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Deriving an atmospheric budget of total organic bromine using airborne in-situ measurements from the Western Pacific during SHIVA

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Abstract

During the SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere) project an extensive dataset of all halogen species relevant for the atmospheric budget of total organic bromine has been collected in the West Pacific region using the FALCON aircraft operated by the German Aerospace agency DLR (Deutsches Zentrum für Luft- und Raumfahrt) covering a vertical range from the planetary boundary layer up to the ceiling altitude of the aircraft of 13 km. In total, more than 700 measurements were performed with the newly developed fully-automated in-situ instrument GHOST-MS (Gas cHromatograph for the Observation of Tracers – coupled with a Mass Spectrometer) by the Goethe University of Frankfurt (GUF) and with the onboard whole-air sampler WASP with subsequent ground based state-of-the-art GC/MS analysis by the University of East Anglia (UEA). Both instruments yield good agreement for all major ($CHBr_3$ and CH_2Br_2) and minor ($CHBrCl$, $CHBrCl_2$ and $CHBr_2Cl$) VSLS (very short-lived substances), at least at the level of their 2 σ measurement uncertainties. In contrast to the suggestion that the Western Pacific could be a major source region for VSLS (Pyle et al., 2011), we found only slightly enhanced mixing ratios of brominated halogen source gases relative to the levels reported in Montzka et al. (2011) for other tropical regions. A budget for total organic bromine, including all four halons,CH_3Br and the VSLS, is derived for the upper troposphere, the input region for the TTL and thus also for the stratosphere, compiled from the SHIVA dataset. With exception of the two minor VSLS $CHBrCl_2$ and $CHBr_2Cl$, excellent agreement with the values reported in Montzka et al. (2011) is found, while being slightly higher than previous studies from our group based on balloon-borne measurements.

1 Introduction

Bromine atoms are very efficient catalysts in destroying stratospheric ozone. In particular bromine atoms are more effective than chlorine atoms by a factor of about 60 (see e.g. Sinnhuber et al., 2009). Therefore, even small amounts of bromine play an important role in stratospheric ozone chemistry. In contrast to chlorine, the sources of bromine to the stratosphere are to a large part of natural origin (e.g. Montzka et al., 2011). The contribution of the so called very short lived species (VSLS), having atmospheric lifetimes of less than half a year, as sources gases (SG) for stratospheric bromine is significant. However, source gas observations of long-lived bromine compounds (Newland et al., 2013; Fraser et al., 1999) and VSLS (Laube et al., 2008; Brinckmann et al., 2012; Montzka et al., 2011) have so far not been able to explain the amount of bromine derived in the stratosphere from observations of BrO and modeling of the ratio of BrO to total bromine (e.g. Dorf et al., 2006; Montzka et al., 2011). Due to the short lifetimes and the high atmospheric variability, the representativeness of the available observations of VSLS source gases remains unclear, as these may vary with region and display seasonal variability.

The major bromine VSLS are dibromomethane (CH_2Br_2) and bromoform ($CHBr_3$), both having mainly oceanic sources (Carpenter et al., 2003), in particular in coastal regions (Quack and Wallace, 2004). In addition there are three mixed bromochlorocarbons contributing to stratospheric bromine: CH_2BrCl, $CHBr_2Cl$ and $CHBr_2Cl$. The mixing ratios of all of these bromine carrying compounds in the atmosphere are well correlated, with the exception of CH_2BrCl. The sources of these compounds to the atmosphere are thus expected to be very similar and mainly of marine origin. Due to the short lifetimes these species have a high atmospheric variability and in addition they are partly destroyed in the troposphere during the transport through the tropical tropopause layer (TTL) into the stratosphere. The fate of the product gases (PG) from the loss reactions in the upper tropical troposphere and TTL is still largely unknown as so far no observations of these are available in the atmosphere. The contribution of PG (so called PGI, product gas injection) to stratospheric bromine thus needs to be determined either from modeling studies or from observations of SG using specific assumptions on the transport into the stratosphere and chemical reactions and washout during this transport process. In contrast to the long lived source gases, the observations from the planetary boundary layer can thus not be used for these short-lived species to constrain the amount of halogen input into the stratosphere.

As mentioned above the sources of bromine VSLS to the atmosphere are largely of natural origin. Consequently, these emissions are expected to display significant geographical variability. They are further prone to changes due to changes in climate or due to land and ocean use, e.g. seaweed farming. It is therefore important to understand the geographical variability and the present day budget of the gases in the atmosphere. For the future, an increasing relative contribution to stratospheric chlorine and bromine from VSLS is expected as anthropogenic long-lived bromine and chlorine source gases are decreasing in the atmosphere. Available observations of VSLS for the tropics have been compiled in Montzka et al. (2011). Especially the data available for the free and upper tropical troposphere are derived from measurement campaigns conducted in the East Pacific and the Caribbean sector of the tropics. The West Pacific is expected to be the most important source region for air transported into the stratosphere (e.g. Newell and Gould-Stewart, 1981; Gettelman et al., 2002; Fueglistaler et al., 2004, 2009; Aschmann et al., 2009). High mixing ratios of brominated VSLS have also been observed occasionally in the atmospheric boundary layer in this region (Pyle et al., 2011) and also upper tropospheric values were enhanced compared to other atmospheric regions (Wisher et al., 2013). Due to the low ozone values observed in the upper troposphere in this region, low OH values and a low oxidation capacity are expected in this region resulting in prolonged lifetimes of many trace species (Kley et al., 1996; Solomon et al., 2005; Rex et al., 2013). A range of different emission inventories (Warwick et al., 2006; Liang et al., 2010; Ziska et al., 2013) has been compared to atmospheric observations (including those presented in this paper) by Hossaini et al. (2013), showing that significant differences in these scenarios exist for the West Pacific region. Here, we thus present an extensive dataset from in-situ measurements using a fully automated gas chromatograph (GC) with mass spectrometric (MS) detection and from whole air sampling system (WASP) with subsequent GC/MS analysis. The in-situ GC/MS is a new development called GHOST-MS (Gas cHromatograph for the Observation of Tracers –

coupled with a Mass Spectrometer) and was deployed for the first time during SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere). The measurements were performed in the West Pacific using the Falcon aircraft operated by the German Aerospace agency DLR (Deutsches Zentrum für Luft- und Raumfahrt) as part of the SHIVA project. Measurements flights were conducted from Miri in Northern Borneo and sampled a wide geographical range, different geophysical conditions and altitudes from the planetary boundary layer to the ceiling altitude of the aircraft of 13 km. The paper is organized as follows. First, we briefly present the SHIVA aircraft campaign in the West Pacific, the instruments used for the observations and the measurement flights performed during SHIVA. We then discuss the data retrieval for the in-situ GC/MS instrument GHOST-MS and the whole air sampling system WASP. Finally, we present the data, compare these to other observations, derive a bromine budget for the West Pacific and derive an estimate of the amount of bromine from VSLS reaching the stratosphere.

2 Origin of data

2.1 The SHIVA – campaign

One scientific aim of SHIVA was to improve the understanding of the influence of VSLS on the stratospheric halogen budget at the present and in the future under the aspect of a changing climate. As part of this project a field campaign in the Western Pacific was conducted in fall 2011. One focus of the campaign was the determination of the oceanic emission strength and the atmospheric mixing ratio of long- and very short-lived brominated substances. Also the atmospheric transport from the boundary layer to the upper troposphere as well as decay processes during this transport was investigated. The field campaign combined a variety of ground, air, ship and satellite based measurements. In this paper we focus on the measurements carried out with the German research aircraft FALCON.

The home base of the aircraft was in Miri on Borneo (Malaysia). From 16 November to 11 December, a total of 16 measurement flights were carried out to determine atmospheric mixing ratios of various trace gases and to study the atmospheric transport processes in this tropical region. An overview of the different flight regions and rationales is given in Table 1. Except for the first flight on 16 November, the instrument GHOST-MS performed very well during the campaign and obtained more than 500 measurements of ambient air in an altitude range from the ground up to 13 km.

Beside the in-situ measurements of halogenated hydrocarbons by the GHOST instrument by the Goethe University Frankfurt (GUF), the University of East Anglia (UEA) also investigated the mixing ratio of these species. For this a combination of the WASP – instrument (Whole Air Sample Pack) with a stationary GC/MS system was used. Overall, 215 samples covering an altitude range from the ground up to 4 km were analyzed during the campaign.

2.2 Instrumental setup

2.2.1 Gas chromatograph for observation of tracers – coupled with a mass spectrometer (GHOST-MS)

The measurement technique for the analysis of VSLS in ambient air is gas chromatography coupled with mass spectrometric detection (GC/MS); the in-situ instrument deployed onboard the Falcon aircraft is called GHOST-MS.

