Br_{org} against O_3 for all FRA-CCS/BOG samples. Data are coloured to show samples with a degree of stratospheric influence. As stated in Sect. 2, tropospheric and stratospherically-influenced samples have been segregated based on a seasonally dependent O_3-threshold. This

Table 2. Summary of tropospheric tropical and extra-tropical 10–12.3 km mid-upper tropospheric means and medians for the bromomethanes and total VSLB-derived organic bromine (VSLB Σ Br$_{org}$) in Central American, South African and Southeast Asian CARIBIC flights (FRA-CCS/BOG, FRA-CPT, FRA-BKK and BKK-KUL) with comparison to literature values. Tropical is defined as between 24.4378° S and 24.4378° N. Values are means with ±1σ, medians in curly brackets and minimum/maximum values in parentheses except for WMO 2010 where medians are not given. Values in square brackets are the number of samples included in the average. All values are given in parts per trillion (ppt).

	Campaign		CHBr$_3$	CH$_2$Br$_2$	CHBr$_2$Cl	CHBrCl$_2$	CH$_2$BrCl	VSLB Σ Br$_{org}$
CARIBIC [1]	C. America	Ex. Trop. [58]	0.52 ± 0.27 {0.45} (0.14–1.4)	0.71 ± 0.11 {0.70} (0.42–0.98)	0.15 ± 0.05 {0.15} (0.08–0.27)	0.23 ± 0.05 {0.22} (0.15–0.38)	0.12 ± 0.02 {0.11} (0.01–0.15)	3.6 ± 1.1 {3.4} (1.7–7.2)
		Tropical [36]	0.52 ± 0.26 {0.49} (0.02–1.1)	0.72 ± 0.14 {0.71} (0.38–1.1)	0.17 ± 0.16 {0.14} (0.04–1.1)	0.27 ± 0.32 {0.21} (0.12–2.1)	0.11 ± 0.03 {0.10} (0.0–0.24)	3.7 ± 1.5 {3.5} (1.4–9.7)
	S. Africa	Tropical [26]	0.48 ± 0.54 {0.35} (0.03–2.8)	0.68 ± 0.14 {0.69} (0.40–0.87)	0.14 ± 0.10 {0.12} (0.05–0.55)	0.24 ± 0.10 {0.22} (0.10–0.56)	0.10 ± 0.02 {0.10} (0.04–0.14)	3.4 ± 2.1 {2.9} (1.4–12)
	S.E. Asia FRA-BKK	Tropical > 15° N [18]	0.28 ± 0.19 {0.25} (0.05–0.58)	0.76 ± 0.14 {0.79} (0.49–0.95)	0.10 ± 0.04 {0.10} (0.04–0.16)	0.17 ± 0.03 {0.16} (0.11–0.22)	0.10 ± 0.01 {0.10} (0.09–0.12)	2.8 ± 0.93 {2.8} (1.6–4.2)
	S.E. Asia BKK-KUL	Tropical 0–15° N [39]	0.56 ± 0.12 {0.56} (0.15–0.81)	0.92 ± 0.08 {0.93} (0.74–1.0)	0.16 ± 0.02 {0.16} (0.08–0.19)	0.21 ± 0.03 {0.21} (0.16–0.31)	0.12 ± 0.01 {0.12} (0.09–0.14)	4.2 ± 0.56 {4.1} (2.4–5.2)
HIPPO-1 [2]	C. America	Tropical [8]	0.44 ± 0.07 {0.44} (0.34–0.58)	0.88 ± 0.02 {0.88} (0.85–0.92)	0.13 ± 0.03 {0.14} (0.09–0.15)	N/A	N/A	3.2 ± 0.33 {3.2} (2.8–3.9)
HIPPO-4 [2]	S.E. Asia	Tropical > 15° N [10]	0.25 ± 0.11 {0.27} (0.00–0.42)	0.69 ± 0.07 {0.68} (0.60–0.83)	0.07 ± 0.02 {0.08} (0.04–0.09)	N/A	N/A	2.2 ± 0.42 {2.3} (1.26–2.6)
		Tropical 0–15° N [7]	0.80 ± 0.24 {0.72} (0.51–1.2)	0.95 ± 0.09 {0.95} (0.83–1.1)	0.16 ± 0.06 {0.16} (0.10–0.21)	N/A	N/A	4.4 ± 0.87 {4.4} (3.2–5.9)
CR-AVE [3]	E. Pacific	Tropical [24]	0.69 ± 0.32 {0.59} (0.32–1.5)	0.96 ± 0.11 {0.96} (0.80–1.2)	0.11 ± 0.02 {0.11} (0.07–0.14)	N/A	N/A	4.2 ± 1.2 {3.8} (2.7–7.0)
WMO2010 [4]		Tropical	0.50 (0.12–1.21)	0.86 (0.63–1.21)	0.11 (0.01–0.36)	0.11 (0.02–0.28)	0.09 (0.03–0.16)	3.5 (1.7–7.4)