The analytical technique of GC/MS is a very versatile technique, widely used in atmospheric sciences for the measurements of halogenated compounds in the troposphere and stratosphere (e.g. Oram et al., 1995; Montzka et al., 1996; Schauffler et al., 2003; Laube et al., 2008; Miller et al., 2008). To our knowledge only one in-situ GC/MS system for airborne application has been described in the literature (Apel et al., 2003). There are very specific requirements and limitations for the operation of such an instrument onboard an aircraft. These include the speed of the chromatography, the dimensions, weight and power consumption of the instrument and the automation of the necessary pre-concentration of ambient air samples.

The principle of the analysis of ambient air is as follows: ambient air is drawn with a two-stage setup of three KNF N 86 KNDCB diaphragm pumps (two in parallel and one in serial) from outside the aircraft, compressed and passed through a chemical drying agent (magnesium perchlorate) in order to remove water vapor without affecting the analytes. Afterwards the air flows through a cooled sample loop at −80 °C, filled with an adsorption material (HayesepD), in order to trap all condensable trace gases on that loop. After a sufficient amount of air (150 mL) is passed through the sample loop, the loop is flash heated and the condensed species are desorbed with a carrier gas on to the separation columns. After the chromatographic separation of the different species on the MXT-1 pre column (7.5 m) and the GS-GasPro main column (22.5 m), the trace species are quantified using a mass spectrometer. To achieve a good temporal resolution, the pre-concentration on the sample loop and the chromatographic separation have to be optimized for speed.

This optimization is realized by several novel approaches during the development of the instrument. To avoid the use of liquid nitrogen or other cryogenics, which would have made the operation of the instrument onboard an aircraft much more complicated, we implemented a free piston Stirling cooler for the cooling of the sample loop. This is a very compact (15 cm × 15 cm × 30 cm), lightweight (3 kg) and efficient cooler (TD08, Twinbird Co.), which provides cooling temperatures down to −100 °C with an electrical power consumption of only 80 W. To our knowledge, Stirling coolers have never been operated before onboard an aircraft in order to be used as cooling agents for sample loops. To achieve fast heating and cooling rates of the separation column, we used a so called LTM-Module ("Lightweight Thermal Mass-Module", Agilent Technologies), which allows realizing heating rates of well over 100 K per minute. This is also a novel in airborne gas chromatography for the analysis of halogenated hydrocarbons.

The mass spectrometer (Agilent MSD 5975) is operated in negative ion chemical ionization (NICI) mode (e.g. Worton et al., 2008) and we can quantify 16 chlorinated, 10 brominated and one iodinated halocarbon in a sample of ambient air within a sample cycle of 4.3 min and a chromatographic runtime of 2.9 min. In this work only the brominated substances will be discussed, a chromatogram of the 10 identified brominated substances is shown in Fig. 1.

In addition to the time resolution, good detection limits, reproducibility and accuracy are necessary in order to resolve the atmospheric variability of the target compounds. The detection limit is calculated via the signal-to-noise ratio for each substance separately. The operation of the mass spectrometer in NICI-model allows the achievement of very low detection limits down to 1 ppq in a sample of 150 mL of air. The precision is determined via repeat measurements of a single calibration gas over a period of several hours. Applying no correction for temporal drifts, the standard deviation of those measurements is a conservative measure for the precision of the instrument. Most of the species are reported relative to the NOAA-ESRL calibration scales (e.g. Hall et al., 2013). For the two halons H-2402 and H-1202 the calibrations are based on intercalibration experiments with the University of East Anglia (UEA). For the short-lived mixed bromochlorocarbons the data are based on a preliminary scale by NOAA, transferred from UEA measurements during the measurement campaign in Borneo. The scale origin for the different substances is given in Table 2 together with the reproducibility and detection limits achieved with GHOST-MS. Note that the accuracy for the calibration gas given in Table 2 is a measure of the precision with which our calibration gases can be linked to absolute calibration scales of NOAA and UEA.

Data processing, e.g. the integration of the signal peaks for the determination of area and height of a peak is performed with self-written software called IAU_ Chrom. The advantage of this software compared to commercially available chromatography software is the sophisticated peak fitting algorithm which fits a probability distribution (Gaussian or Gumble function) to a peak in the predefined peak window. This is a very stable and reproducible method, especially for signal peaks with small signal-to-noise ratios or overlapping peaks.

2.2.2 Whole Air Sample Pack (WASP)

The WASP consists of thirty pyrex tubes (5 cm diameter, 35 cm long, approximately 700 mL) with 6 mm inlet and outlet tubes. The tubes are connected via PFA unions and tubing to two 1/8″ (approx. 3.2 mm) Valco STF 16-way flow-through valves.

Inlet air was compressed with a KNF AN18 series diaphragm pump with a PTFE diaphragm and a needle valve on the WASP vent was used to regulate the fill pressure. The final fill pressure was typically 40 psi (approx. 2800 hPa), although this was reduced at high altitudes due to the limitation of the pump. The sample tube was continually being flushed at elevated pressure until it was isolated by moving the Valco valve to a new position when a new sample flask was exposed and flushed. The flow rate of the flushing air was altitude dependent and so the averaging time for the flask sample being < 20 s at sea level up to 180 s at 4 km.

Between flights the WASPs were cleaned by a series of evacuation/fill/flush cycles (using zero grade nitrogen) and left at atmospheric pressure. Occasional blanks were performed on random sample flasks after cleaning with no problems found.

Samples were analyzed on a Dual-MS GC/MS system. Analytes were separated with a temperature programmed 105 m RTX-502.2 column (0.32 mm id, 1 µm film) at constant flow, which allowed the separation of all five bromomethanes. The column effluent was split using a silco-treated Valco 1/32″ (approx. 0.8 mm) Y-connector in a 50 : 50 ratio into two Agilent 5973N mass spectrometers, one in electron ionization (EI) mode and one in negative ion chemical ionization (NICI) mode. Bromomethanes, other halocarbons and alkyl nitrates were measured on the negative ion channel, whilst a limited range of hydrocarbons and a range of additional halocarbons were measured on the EI channel. Carbon tetrachloride, bromoform and CFC-113 were analyzed on both channels, and no significant differences in measured mole fractions were observed between the two channels.

1200 mL samples, dried with a 72″ counter-flow nafion dryer, were pre-concentrated prior to injection onto the GC column with a Markes Unity thermal desorption system using a carbographB/carboxen 1003 sample trap held at −10 °C. Injection from the trap was performed by heating the trap to 250 °C for 15 min. Working standards were analyzed after every 5 samples, and a helium blank run once per day. Analytical precision, determined from 7 consecutive measurements of the standard, was typically 3 % ($1\,\sigma$) for the bromomethanes and organic nitrates, and around 10 % ($1\,\sigma$) for hydrocarbons. Limits of detection (based on analytical precision and blanks) varied between compounds, but for bromomethanes, most halocarbons and organic nitrates they were typically < 0.01 ppt.

Full details of the use of the Markes Unity system coupled to negative ion GCMS can be found in Worton et al. (2008).

2.3 Data correction

The chromatographic system of the GHOST-MS cannot resolve the two substances CH_2Br_2 and $CHBrCl_2$ within a regular chromatographic run as used on the aircraft, as these substances coeluate on the separation column of the GC/MS system due to their very similar boiling point. For the further data analysis, e.g. for the calculation of the budget of total organic bromine, it is necessary to know the fraction each of the two species contributes to the total peak area. While this can be done easily for the calibration gas using a slower temperature programming in the laboratory and thus separating the two peaks, it is not possible for ambient air measurements due to the limited amount of time available for the separation. The fractions of the peak area determined by this experiment for our calibration gas are $C_{\mathrm{CH2Br2}} = 0.6494 \pm 0.0097$ and $C_{\mathrm{CHBrCl2}} = 0.3506 \pm 0.0097$. The corresponding mixing ratio in the calibration gas for these peak fractions are (3.25 ± 0.11) ppt for CH_2Br_2 and (2.08 ± 0.07) ppt for $CHBrCl_2$.

For the separation of the contribution of both substances to ambient air observations, we assume that a linear relationship exists between the mixing ratios of CH_2Br_2 and $CHBrCl_2$ as described e.g. in Yokouchi et al. (2005), Brinckmann et al. (2012). The relationship used for the SHIVA observations is based on simultaneous measurements performed by the UEA on glass flasks sampled onboard the FALCON and analyzed afterwards using a GC/MS system set up at the aircraft hangar in Miri. From these measurements, the linear relation between the mixing ratio of CH_2Br_2 and $CHBrCl_2$ has been determined as (all units in ppt).

$$[CHBrCl_2] = 0.3239 \cdot [CH_2Br_2] - 0.0498 \quad (1)$$

Assuming such a linear relationship between the mixing ratios of these two species and taking into account the relative sensitivity of the system to both compounds, which is known from laboratory measurements, the contribution to the peak area can be separated and both species can be quantified, as explained in detail in Sala (2014).

Further to the separation of the double peak from CH_2Br_2 and $CHBrCl_2$ the GHOST-MS as operated during SHIVA displays a memory effect, i.e. the preceding sample is not entirely flushed from the system and the instrument thus has a "memory". Only the substances CH_2Br_2, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ are affected by this memory effect, the strength of which increases with increasing boiling point of the substance. This memory effect was quantified using laboratory measurements and the data were corrected accordingly. Finally it was noted that due to a late eluting peak from the calibration gas, the sensitivity of the system was somewhat reduced immediately after the calibration gas measurements. This too was quantified by laboratory measurements and the results were corrected accordingly. The quantification and the entire procedure for the corrections explained here are described in detail in Sala (2014). The maximum correction which was necessary was up to 65 % for some $CHBr_3$ data points, while typically the correction was less than 10 %.

2.4 Data origin and definition of altitude intervals

For the interpretation of the measurements it is convenient to group the data into different altitude intervals and to consider these intervals separately. In this work, we focus on measurements near the source regions of VSLS – the boundary layer – as well as measurements in the upper troposphere. For the comparison with other data sets, it is also important to know the geographical origin of the data.

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The data given in Montzka et al. (2011) for the upper tropical troposphere cover an altitude range of 10 to 12 km (Table 1–7 in Montzka et al., 2011) and originate from a variety of measurement campaigns which are listed in detail in Montzka et al. (2011). The measurements of the upper troposphere during SHIVA cover an altitude range from 10 km to the maximum cruise altitude of the FALCON aircraft of approximately 13 km.

The altitude range of 2 to 10 km covers the so called free troposphere. This interval is used for the data reported in Montzka et al. (2011) as well as for the SHIVA data.

The data for the marine boundary layer used in Montzka et al. (2011) are adapted from Law and Sturges et al. (2007) for the marine boundary layer, which include all data below 1 km. These data originate from a variety of measurement campaigns with samples taken in the entire Pacific, as well as the Atlantic and the Indian Ocean (see Law and Sturges et al., 2007 for details).

The diverse spatial sources and the variety of the instruments and calibrations scales contributing to the data in Montzka et al. (2011) have to be taken into account when comparing those data with the measurements presented here. See e.g. Hall et al. (2013) for an intercomparison of different halocarbon measurement scales.

To determine the altitude of the boundary layer during SHIVA, the profiles of potential temperature, relative humidity and wind speed are used to calculate an average value (S. Fuhlbrügge, IFM Geomar, Kiel, Germany, personal communication, 2013). At the transition between boundary layer and free troposphere, potential temperature increases with altitude, whereas relative humidity and wind speed mostly decrease (Roedel, 2011). The three meteorological parameters are obtained from the basic instrumentation of the FALCON as well as from frequent radiosonde launches from the RV SONNE. The data from the FALCON result in an average boundary layer height of 450 m, which is a rough estimate for the whole flight track, because the transition between the boundary layer and the free troposphere is only determined during takeoff and landing, when passing the boundary layer. The radiosonde launches give information about the boundary layer altitude, which is somewhat away in space and time from the different flight tracks. The average value of 300–500 m from these radiosonde releases is in a good agreement with the altitude of 450 m calculated from the FALCON measurements (S. Fuhlbrügge, IFM Geomar, Kiel, Germany, personal communication, 2013).

For the interpretation of the results we distinguish between different variables. The mean value in a given altitude interval is the arithmetic mean of all data points in that interval. The corresponding absolute standard deviation, or scatter, is determined by two factors: the measurement precision of the instrument and the atmospheric variability. These two variables are statistically not linked with each other and can therefore be combined via Gaussian error propagation.

$$\text{scatter} = \sqrt{\text{precision}^2 + \text{variability}^2} \tag{2}$$

and therefore

$$\text{variabilty} = \sqrt{\text{scatter}^2 - \text{precision}^2} \tag{3}$$

For further considerations, the atmospheric variability is used as specified by the calculated value given in Eq. (3). The measurement precision of the instrument is taken from Table 2.

3 Results

3.1 Altitude profiles of VSLS

In this chapter, we present the altitude profiles for the five VSLS measured by the in-situ GC/MS instrument GHOST-MS from GUF and by the ground-based GC/MS instrument from the UEA analyzing the WASP canisters. Both instruments were flown in parallel on board of the FALCON aircraft. In order to derive the total organic bromine budget, we further take into account the longer-lived bromine species, i.e. halons and

CH_3Br measured by the GHOST-MS instrument. The mean mixing ratio as well as the atmospheric variability in the different altitude intervals defined in Sect. 2.4 will be discussed. We consider the results from measurements in the planetary boundary layer (PBL, 0–450 m), in the free troposphere (FT, 2–10 km) and in the upper troposphere (UT, 10–13 km). The data from the UEA instrument only covers the range up to ∼ 4 km due to a problem with the WASP pumping system.

The results for the major and minor VSLS derived from both instruments, GHOST and WASP are summarized in Table 4. For the WASP instrument the vertical extension of the data is limited and therefore mean values, scatter and variability could only be calculated for the planetary boundary layer.

Given the measurement uncertainties of both instruments, the agreement between WASP and GHOST data is within the expected range for all species. On average the values for CH_2Br_2 observed by GHOST-MS are slightly larger, while WASP $CHBr_3$ are higher than GHOST measurement. The difference of about 20 % for $CHBr_3$ between GHOST and WASP are just in the range of the overall measurement uncertainty of both instruments (shown in Tables 2 and 3). For the mixed bromochlorocarbons overall reasonable agreement is observed within the expected uncertainties. One can argue that the observed differences are partly caused by the fact that especially the shortest lived VSLS have a high spatial and temporal variability in the planetary boundary layer and that both instruments did not measure (GHOST) or sample (WASP) simultaneously. A more detailed analysis of vertical distribution is given in the following sections.

3.2 Major VSLS: CH_2Br_2 and $CHBr_3$

The mean mixing ratio of CH_2Br_2 in the PBL is found to be 1.19 ppt for the GHOST and 1.15 ppt for the WASP data with a moderate atmospheric variability of ±17 % and 11 % respectively (see Table 4). It is obvious from Fig. 2 that the CH_2Br_2 mean values as well as the variability (shown for better visualization only as the 95 % percentiles for the WASP data) derived from UEA and GUF show an excellent agreement over the whole overlapping range of both instruments from 0–4 km. Within the UT, the mean mixing ratio is 0.90 ppt with an atmospheric variability of ±13 %. The decay between PBL and UT is 24 % – only for the GHOST data. In the following sections, the analysis between PBL, FT and UT mixing ratios will be done for reason of consistency only with the GHOST dataset.

With a typical free tropospheric lifetime of 123 days (Montzka et al., 2011), CH_2Br_2 is one of the longer lived VSLS. Therefore, it is expected that this substance has a relatively homogenous distribution above the PBL. Within the FT, the mean mixing ratio as well as the atmospheric variability show the lowest values of all VSLS with a mean mixing ratio of 0.88 ppt and a variability of ±8 %, respectively. It is clear to see that the flight 20111119a, blue data points in Fig. 2, shows exceptionally high mixing ratios in the free troposphere. For this reason the CH_2Br_2 (as well as for CH_2BrCl and $CHBrCl_2$) mixing ratios from this flight have been excluded from calculation of the mean values shown in Table 4.

A possible explanation for the lower mixing ratios and lower atmospheric variability in the free troposphere compared to the upper troposphere is that the FT is less affected by direct convective outflow than the UT. Deep convection in the tropics can transport air masses with high mixing ratios from the lowest atmospheric layers within a relatively short timescale to the upper layers of the troposphere. The region of main convective outflow is located at altitudes between about 10 and 13 km (see e.g. the discussion in Gettelman and Forster, 2002).

Two flights performed towards the end of the campaign (20111211a and b) probed the outflow from several large convective cells at an altitude of approximately 11 km. Both of these flights show a slightly enhanced mean mixing ratio in the altitude interval between 10 and 11 km as indicated by the olive green line in Fig. 2. The altitude profile can also provide information on the level of entrainment, which describes the part of the atmosphere in which air is mixed into the convective cells. The mixing ratios measured in the FT between 2 km and 10 km are, except for flight 20111119a, lower than the highest mixing ratios observed in the UT. This suggests that the entrainment of air masses into convective cells occurs mainly below 2 km, where higher mixing ratios can be found. This will be discussed in more detail with respect to the observations of $CHBr_3$.