[1] 10–12.3 km mid-upper tropospheric means ±1σ and ranges.
[2] Wofsy et al. (2012). Averages at 9–12 km altitude. VSLB Σ Br$_{org}$ does not include CHBrCl$_2$ and CH$_2$BrCl.
[3] VSLB Σ Br$_{org}$ derived from CHBr$_3$, CH$_2$Br$_2$ and CHBr$_2$Cl only.
[4] 10–12 km. Montzka and Reimann (2011)

"chemical tropopause" (CT) lies ∼ 800 m below the thermal tropopause (Bethan et al., 1996) and approximates to a CT at 100 ppb O$_3$ and an upper limit to the mixed ExTL of ∼ 500 ppb O$_3$. Therefore, between the CT and thermal tropopause there is significant impact from stratospheric air. All five VSLB show a sharp decrease in mixing ratio around 100–200 ppb O$_3$ corresponding to the transition from the troposphere to the ExTL. Above 200 ppb O$_3$ mixing ratios do not decrease greatly indicating that this layer is still show-

ing some degree of mixing with the troposphere or the influence of quasi-horizontal transport from the tropics. All tropical samples are below the CT due to the restricted altitude range of the aircraft.
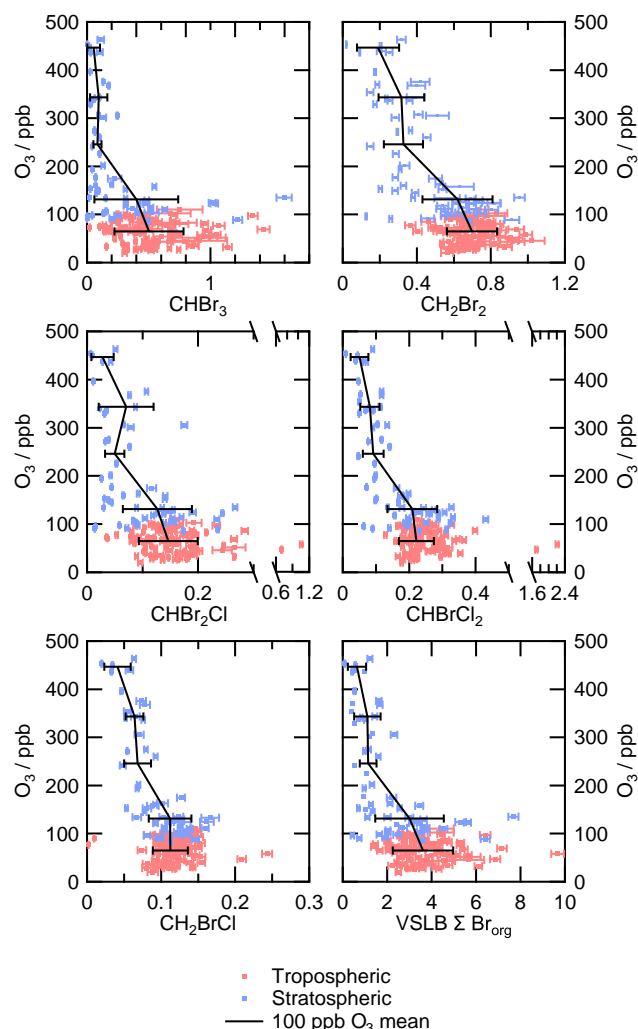
An alternate method of viewing the chemical structure within the ExTL is to define a vertical height above the tropopause based on simultaneously measured O$_3$ mixing ratios. O$_3$ mixing ratios can be translated into vertical distance above the thermal tropopause (zO_3) by comparison to