With a free tropospheric lifetime of about 24 days (Montzka et al., 2011), $CHBr_3$ has the shortest atmospheric lifetime of all brominated VSLS. The altitude profile observed during SHIVA is shown in Fig. 3. $CHBr_3$ features larger variations than CH_2Br_2 at all altitude intervals. The mean mixing ratio in the PBL is 1.43 ppt for the GHOST and 1.9 ppt for the WASP dataset with corresponding atmospheric variability of ±37 % and ±28 %. As discussed above, the mean values in the PBL are just in the range of the uncertainties. Part of the difference could also be explained due to both instruments not always sampling the same air. In the lower FT, where WASP data are still available, the median and the variability for both instruments agree quite well inside the uncertainties. The highest mixing ratios of $CHBr_3$ were found to be 3.42 ppt (measured by GHOST-MS, near Miri) and 3.78 ppt (measured by WASP, Strait of Malacca) respectively. In the free troposphere the mean mixing ratio decreases to 0.56 ppt and at the same time the atmospheric variability decreases to ±28 %, much less pronounced than in the PBL. The altitude profile of $CHBr_3$ shows a much stronger vertical gradient than the profile of the longer lived substance CH_2Br_2. The decrease in the mean mixing ratio between PBL and FT for $CHBr_3$ is 61 % and thus, as expected, significantly higher than for CH_2Br_2, for which the mean mixing ratio decreases by only 26 %. At altitudes between 10 km and 13 km (Box A in Fig. 3) both, the mean mixing ratio (0.61 ppt) and the atmospheric variability (±33 %), increase again in the upper troposphere compared to the free troposphere. The decay in mixing ratio between PBL and UT is 57 % for $CHBr_3$ in contrast to only 24 % observed for CH_2Br_2.

In contrast to the profile of CH_2Br_2, the profile of $CHBr_3$ shows a region in the upper part of the free troposphere with enhanced mixing ratios compared to the lower part of the free troposphere. This region is marked with the Box B in Fig. 3 and is located at an altitude of 8–9.5 km. For the complete free troposphere (2–10 km), we found a mean mixing ratio of 0.56 ppt with an atmospheric variability of ±28 %. The measurements in the altitude range marked with Box B also show an enhanced mean mixing ratio

(0.62 ppt) and an enhanced atmospheric variability (±37 %) with respect to the FT. This indicates that convective outflow detraining in the upper part of the FT can influence $CHBr_3$ while this is not significant for the longer lived CH_2Br_2 which shows a much smaller vertical gradient.

The mixing ratios of $CHBr_3$ in the FT are almost entirely below the value marked with the red dotted line in Fig. 3. As already suspected for CH_2Br_2, the air masses with the high mixing ratios (Boxes A and B) must originate from atmospheric regions with higher mixing ratios. These are the regions below 2 km, shown by the Box C in Fig. 3.

3.3 Minor VSLS: CH_2BrCl, $CHBr_2Cl$ and $CHBrCl_2$

The altitude profile of CH_2BrCl (shown in Fig. 4) shows a rather compact distribution with the exception of the observations from flight 20111119a. During this flight, very high mixing ratios were measured by the GHOST-MS instrument. These are a factor of 2.5 higher than the mixing ratios measured during the rest of the campaign. It cannot be excluded, that this was due to some kind of measurement error of the instrument, but we have no indication for a malfunction during that particular flight.

Several studies (e.g. Brinckmann et al., 2012) reveal a poor correlation between CH_2BrCl and the other brominated VSLS. This indicates that the sources for CH_2BrCl differ significantly from those of the other VSLS. Therefore, a possible explanation might be that this flight was performed closer to a singular source of CH_2BrCl than any other flight. However, enhanced mixing ratios for other VSLS (CH_2Br_2 and $CHBrCl_2$) are also derived for this flight. As these enhanced mixing ratios seemed not to be typical in this part of the Western Pacific, the data from flight 20111119a are not included in the calculation of the tropical background distribution.

With a typical local lifetime of 137 days in the lower troposphere, CH_2BrCl has the longest lifetime of all brominated VSLS. With a mean mixing ratio in the PBL of 0.11 ppt for GHOST and 0.15 ppt for WASP, decreasing by 18 % down to 0.09 ppt in the upper troposphere, CH_2BrCl is also the substance with the lowest mixing ratio of all brominated VSLS. Given the relative large uncertainties in the calibration for both data sets, 15 % (GUF) and 9 % (UEA) (see also Tables 2 and 3), the mean values given in Table 4 as well as the median in Fig. 4 matches. However, the WASP data set from UEA seems to have substantially higher variability in the PBL and the lower FT.

The relatively small decrease between the PBL and the free and upper troposphere can be explained by the relatively long lifetime, which leads to a rather homogeneous distribution of CH_2BrCl in the observed altitudes. Another explanation for the low and rather homogeneous mixing ratios in the boundary layer could be that the measurements – except for flight 20111119a – have not probed air masses close to the source regions of CH_2BrCl. The atmospheric variability in the PBL is ±21 % for the GHOST and 33 % for the WASP dataset, ±8 % in the FT and ±15 % in the UT (only GHOST data). The vertical distribution and the atmospheric variability in the three compartments are comparable to those of CH_2Br_2 in agreement with the very similar lifetimes of both species.

The mean mixing ratio of $CHBrCl_2$, which has a free tropospheric lifetime of 78 days, shows a decrease with altitude from 0.34 ppt in the PBL to 0.24 ppt in the UT, which corresponds to a percental decrease of 26 %. The atmospheric variability is ±20 % and ±16 %, respectively, in the free and upper troposphere, which is slightly larger than the variability of the longer lived species CH_2Br_2 and CH_2BrCl but smaller than for the two shorter lived species $CHBr_2Cl$ and $CHBr_3$.

As for CH_2Br_2, the agreement is excellent between the $CHBrCl_2$ observations in the PBL from UEA and GUF during SHIVA as can be seen in Fig. 5 and Table 4. This is partly related to the fact that the mixing ratios of $CHBrCl_2$ for GHOST rely on its linear relation with CH_2Br_2 (see Eq. 1) derived from the UEA observations during SHIVA, as both species cannot be chromatographically separated by the GHOST instrument.

$CHBr_2Cl$ has a lifetime of less than two month in the free troposphere. The mean mixing ratios in the PBL are 0.32 ppt for GHOST, and 0.33 ppt for WASP data. The decrease in the mixing ratio of 41 % between the PBL and the upper troposphere, as well as the atmospheric variability with ±34 % (PBL) and ±21 % (UT) is already quite pronounced. While the mixing ratio in the UT is the second lowest of all species discussed here, the effect on stratospheric bromine depletion is probably in the range as the sum of the two longer lived minor VSLS $CHBrCl_2$ and CH_2BrCl that has together about twice the mixing ratio of $CHBr_2Cl$ in the UT, but carries only one bromine atom.

3.4 Long lived bromine source gases: halons and CH_3Br

Due to their long atmospheric lifetime, it is expected that the mixing ratios of the halons are very homogeneous in the troposphere and no vertical gradient between the PBL and the UT is expected in the absence of tropospheric sinks. We note that this is the case for H-1301 with a tropospheric lifetime of more than 10 000 yr (Newland et al., 2013). H-1211 and H-2402 have small photolytic sinks in the troposphere with lifetimes of 25 and 41 yr respectively (Newland et al., 2013). H-1202 is the only halon with a comparatively low tropospheric lifetime of about 3 yr (Newland et al., 2013) and thus has a significant sink in the troposphere due to photolysis. The observed vertical distributions of the four halons are shown in Fig. 7, the corresponding mixing ratios are listed in Table 5.

The mean mixing ratio for H-1301 (see Fig. 7a) is 3.19 ppt in the PBL and 3.28 ppt in the upper troposphere. For H-1301, the standard deviation of the atmospheric measurements is less than the measurement precision shown in Table 2. Consequently, no physically reasonable atmospheric variability can be calculated, because the value in the radicand in Eq. (3) becomes negative. It can therefore be assumed that the measured atmospheric variability is obscured by the measurement precision of the instrument. We note that while H-1301 is also widely used as fire extinguishing agent onboard passenger aircraft in fixed installations, no enhancement of this compound was observed at any of the rather small airports used for the refueling stops. The difference between the PBL and the UT values is not significant within our uncertainties.

In the upper troposphere, H-1211 (see Fig. 7b) has a mean mixing ratio of 4.16 ppt with an atmospheric variability of ±3 %. The mean mixing ratio in the PBL is 4.29 ppt with an atmospheric variability of ±9 %. Some of the measurements conducted at the ground show significantly higher values than the mean value. The highest mixing ratio measured at the ground level is 6.88 ppt of H-1211. All observations of significantly enhanced H-1211 levels were made during refueling stops of the aircraft at airports in Malaysia (e.g. Tawau). During the refueling process on the runway the measurements were continued. H-1211 was mainly used as a fire suppressant in portable fire extinguishers in aircrafts (see e.g. HTOC, 2011). It is very likely, that small leakages in those fire extinguishers lead to the observed locally enhanced mixing ratios at the airports.