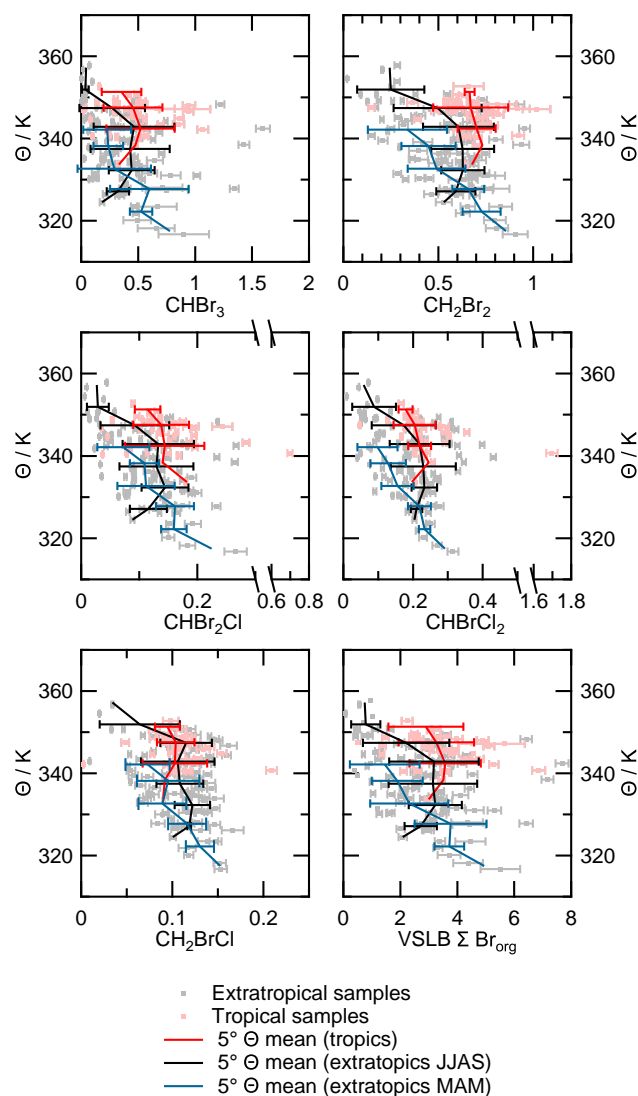
Fig. 4. Plots of VSLB and total VSLB-derived bromine (VSLB Σ Br$_{org}$) for Central American flights against potential temperature (Θ) with 5 K means. 5 K means with 1 σ error bars representing variability are separated into extra-tropical from March, April and May (MAM); extra-tropical from June, July, August and September (JJAS) and tropical samples from all months. Where fewer than three data points were available for averaging, error bars have not been added. Error bars on sample data points represent analytical uncertainties. All VSLB values on the horizontal axes are given in ppt.

Fig. 5. Plots of VSLB and total VSLB-derived bromine (VSLB Σ Br$_{org}$) for all samples on Central American flights against O$_3$ with 100 ppb binned means ± 1 σ error bars representing variability. Error bars on sample data points represent analytical uncertainties. Data points have been separated by colour into tropospheric samples and those with stratospheric influence (see Sect. 3). All VSLB values on the horizontal axes are given in ppt.

monthly mean O$_3$ sonde-based profiles (Sprung and Zahn, 2010). Being a relatively long-lived tracer, O$_3$ follows the vertical movement of the tropopause. Therefore, zO$_3$ removes vertical variations in the thermal tropopause from trace gas profiles as shown in Sprung and Zahn (2010).

Figure 6 shows plots for all FRA-CCS/BOG samples of the five VSLB and VSLB Σ Br$_{org}$ with the height above the thermal tropopause as calculated for CARIBIC following

the definition given in Zahn and Brenninkmeijer (2003). Due to the limited cruising altitude range of the aircraft, height above the thermal tropopause is only available for extra-tropical samples. There is a high degree of variation within 0.5 km of the tropopause with a lesser degree of variation above 0.5 km. VSLB Σ Br$_{org}$ decreases from a mean value of 2.3 ppt at 0–0.5 km above the tropopause to < 0.5 ppt above 3 km although this number is based on only two samples. This level is at the upper extent of the mixed ExTL layer and puts an upper limit on the quantity of organic-derived bromine entering the lower extra-tropical stratosphere. This, of course, does not give an indication of the quantity of
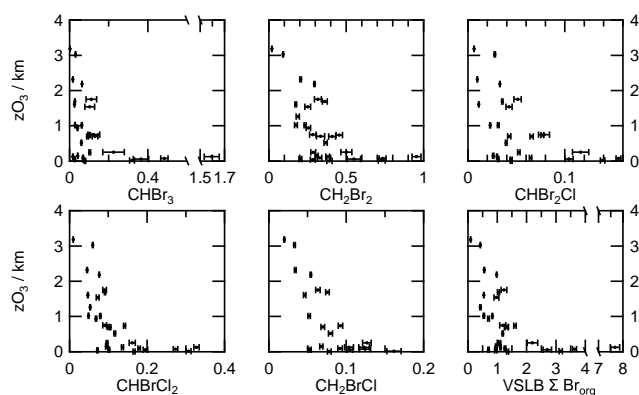
Fig. 6. Plots of VSLB and VSLB-derived total bromine (VSLB Σ Br_{org}) for Central American flights with O_3-derived height above the thermal tropopause (zO_3) as defined by Zahn and Brenninkmeijer (2003). Error bars represent analytical uncertainties. The tropopause is defined as $zO_3 = 0$ (see Sect. 3.1.3). All VSLB values on the horizontal axes are given in ppt.

product gases (derived from photochemical processing of VSLB) transported into this region.

3.2 South African flights

The South African (FRA-CPT) CARIBIC route partly samples air masses with similar origins to the Central American route (Fig. 2 and Sect. 3.1). However, there is also greater latitudinal range over FRA-CPT providing the opportunity to samples air masses from both hemispheres as well as air masses from the African continent and further east.