H-2402 (see Fig. 7d) has an overall mean atmospheric mixing ratio of 0.43 ppt, with no observable difference between the PBL and the UT. Also the atmospheric variability with a value of ±3 % is quite low. As this compound is used nearly exclusively in the states of the former Soviet Union (Newland et al., 2013) and the observations in Malaysia are far from the source region, no direct sources are expected even at airports.

H-1202 (see Fig. 7c) is the substance with the most pronounced atmospheric variability of all halons. With a mean mixing ratio of 0.028 ppt in the PBL, the variability is ±17 %. In the upper troposphere, the mean mixing ratio decreases down to 0.026 ppt, still showing an atmospheric variability of ±8 %. This behavior is expected compared to the other halons as H-1202 is the shortest lived of the four substances. The rather short tropospheric lifetime of about 3 yr is thus obviously not sufficient to lead to a significant vertical gradient but it is reflected in an enhanced variability with respect to the other halons.

CH_3Br is the most abundant brominated substance in the atmosphere with a tropospheric lifetime of 0.8 yr. The altitude profile of the measurements is shown in Fig. 8, the mixing ratios in the different altitude intervals are listed in Table 5. A mean mixing ratio of 8.79 ppt in the PBL was observed with an atmospheric variability of ±38 %. Within the PBL, some very high mixing ratios have been observed. The highest value was 28.77 ppt. These high values, as well as the pronounced variability, could be explained by measurements near to sources of CH_3Br. In the upper troposphere, the mean mixing ratio decreases by 16 % down to 7.35 ppt, the atmospheric variability is ±7 %, thus significantly lower than in the planetary boundary layer.

3.5 Comparison of the dataset with data given in WMO 2010

In this section we compare the dataset obtained during SHIVA with the tropical VSLS data compiled in the last WMO report (Montzka et al., 2011). Furthermore, we derive a budget of the total organic bromine in the upper troposphere over the western Pacific region from our measurements.

3.5.1 Measurements in the boundary layer

Available measurements of VSLS from the marine boundary layer up to the tropical tropopause are summarized in Montzka et al. (2011), divided into six different altitude intervals. These data were obtained from different campaigns, as mentioned in Sect. 2. We compare our measurements with the data given for the marine boundary layer (listed in Table 6) and the upper troposphere (listed in Table 7). Note the slightly different definitions for the altitude intervals as explained in detail in Sect. 2.4. Measurements from the ground up to 1000 m are summarized as marine boundary layer in Montzka and Reimann et al. (2011), whereas the marine boundary layer was found to be on average between 0 and 450 m during SHIVA.

For the comparison with the boundary layer values, the median instead of the arithmetic mean is used to ensure data comparability between the SHIVA and Montzka et al. (2011) data sets.

The median values shown in Table 6 for the different VSLS in the boundary layer tend to be somewhat lower during the SHIVA campaign than the values published in Montzka et al. (2011). Within the one sigma measurement uncertainty the median value of CH_2Br_2, $CHBrCl_2$ and $CHBr_2Cl$ for both instruments agrees with the median given in Montzka et al. (2011). Assuming twice the measurement uncertainty, an agreement is also found for $CHBr_3$.

A very large discrepancy is observed for CH_2BrCl between values of both instrument during SHIVA and the values reported by WMO. Even the ranges observed with the GHOST and WASP instruments during SHIVA and the range given in Montzka et al. (2011) do not overlap. This discrepancy may be due to the fact that CH_2BrCl is not correlated with the other VSLS and therefore entirely different sources could have been seen during the different campaigns without affecting the remaining VSLS. The boundary layer value for CH_2BrCl in Montzka et al. (2011) is directly transferred from (WMO, 2007) and it is also much higher than the free tropospheric and upper tropospheric values given in Montzka et al. (2011). This may be an indication that this value is based on a calibration scale which is not compatible with our measurements conducted by UEA and GUF. Overall the observed data ranges in the PBL for all 5 brominated VSLS during SHIVA are smaller than the ranges reported in Montzka et al. (2011). However, the ranges given in Montzka et al. (2011) are calculated in a slightly different way, as they are based on observations from different campaigns, regions and seasons, making this comparison difficult.

3.5.2 Measurements in the upper troposphere

In Montzka et al. (2011) the interval between 10 and 12 km is defined as the upper troposphere. During SHIVA, the aircraft operated at a maximum altitude of 13 km. As we see no further decay in mixing ratio of all organic brominated compounds between 12 km and 13 km during SHIVA, we use the range of 10 to 13 km for the upper troposphere in order to obtain better statistics. Observations in the same region have recently been published by Wisher et al. (2013).

Our observations in the upper troposphere during SHIVA, the data for S.E. Asia (0–15° N) published in Wisher et al. (2013) and the data given by Montzka et al. (2011) are summarized in Table 7. The data from Wisher et al. (2013) show a very good agreement with our measurements presented here for all VSLS.

Comparing our measurements with the data given in Montzka et al. (2011), they agree within a single measurement uncertainty with the values, with the exception of $CHBr_2Cl$ and $CHBrCl_2$. In particular the values of $CHBrCl_2$ presented in this work are about a factor of 2 higher than the WMO data. However, for both substances the range of the observations is in very good agreement with the values of (0.23 ± 0.13) ppt for

$CHBrCl_2$ and (0.15±0.08) ppt for $CHBr_2Cl$ reported by Wisher et al. (2013) derived from CARIBIC air samples. The discrepancy for these two minor VSLS given in Montzka et al. (2011) is not well understood. It might be due to calibration uncertainties as well as due to natural variability in the different sampling regions and seasons.

The ratio between the values measured in the upper troposphere and the boundary layer, which is the source region for the TTL, is a measure, of the chemical decay between both reservoirs. This ratio is shown in Table 8 for the values compiled in Montzka et al. (2011) and our observations during SHIVA. In general, it is expected that the decay is stronger for shorter lived compounds. Overall, the observed gradient in the mixing ratios of the VSLS between the two altitude intervals is weaker during SHIVA. The greatest discrepancy between the two datasets is found for CH_2BrCl. The decline of this substance given by Montzka et al. (2011) is more than four times larger than derived from the SHIVA observations. A decay of the same order as observed for CH_2Br_2 and a significantly smaller decay than observed for the shorter lived $CHBr_3$ would be expected for CH_2BrCl due to its lifetime. Two other substances presented in Montzka et al. (2011), $CHBrCl_2$ and $CHBr_2Cl$, also feature a surprisingly strong negative vertical gradient.

The best estimate of the typical free tropospheric lifetime of the VSLS is in the range from 137 days (CH_2BrCl) to 24 days ($CHBr_3$). Due to this rather narrow range of tropospheric lifetimes the different substances should display rather similar decay rates. In the SHIVA dataset, the decay is in the range of 20–30 % for all substances except for the two shortest lived species, $CHBr_2Cl$ and $CHBr_3$. This may be due to the different chemical degradation processes. Both species have significant photochemical loss and in the case of $CHBr_3$ photolysis, which is mostly independent of altitude, is the dominant loss process. The chemical degradation via the OH-radical is dominant for the other VSLS. However, the rate constants for the reaction with the OH-radical show a strong temperature dependence (Hossaini et al., 2010; Orkin et al., 2013) and this loss process is thus much less efficient at higher altitudes due to decreasing temperature. The decay rates based on the data compiled in Montzka et al. (2011) show a much more inhomogeneous pattern. In particular, no relationship between the decay between PBL and UT and the lifetime is observed for the data compiled in Montzka et al. (2011), while our observations clearly show that for the VSLS the vertical gradient between both reservoirs is anti-correlated to their lifetime.

These large differences in the degradation rates for the WMO data are most probably caused by inconsistent calibration gas scales and the combination of observations from different regions and periods. In particular for the mixed bromochlorocarbons CH_2BrCl, $CHBrCl_2$ and $CHBr_2Cl$ no consistent and internationally intercompared calibration scale exist. This is so far only available to a certain degree for CH_2Br_2 and $CHBr_3$ (Hall et al., 2013; Jones et al., 2011). In contrast the SHIVA data derived from GUF with the GHOST instrument presented here rely on the same calibration gas scale for the different altitude regions and are from one period and region. This emphasizes the need for a consistent scale for VSLS species and for vertically resolved observations from different regions and during different seasons.

Table 9 shows the mixing ratios of the long-lived halons and CH_3Br obtained during SHIVA and compared with calculated tropospheric mean values for the end of 2011. The global tropospheric mean values are derived from different ground based measurements at remote locations from the NOAA-ESRL network (Montzka et al., 2003). For the comparison, we use our data from the free and upper troposphere, since it can be assumed, that these air masses are not influenced by local sources from the boundary layer. In addition, the changes in mixing ratio between the boundary layer and the free troposphere are insignificant for these long-lived substances compared to the VSLS. Therefore, the long-lived substances are not significantly affected by convective transport from the boundary layer in the free and upper troposphere.