Analyses for three flights were available for CARIBIC route FRA-CPT (one return flight and one out-bound flight). Latitudinal profiles for these flights are shown in Fig. 7 with 10° latitudinal means of tropospheric data above 10 km altitude. When all the data is binned latitudinally, there is some degree of latitudinal gradient in all VSLB with higher values in the northern mid-latitudes declining towards the southern mid-latitudes (see Fig. 7). For example, mean $CHBr_3$ drops from 0.73 ppt to 0.16 ppt and CH_2Br_2 from 0.80 ppt to 0.48 ppt. These two compounds are the main contributors to VSLB Σ Br_{org} which drops from 4.5 ppt to 1.8 ppt. However, higher mixing ratios in the northern mid-latitudes derive from one FRA-CPT flight leg in February 2011 (the other return flight was in October 2009). Five and eight-day back trajectories shows that air in the northern mid-latitudes originated, on this flight leg, from further south within the Central American tropics rather than from the North American continent and North West Atlantic as in the return flight. Elevated mixing ratios of $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl at 25–35° S are from the return flight and show a possible influence from the east coast of South America. It is likely that the inter-hemispheric gradient in Fig. 7 is a product of regional influences and the limited temporal range of the data
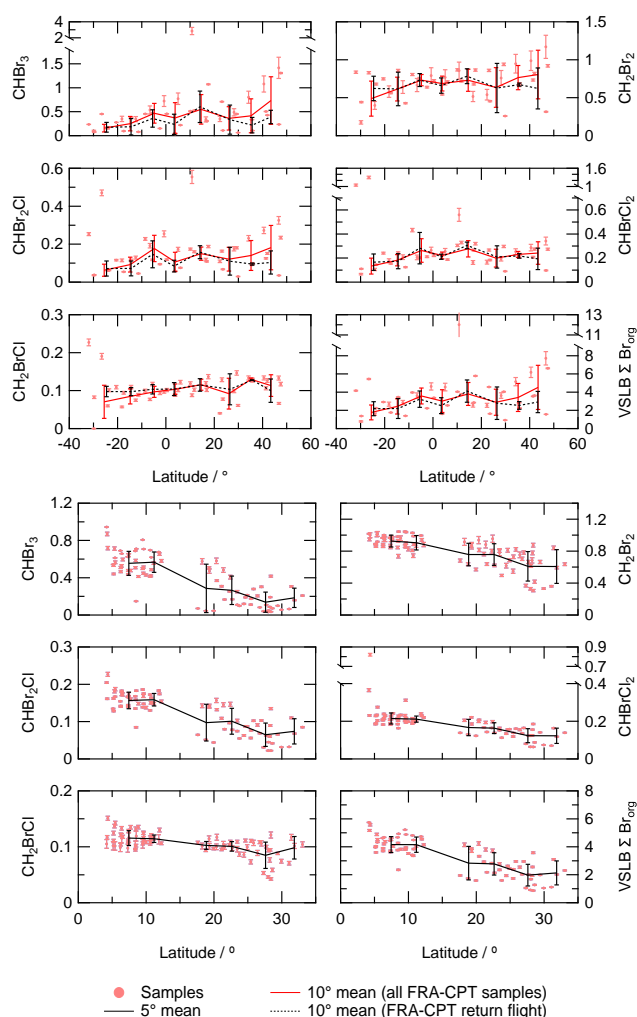
Fig. 7. Latitudinal distributions in South African (top) and Southeast Asia (bottom) flights of VSLB and total VSLB-derived bromine (VSLB Σ Br_{org}) with 10° (South African flights) and 5° (Southeast Asia) latitudinal means of tropospheric samples above 10 km altitude with 1σ error bars representing variability. Latitudinal averages for South African flights are are shown for all samples and for samples collected on the return flight (see Sect. 3.2). All samples in both routes are tropospheric (following the definition in Sect. 3) with error bars representing analytical uncertainties. All VSLB values on the horizontal axes are given in ppt.

rather than representing a larger-scale gradient. For comparison, over all HIPPO campaigns (HIPPO-1 and −4 are summarised in Table 2, see also Sects. 3.1.1 and 3.3) there is no comparable inter-hemispheric gradient over a similar latitudinal and altitudinal range.

If the February 2011 flight leg is excluded from the dataset (as in Fig. 7), there is no discernible inter-hemispheric latitudinal gradient. However, there is a possible increase in mixing ratios in all except CH_2BrCl in the tropics, e.g. $CHBr_3$ is enhanced by up to ~ 0.4 ppt. This increase is small when variability is taken into account with limited sampling.