The mixing ratios for the long-lived substances show an overall very good agreement with the H-1301, H-1211, H-2402 and CH_3Br data published by Montzka et al. (2003), (updated) and the H-1202 data published by Newland et al. (2013). H-1211 and H-1202 show slightly higher mixing ratios during SHIVA, but they still agree within the 2 σ uncertainty. For the remaining three substances we find a match within the 1 σ measurement uncertainty. Except H-2402, all substances measured during SHIVA show a slightly enhanced mixing ratio. This may be due to the fact, that occasionally slightly polluted air was sampled during the SHIVA campaign and therefore even the measurements in the free and upper troposphere do not reflect completely remote air masses. This is consistent with the vertical profiles presented in Figs. 2 and 3, showing that convection can locally transport boundary layer air to the free and upper troposphere. Another circumstance which has to be taken into account is the link of our calibration gas scale to the NOAA-Scale. In the International Halocarbons in Air Experiment (IHALACE) (Hall et al., 2013), which was carried out from 2004 to 2006, our laboratory reported slightly higher mixing ratios for H-1301 and H-1211 compared to the NOAA laboratory.

3.6 Budget of total organic bromine in the upper troposphere

Table 10 shows a comparison of the total organic bromine budget for the upper troposphere derived from GHOST measurements during SHIVA and "WMO data" reported in Montzka et al. (2011). The data from SHIVA is slightly higher than that derived in Montzka et al. (2011) for the total organic bromine, although consistent within the uncertainties. The SHIVA results for the five VSLS are also in very good agreement with airborne observations presented in Wisher et al. (2013) for the same region. The halons show an elevated mixing ratio by 2.6 %, the mixing ratio for CH_3Br and the VSLS are elevated by 5.6 % and 20 %, respectively. The total organic bromine calculated for the SHIVA dataset is 7 % higher than those of Montzka et al. (2011). The contribution of the VSLS given by the SHIVA dataset is (4.35 ± 0.60) ppt for the upper troposphere. This is 0.71 ppt or 20 % higher than the value given in Montzka et al. (2011), and thus slightly outside our estimated uncertainty range, supporting the finding that the Western Pacific may be a slightly outstanding source region for VSLS (Wisher et al., 2013). Regarding the individual substance classes, the halons contribute most (42 % SHIVA, 43 % WMO) to the total organic bromine. CH_3Br has a smaller contribution (37 % for both datasets). The smallest contribution to the total organic bromine in the upper troposphere is from VSLS (21 % SHIVA, 21 % WMO). In general, the overall agreement between the total organic bromine found during SHIVA and reported by Montzka et al. (2011) is still in the range of 1 σ uncertainty, especially the partitioning between the three substance classes is nearly the same. The altitude profile of total organic bromine is shown in Fig. 9.

3.7 Budget of total organic bromine at the LZRH

In order to obtain information about the quantity of total organic bromine entering the stratosphere, we consider the budget at the Level of Zero Radiative Heating (LZRH), in a similar way as suggested in Montzka et al. (2011). Air masses reaching this level are expected to enter the stratosphere. Under this condition, it is assumed that also product gases released from source gases above this level are transported into the stratosphere. According to Gettelman et al. (2004) the LZRH is located between 15 km and 15.6 km, an altitude which could not be reached during SHIVA. The maximum altitude reached during the SHIVA campaign was about 13 km. To obtain information about the mixing ratios of the substances and therefore a bromine budget at the LZRH, we make the following assumptions: (i) for the long lived halons as well as for CH_3Br we assume, that there is no change in the mixing ratio between the upper troposphere and the LZRH and (ii) for the substance class of VSLS, we estimate that the degradation between these two altitude intervals derived from the data presented in Montzka and Reimann et al. (2011) is representative for our observations too. Therefore, we compare the values given for the individual substances in Montzka et al. (2011) for the upper troposphere and the LZRH (Tables 1–7 in Montzka et al. (2011) and calculate a percental degradation rate. With these assumptions, we can use our measurements in the upper troposphere to estimate values for the LZRH during the SHIVA campaign. The results for these calculations are shown in Table 11.

The values for CH_2BrCl given in Montzka et al. (2011) for the different altitude intervals originate from different campaigns. This may explain the – physically not very meaningful – increase in mixing ratio by 11 % between the UT and the LZRH. Therefore, the mixing ratio of CH_2BrCl is assumed to be constant between these two levels for the SHIVA dataset. For the remaining VSLS a decline between the UT and the LZRH is observed in the data compiled in Montzka et al. (2011), which is most pronounced for $CHBr_3$ with a value of 56 %.

In analogy to the bromine budget for the UT presented in Sect. 3.6, we calculate a budget of the total organic bromine at the LZRH using the calculated values given in Table 11. The results of this LZRH bromine budget are presented in the Table 12 and compared with different data published in the literature. Within their degree of measurement uncertainty, the values of the different substance classes and the overall amount of total organic bromine calculated for the SHIVA campaign agree with the data given in Montzka et al. (2011).

We also compare our calculated data for SHIVA with the results of two measurement campaigns using balloon borne whole air samplers, which were carried out by the Goethe University Frankfurt (GUF). These two campaigns were carried out in 2005 (Laube et al., 2008) and 2008 (Brinckmann et al., 2012) in Teresina, Brazil (5° S). Using a cryogenic whole air sampler (e.g. Engel et al., 1997), samples at an altitude of 15.20 km (year 2005) and 14.85 km (year 2008) have been taken during these campaigns and analyzed afterwards using a GC/MS system in the laboratory in Frankfurt. The analysis for a broad variety of halocarbons was done half a year (2005) and two month (2008) after the samples were taken. For the long-lived substances very good agreement is achieved between the data calculated for SHIVA and observed mixing ratios during the Teresina campaigns. For the substance class of VSLS, Brinckmann et al. (2012) found a lower value at the LZRH, which is still in agreement within its measurement uncertainty with the value of (2.88 ± 0.60) ppt calculated from the SHIVA data. The mixing ratio of VSLS at the LZRH found by Laube et al. (2008) is substantially lower (1.25 ppt) than expected by other studies and our calculations. This low mixing ratio is most probably due to the long period which elapsed between sampling and analysis of the air samples. As shown by Laube (2008) and verified by Brinckmann (2011), a decomposition of short-lived substances can occur in the stainless steel sampling canisters. The decrease cannot be quantified, as it is – among other things –

a function of water vapor content, sample pressure and the surface conditions of the individual sample canister. These things are highly variable and therefore difficult to characterize. Another aspect may be due to the slightly higher sampling altitude (and therefore longer transport time of the air mass into this region) of the measurement from the year 2005.

4 Conclusions

During the measurement campaign in Malaysia, which took place in November and December 2011, more than 500 samples of ambient air have been measured with the in-situ GHOST-MS instrument of GUF and about 215 air samples have been collected with the WASP instrument onboard the research aircraft FALCON and analyzed afterwards with a state-of-the art GC/MS system by the UEA. In total 16 scientific flights have been performed in the boundary layer as well as in the free and upper troposphere. From these air samples, mixing ratios of four long-lived halons, methyl bromide and five very short-lived substances, including the two major VSLS dibromomethane and bromoform have been determined.

The independent observations of VSLS derived from UEA and GUF show very good agreement inside the 2 σ measurement uncertainty over the whole overlapping vertical range of both instruments (see Figs. 2–5).

The atmospheric variability in the different altitude intervals increases with decreasing lifetime of a VSLS, Also the decrease in mixing ratio between PBL and FT and PBL and UT is stronger the shorter the lifetime of a VSLS is, which leads to a very pronounced altitude profile for the shortest lived VSLS. Within the boundary layer, the highest mixing rations of VSLS have been found.

Using the mean mixing ratios in the upper troposphere, a budget of the total organic bromine was determined by multiplying the mixing ratio of each substance with the number of their bromine atoms. The calculated values of the total organic bromine in the upper troposphere is (20.01 ± 1.77) ppt and the total amount from VSLS is (4.35 ±

0.59) ppt. Both values are higher than the ones reported by Montzka et al. (2011), but only the latter is slightly outside the range of 1 σ uncertainty.

Regarding the entry of bromine in the stratosphere, the estimation of the bromine content at the LZRH gives a value of (18.54 ± 1.78) ppt and a value of (2.88 ± 0.60) ppt from VSLS, reflecting a fraction of 16 % of the total bromine budget. The amount of total organic bromine from VSLS at the LZRH is only 0.18 ppt higher than the value published in Montzka et al. (2011), while being slightly higher than previous estimates from our group based on balloon-borne measurements over Teresina/Brazil.

When comparing the data obtained during SHIVA with those published in Montzka et al. (2011), which are mainly from measurement campaigns in the central and eastern Pacific, generally a good agreement in the mixing ratios is found, with our measurements showing slightly enhanced total organic bromine. The main exceptions to the good agreement are the CH_2BrCl in the boundary layer, where we find much lower values and $CHBrCl_2$ in the upper troposphere, where our measurements suggest higher mixing ratio. Slightly higher mixing ratios of short-lived bromine species for the upper troposphere of the West Pacific have recently also been suggested by Wisher et al. (2013) in comparison to observation carried out over Central America and Africa. As noted e.g. by Ashfold et al. (2012) natural variability like e.g. the phase of the ENSO and seasonality may affect the sources and sinks of VSLS and the transport into the UT. Altogether, this shows that the West Pacific may be a preferred region for VSLS transport to the stratosphere. However, the total organic bromine and the total amount of VSLS at the LZRH calculated from the SHIVA dataset give only a weak indication of enhanced source gas injection of organic bromine into the stratosphere. More vertically resolved observations are crucially needed to sample the entire range of natural variability and to confirm this possible role of the Western Pacific as a source region for stratospheric halogens from short-lived species.

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Table 1. Overview over the 16 measurement flights during the field campaign of SHIVA (Pfeilsticker, K. and the SHIVA consortium, The SHIVA Western Pacific campaign in November and December 2011, Post-campaign Activity Report, 2011, modified).

Flight	Take off and landing (UT)	Rationale	Region
20111116a	04:13 07:28	MBL sampling, deep profile	Coast between Miri and Kuching
20111119a	03:57 06:43	MBL sampling, comparison RV *Sonne* and local boat	Coast between Miri and Kuching, Kuching bay
20111119b	08:12 10:47	Outflow sampling of deep convection	Coast north of Brunei
20111121a	06:33 10:24	Lagrangian experiment: RV *Sonne – Falcon*	Coast near Bintulu
20111122a	03:05 06:00	Lagrangian experiment: RV *Sonne – Falcon*	Coast near Sibu
20111123a	03:09 05:25	MBL sampling	Coast between Semporna and Sandakan
20111126a	04:10 06:17	Deep profile upwind Borneo	Sulu sea
20111126b	08:53 09:43	Transfer back to Miri	Sandakan – Miri middle troposphere
20111202a	07:03 09:30	Outflow sampling of deep convection	South-west of Miri
20111207a	03:00 05:30	MBL sampling	Semporna – Tawau
20111207b	06:23 09:17	Deep vertical profile, UTLS survey	Bay of Kuching
20111208a	02:07 05:11	Sampling of outflow from deep convection	Coast Kudat – Sandakan
20111209a	03:58 06:43	MBL sampling, vertical transport by shallow convection	North-eastern coast of Borneo
20111209b	08:12 10:47	Sampling of outflow from deep convection	North-eastern coast of Borneo
20111211a	03:00 06:15	MBL and convective outflow sampling	Strait of Malacca
20111211b	07:41 10:20	MBL and convective outflow sampling	Strait of Malacca

Table 2. Overview of detection limits and the measurement precision of GHOST-MS and the origin and the accuracy of the used calibration gas scale for the different brominated substances.

substance	detection limit [ppq]	average precision of measurements	accuracy of calibration gas	calibration scale origin
H-1301	12	4.6 %	6.2 %	NOAA, 2006
H-1211	1	2.1 %	2.2 %	NOAA, 2006
CH_3Br	294	9.0 %	7.8 %	NOAA, 2003
H-1202	1	5.1 %	8.6 %	UEA, 2009
H-2402	1	2.4 %	4.0 %	UEA, 2009
CH_2BrCl	6	9.8 %	15.0 %	NOAA, prel.
CH_2Br_2	1	3.4 %	10.8 %	NOAA, 2004
$CHBrCl_2$	1	3.4 %	14.0 %	NOAA, prel.
$CHBr_2Cl$	1	4.3 %	9.7 %	NOAA, prel.
$CHBr_3$	3	5.7 %	17.7 %	NOAA, 2003

Table 3. Overview of detection limits and the measurement precision of WASP and the origin and the accuracy of the used calibration gas scale for the different brominated substances. The accuracies are updated from Wisher et al. (2013).

substance	detection limit [ppq]	average precision of measurements	accuracy of calibration gas	calibration scale origin
CH_2BrCl	5	6 %	9 %	NOAA, prel.
CH_2Br_2	1	3 %	7.8 %	NOAA, 2004
$CHBrCl_2$	0.8	3 %	9.9 %	NOAA, prel.
$CHBr_2Cl$	1	3 %	6.7 %	NOAA, prel.
$CHBr_3$	1	3 %	6 %	NOAA, 2003

Table 4. Overview over the averaged mixing ratio of the VSLS in the planetary boundary layer, the free and upper troposphere. The scatter is the absolute standard deviation of all measurements for the given mean value. The (atmospheric) variability is calculated as given in Eq. (2). The lifetime is given for the free troposphere (Montzka et al., 2011). For CH_2BrCl, the data of flight 20111119a is not taken into the calculation for the mean value in all three altitude ranges, as the mixing ratios during that flight are much higher (factor 2.5) than during the rest of the campaign (see also Fig. 3). Therefore we state, that these high values are not representative for the mixing ratio of CH_2BrCl during the campaign. For the calculation of the mean value of CH_2Br_2 and $CHBrCl_2$ in the free troposphere, flight 20111119a is also not considered for the same reasons (see Figs. 1 and 4).

		upper troposphere		free troposphere		planetary boundary layer			
substance	lifetime [days]	GHOST				GHOST		WASP	
		mean ± scatter [ppt]	variability	mean ± scatter [ppt]	variability	mean ± scatter [ppt]	variability	mean ± scatter [ppt]	variability
CH_2BrCl	137	**0.09** ±0.02	±15 %	**0.09** ±0.02	±8 %	**0.11** ±0.02	±21 %	**0.15** ±0.05	±33 %
CH_2Br_2	123	**0.90** ±0.12	±13 %	**0.88** ±0.08	±8 %	**1.19** ±0.21	±17 %	**1.15** ±0.14	±11 %
$CHBrCl_2$	78	**0.25** ±0.04	±16 %	**0.24** ±0.03	±12 %	**0.34** ±0.07	±20 %	**0.33** ±0.07	±21 %
$CHBr_2Cl$	59	**0.19** ±0.04	±21 %	**0.18** ±0.06	±33 %	**0.32** ±0.11	±34 %	**0.33** ±0.09	±27 %
$CHBr_3$	24	**0.61** ±0.20	±33 %	**0.56** ±0.17	±28 %	**1.43** ±0.53	±37 %	**1.90** ±0.55	±28 %

Table 5. Overview over the mean mixing ratios of the long-lived halons and CH_3Br in the planetary boundary layer and the upper troposphere as observed during SHIVA. The scatter is the absolute standard deviation of all measurements around the given mean value. The atmospheric variability is calculated as given in Eq. (3). For H-1301, no meaningful variability can be calculated (noted by n/a), as the scatter of the atmospheric measurements is smaller than the measurement precision of the instrument during the flight that can only be estimated in the laboratory (see Sect. 2.2). Lifetimes for the halons are adapted from Newland et al. (2013) and the lifetime of CH_3Br is taken from Montzka et al. (2011).

substance	tropospheric lifetime [years]	upper troposphere mean ± scatter [ppt]	upper troposphere atmospheric variability	planetary boundary layer mean ± scatter [ppt]	planetary boundary layer atmospheric variability
H-1301	> 10 000	**3.28** ± 0.13	n/a	**3.19** ± 0.14	n/a
H-1211	25	**4.16** ± 0.14	±3 %	**4.29** ± 0.40	±9 %
H-1202	3	**0.026** ± 0.002	±8 %	**0.028** ± 0.005	±17 %
H-2402	41	**0.43** ± 0.02	±3 %	**0.43** ± 0.02	±3 %
CH_3Br	0.8	**7.35** ± 0.86	±7 %	**8.79** ± 3.39	±38 %

Table 6. Comparison of the boundary layer measurements during SHIVA derived independently from GHOST (GUF) and WASP (UEA) instrument with data compiled in Montzka et al. (2011). The measurement uncertainty (1σ) given for the SHIVA data is the sum of scale accuracy and instrumental measurement precision, excluding atmospheric variability. The range for the SHIVA data represents the 2.5 to 97.5 percentiles of the observed distribution.