Therefore, these results should be taken as suggesting the possibility of a tropical enhancement over Africa rather than being definitive. This is perhaps present in the latitudinal averages across all data but obscured by the apparent latitudinal gradient. The HIPPO campaigns show increased mixing ratios around the equator compared to the extra-tropics (e.g. $CHBr_3$ increases from ~ 0.2 ppt at $50°$ N to ~ 0.6 ppt in the tropics); a similar enhancement to the CARIBIC data. It should be noted that the HIPPO campaign was exclusively in the Pacific region. Therefore, it is not directly comparable to the CARIBIC FRA-CPT route except in discussing global patterns. The source of this tropical enhancement is not clearly given by five-day back trajectories (Fig. 2). There is an indication in the back trajectories of strong uplift from the east coast and continental Africa around the equator. One sample in this region shows high levels of $CHBr_3$ (2.85 ppt), $CHBr_2Cl$ (0.55 ppt) and $CHBrCl_2$ (0.56 ppt). Back trajectory analysis for this sample indicates possible influence from the east coast of Africa in the region of Somalia and/or the Arabian Sea. This samples is from the February 2011 flight leg but is representative, from back trajectory analysis, of air around the equator.

Mean mixing ratios for the tropical mid-troposphere at 10–12.3 km are presented in Table 2. Values for the extra-tropical region are not given due to limited data coverage. The values given in Table 2 for $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl agree well, within the uncertainties, with tropical troposphere values for the Central American flights and, therefore, with WMO 2010; CH_2Br_2 is ~ 0.2 ppt lower. Ranges for $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl are similar to WMO 2010 however, the maximum value for $CHBr_3$ in CARIBIC is ~ 1.6 ppt higher than in WMO 2010 and maximum CH_2Br_2 is ~ 0.4 ppt lower.

3.3 Southeast Asia flights

The tropical West Pacific is considered a potentially important region for transport of VSLB into the stratosphere (e.g. Aschmann et al., 2009). Frequent and intense convection provides an efficient pathway for boundary layer air to be transported to the TTL (e.g. Fueglistaler et al., 2009). Additionally, emissions in the region are poorly sampled, including those of farmed macroalgae species. These could impact on future VSLB emissions due to interest in increasing seaweed aquaculture in the region (Leedham et al., 2013).

Flights between FRA and KUL consist of two legs; FRA-BKK and BKK-KUL (collectively FRA-BKK-KUL). As bottle samples are only collected at cruising altitude and not during take-off or landing, there is a discontinuity in data coverage in the region of Bangkok. This route intersects air masses, over the FRA-BKK leg, with a range of origins (Fig. 2). The BKK-KUL leg samples a less diverse range of air masses mainly originating over Indonesia and the South China Sea.

A total of three return flights were analysed along the FRA-BKK-KUL route providing good coverage in a region of the tropics that is considered important for VSLB emissions (e.g. Ashfold et al., 2014). Latitudinal profiles for these flights are shown in Fig. 7 with $5°$ latitudinal means of tropospheric samples above 10 km altitude. All five compounds show distinctly higher mixing ratios within $15°$ N of the equator than at higher latitudes with $CHBr_3$ at ~ 0.6 ppt below $15°$ N compared to ~ 0.3 ppt at $15–30°$ N. This partly reflects the origins of air masses in this region; back trajectories indicate that most air masses on the BKK-KUL leg of the flight have been uplifted from the South China Sea and Western Pacific Ocean. In contrast, the FRA-BKK leg is dominated by long-range, higher altitude transport from over the Atlantic and North American, European, Asian and African continents with a small number of samples near Bangkok uplifted from Indonesia (see Fig. 2). Additionally, as the VSLB are mainly marine sourced, the FRA-BKK leg of the route, which passes over Europe and Asia, might be expected to show relatively lower mixing ratios.

Samples from $0–5°$ N are from below 10 km altitude and are not included in the latitudinal means however, two of the samples show slightly higher mixing ratios than $5–15°$ N for $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$. Back trajectories indicate that the air masses originated off the coast of Malaysia in one case and west of Sumatra in the other.

Average values for the tropical troposphere for the FRA-BKK leg and for the BKK-KUL leg are included in Table 2. Values for the extra-tropical region are not given due to limited data coverage. Means over the FRA-BKK leg for $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl agree well with the Central American and South African flights. CH_2Br_2 (0.76 ppt) is 0.08–0.11 ppt higher and $CHBr_3$ (0.28 ppt) is ~ 0.2 ppt lower than Central American and South African flights. This reflects the mix of long and short-scale transport from various regions covered on this leg of the flight and is not representative of emissions and vertical transport from tropical regions.

Mean mixing ratios for $CHBr_3$ (0.56 ppt), $CHBr_2Cl$ (0.16 ppt), $CHBrCl_2$ (0.21 ppt) and CH_2BrCl (0.12 ppt) for the BKK-KUL leg are similar to the South African and Central American CARIBIC routes and agree well within the errors. However, CH_2Br_2 (0.92 ppt) is 0.24–0.27 ppt higher than in the South African and Central American flights. This indicates that there is a greater emission of CH_2Br_2 in the Southeast Asian Pacific tropics than in either the Western Atlantic or African tropics. Emissions of the other VSLB are more similar. Caveats relating to data limitations, including seasonality, are the same as those discussed in Sect. 3.1.1.

The HIPPO-4, HIAPER Pole-to-Pole Observations (Wofsy, 2011; Hossaini et al., 2013) took place in June and July 2011. HIPPO-4 mixing ratios are on the NOAA scale and are directly comparable to CARIBIC. HIPPO values are based on a subset of all measurements made during the campaign available from the HIPPO data archive (Wofsy et al., 2012). Part of the campaign took place in the

region of Indonesia and the Philippines, further east than the CARIBIC BKK-KUL leg. Average mixing ratios for this campaign are shown in Table 2. All mixing ratios are on the NOAA scale. 0–15° N means for CH_2Br_2, $CHBr_2Cl$ and VSLB Σ Br_{org} agree well with BKK-KUL. $CHBr_3$ is higher in HIPPO-4 (0.80 ppt) than in BKK-KUL (0.56 ppt) but this is within the variability.

We suggest that there are two possible reasons for this enhancement in tropical CH_2Br_2 between BKK-KUL and Central America or South African flights.

1. The $CHBr_3/CH_2Br_2$ emission ratio might differ between the regions. The enhancement in CH_2Br_2 in BKK-KUL is not accompanied by a similar enhancement in $CHBr_3$ and might indicate a lower $CHBr_3$ emission ratio, relative to CH_2Br_2, in Southeast Asia. This is not the case in the literature where $CHBr_3/CH_2Br_2$ emission ratios have been reported as broadly consistent over a range of tropical regions (e.g. Brinckmann et al. 2012; Yokouchi et al. 2005; O'Brien et al. 2009). Additionally, $CHBr_2Cl$ is similar across the tropical regions sampled, indicating that the Southeast Asian emission ratio is lower for $CHBr_2Cl$. This emission ratio is known to vary regionally, e.g. Brinckmann et al., O'Brien et al. and Yokouchi et al. report varying emission ratios relative to CH_2Br_2 (0.35, 0.46 and 0.7 respectively). Verification of the emission ratios relative to CH_2Br_2 in this study is not possible as measurements were too far removed from source to provide a reliable estimate. This hypothesis is based on the assumption that there is no effect, in our data, of seasonality or inter-annual variability.

2. The local lifetime of CH_2Br_2 might be longer in Southeast Asia. Montzka and Reimann (2011) give the local lifetime (τ_{local}) of CH_2Br_2 as 120 days. This lifetime is dominated by reaction with hydroxyl (OH) radical ($\tau_{OH} = 123$ days, $\tau_{photolysis} = 5000$ days). $CHBr_3$ ($\tau_{local} = 24$ days) is more influenced by photolysis ($\tau_{OH} = 76$ days, $\tau_{photolysis} = 36$ days). Therefore, it could be expected that, within the troposphere, a region of low OH mixing ratios would lead, after significant photochemical processing, to an enhancement in CH_2Br_2 without a significant, concomitant depletion of $CHBr_3$. The mixed halomethanes could be expected to show a similar behaviour, however, the magnitude of this effect would be too small to discern from the analytical uncertainties.

4 Enhancements in the mixed bromochloromethanes

We have observed on a few occasions, enhanced mixing ratios of mixed bromochloromethanes ($CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl) without significant enhancements of $CHBr_3$ or CH_2Br_2, e.g. between 10 and 20° N in the Central American flights and 30–40° S in the South African flights. These samples also show enhancements in chloroform ($CHCl_3$), toluene and benzene. This hints at a possible anthropogenic source of trihalomethanes although a biogenic source cannot be ruled out. Disinfection of seawater, freshwater and wastewater is a known anthropogenic source of halomethanes (Quack and Wallace, 2003, and references therein). However, it would be expected that $CHBr_3$ would show an enhancement if this was the case. Due to the altitude of the CARIBIC aircraft and the limitations of following a commercial flight-path, it is not possible to attribute these elevated samples to a distinct source. However, we believe that there is some indication of a source of mixed bromochloromethanes that is independent of $CHBr_3$ and CH_2Br_2.

5 Summary and conclusions

We report the mixing ratios of five brominated VSLS in samples collected on three routes of the CARIBIC aircraft during 2009–2013. Across the three routes analysed, mean tropical mid-UT mixing ratios were: $CHBr_3$, 0.43 ppt; CH_2Br_2, 0.74 ppt; $CHBr_2Cl$, 0.14 ppt; $CHBrCl_2$, 0.23 ppt and CH_2BrCl, 0.11 ppt. Total bromine across all routes in the tropical mid-UT was 3.4 ± 1.5 ppt. These values agree well with values reported in the 2010 WMO O_3 assessment (Montzka and Reimann, 2011). Using a 2008 value of 15.2 ± 0.2 ppt for bromine from Halons and methyl bromide (Montzka and Reimann, 2011), VSLB across all routes accounts for $\sim 19\%$ of total bromine. As the anthropogenic contribution to atmospheric bromine (mainly halons and methyl bromide) is expected to decrease, coupled with the potential changes in emissions due to climate change (e.g. increases in wind speeds, ocean temperatures etc.), emissions of VSLB are likely to become proportionally more significant in the future.

For each of the tropical regions covered in this study, mid-UT VSLB Σ Br_{org} was 3.7 ppt for FRA-CCS/BOG, 3.4 ppt for the FRA-CPT and 4.2 ppt for BKK-KUL. Mixing ratios of $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl were similar between these three routes: CH_2Br_2 was relatively enhanced in the Southeast Asian flights and is the main contributor to the 0.5–0.8 ppt enhancement of total organic bromine compared to Central American and South African tropical mixing ratios.

The percentage contribution of the three minor VSLB ($CHBr_2Cl$, $CHBrCl_2$ and CH_2BrCl) to total organic bromine derived from the species analysed across all routes in the tropical mid-UT was $18 \pm 4.8\%$ (range 11–46); $CHBr_3$ and CH_2Br_2 together contributed $82 \pm 4.8\%$ (54–89). Individual contributions were $34 \pm 13\%$ (4.7–71) for $CHBr_3$, $48 \pm 12\%$ (14–73) for CH_2Br_2, $7.8 \pm 2.0\%$ (2.8–22) for

CHBr$_2$Cl, 6.9 ± 3.0 % (3.8–25) for CHBrCl$_2$ and 3.6 ± 1.3 % (0.0–7.2) for CH$_2$BrCl.

Considering that these measurements were made at 10–12 km, below the tropical tropopause layer (TTL) ($\sim$ 12–17 km), further decomposition will occur during ascent in to the stratospheric overworld. This implies that these values constrain the contribution of VSLB to stratospheric bromine to the lower end of 6 (3–8) ppt of stratospheric BrO required by WMO 2010 to balance the stratospheric bromine budget. Though this study is limited latitudinally, altitudinally and temporally, the large range and number of regular flights means that the CARIBIC passenger aircraft will continue to be an important source of UTLS and free tropospheric data in the future.

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