	WMO, 2010		SHIVA, 2011			
substance	marine boundary layer		planetary boundary layer			
			GHOST		WASP	
	median [ppt]	range [ppt]	median ± uncertainty [ppt]	range [ppt]	median ± uncertainty [ppt]	range [ppt]
CH_2BrCl	**0.5**	0.4–0.6	**0.11** ± 0.02	0.07–0.29	**0.12** ± 0.01	0.10–0.26
CH_2Br_2	**1.1**	0.7–1.5	**1.14** ± 0.21	0.94–1.62	**1.10** ± 0.06	0.96–1.48
$CHBrCl_2$	**0.3**	0.1–0.9	**0.33** ± 0.05	0.26–0.48	**0.32** ± 0.02	0.23–0.52
$CHBr_2Cl$	**0.3**	0.1–0.8	**0.28** ± 0.11	0.20–0.62	**0.32** ± 0.02	0.22–0.59
$CHBr_3$	**1.6**	0.5–2.4	**1.24** ± 0.22	0.60–2.54	**1.81** ± 0.10	1.23–3.35

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Table 7. Comparison of the upper troposphere measurements during SHIVA from GHOST with data compiled in Montzka et al. (2011) and data published in Wisher et al. (2013) from South East Asia (0–15° N).The measurement uncertainty (1σ) given for the SHIVA data is the sum of scale accuracy and instrumental measurement precision, excluding atmospheric variability. The range for the SHIVA data represents the 2.5 to 97.5 percentiles of the observed distribution.

substance	WMO upper troposphere (10–12 km)		SHIVA upper troposphere (10–13 km)		CARIBIC upper troposphere (> 10 km)	
	mean [ppt]	range [ppt]	mean ± uncertainty [ppt]	range [ppt]	mean ± uncertainty [ppt]	full range [ppt]
CH_2BrCl	**0.09**	0.03–0.16	**0.09** ± 0.02	0.06–0.26	**0.12** ± 0.01	0.09–0.14
CH_2Br_2	**0.86**	0.63–1.21	**0.90** ± 0.12	0.71–1.22	**0.92** ± 0.08	0.74–1.00
$CHBrCl_2$	**0.11**	0.02–0.28	**0.25** ± 0.04	0.19–0.35	**0.21** ± 0.03	0.16–0.31
$CHBr_2Cl$	**0.11**	0.01–0.36	**0.19** ± 0.04	0.12–0.27	**0.16** ± 0.02	0.08–0.19
$CHBr_3$	**0.50**	0.12–1.21	**0.61** ± 0.11	0.28–1.01	**0.56** ± 0.12	0.15–0.81

Table 8. Comparison of the decay of the VSLS between boundary layer and upper troposphere. The lifetime is given for the free troposphere (Montzka et al., 2011).

substance	free tropospheric lifetime [days]	decay WMO	decay SHIVA
CH_2BrCl	137	−82 %	−18 %
CH_2Br_2	123	−22 %	−24 %
$CHBrCl_2$	78	−63 %	−26 %
$CHBr_2Cl$	59	−63 %	−41 %
$CHBr_3$	24	−69 %	−51 %

Table 9. Overview of the most important long-lived brominated substances. The global tropospheric mean for H-1301, H-1211, H-2402 and CH_3Br are an update of Montzka et al. (2003), H-1202 is taken from Newland et al. (2013). The measurement uncertainty is the sum of scale accuracy and instrumental measurement precision. The atmospheric variability is not contained in the value.

substance	global tropospheric background (late 2011)	SHIVA, free and upper troposphere (2–13 km) (mean ± uncertainty)
H-1301	3.19 ppt	(**3.23** ± 0.21) ppt
H-1211	3.97 ppt	(**4.15** ± 0.10) ppt
H-2402	0.45 ppt	(**0.43** ± 0.02) ppt
H-1202	0.020 ppt	(**0.025** ± 0.002) ppt
CH_3Br	6.96 ppt	(**7.50** ± 0.64) ppt

Table 10. Comparison of the total organic bromine in the upper troposphere between SHIVA and WMO data. The data given for the global average of H-1301, H-1211, H-2402 and CH_3Br is an update of Montzka et al. (2003), H-1202 is taken from Newland et al. (2013) and the VSLS data is from Montzka et al. (2011). For the calculation of the total organic bromine, the mean mixing ratio (given in Table 7 and Table 9) of an individual substances is multiplied by its number of bromine atoms. The measurement uncertainty is the sum of scale accuracy and instrumental measurement precision.

	global average, year 2011		SHIVA, year 2011	
substance class	Br_{org} [ppt]	percentage of total Br_{org}	Br_{org} ± measurement uncertainty [ppt]	percentage of total Br_{org}
Halons	**8.10**	43 %	**8.31** ± 0.58	(42 ± 3) %
CH_3Br	**6.96**	37 %	**7.35** ± 0.60	(37 ± 3) %
VSLS	**3.64**	20 %	**4.35** ± 0.60	(21 ± 3) %
ΣBr_{org}	**18.70**	100 %	**20.01** ± 1.78	100 %

Table 11. Mixing ratio of the VSLS in the upper troposphere and the LZRH. The decay shows the decrease in mixing ratio between the upper troposphere and the LZRH given in Montzka et al. (2011). With these decay rates, the expected mixing ratios for the LZRH during SHIVA are calculated. The mixing ratio of CH_2BrCl is kept constant, as there is no physical indication for an increase as given in the WMO-data.

	mean mixing ratio WMO [ppt]		decay	mean mixing ratio SHIVA [ppt]	
substance	upper troposphere	LZRH		upper troposphere	LZRH, calculated
CH_2BrCl	0.09	0.10	(+11 %)	0.09	0.09
CH_2Br_2	0.86	0.74	−14 %	0.90	0.77
$CHBrCl_2$	0.11	0.10	−9 %	0.25	0.23
$CHBr_2Cl$	0.11	0.06	−45 %	0.19	0.10
$CHBr_3$	0.50	0.22	−56 %	0.61	0.27

Table 12. Budget of total organic bromine at the LZRH with the contribution of different substance classes. The VSLS value for the SHIVA campaign is calculated from the estimate described in Table 8 using the decay in mixing ratio between UT and LZRH. The values given for SHIVA are (mean mixing ratio ± measurement uncertainty). The measurement uncertainty is the sum of scale accuracy and instrumental measurement precision. The global average values (see also Table 7 and Table 9) are from Montzka et al. (2003)[1] (updated) and Newland et al. (2013)[2] (for H-1202), and Montzka et al. (2011)[3]. The values given for Teresina are from Brinckmann et al. (2012)[4] and Laube et al. (2008)[5].

substance class	SHIVA, Malaysia 2011 (calculated)	global average 2011	Teresina, Brazil 2008[4]	Teresina, Brazil 2005[5]
Halons	(8.31 ± 0.58) ppt	8.10 ppt[1,2]	8.17 ppt	8.29 ppt
CH_3Br	(7.35 ± 0.60) ppt	6.96 ppt[1]	7.40 ppt	6.68 ppt
VSLS	(2.88 ± 0.60) ppt	2.70 ppt[3]	2.25 ppt	1.25 ppt
Σ_{Br}	**(18.54 ± 1.78)** ppt	**17.76** ppt	**(17.82 ± 0.66)** ppt	**(16.22 ± 1.10)** ppt

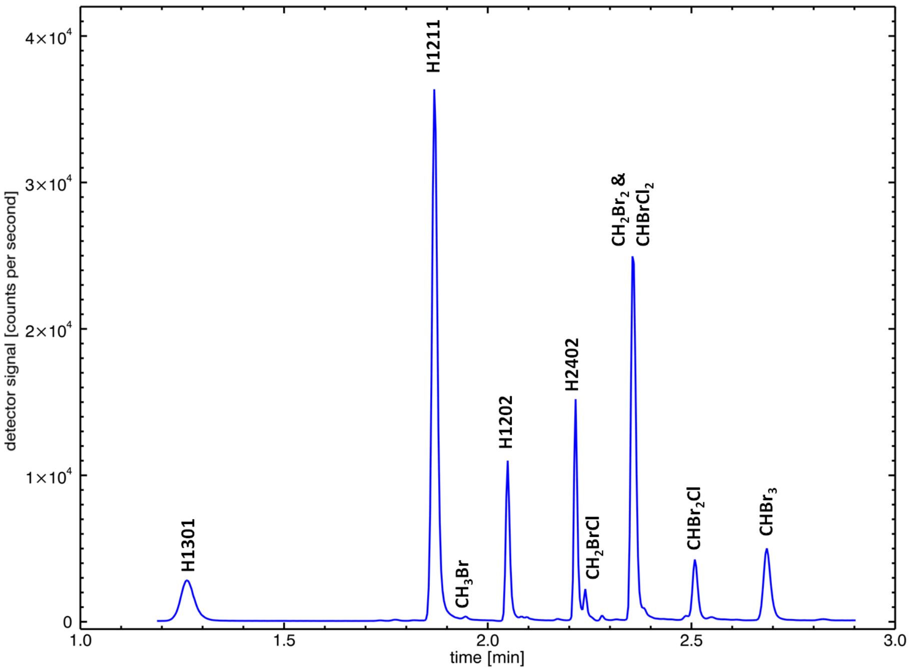

Fig. 1. NICI – Chromatogramm (m/z 79) of GHOST-MS.

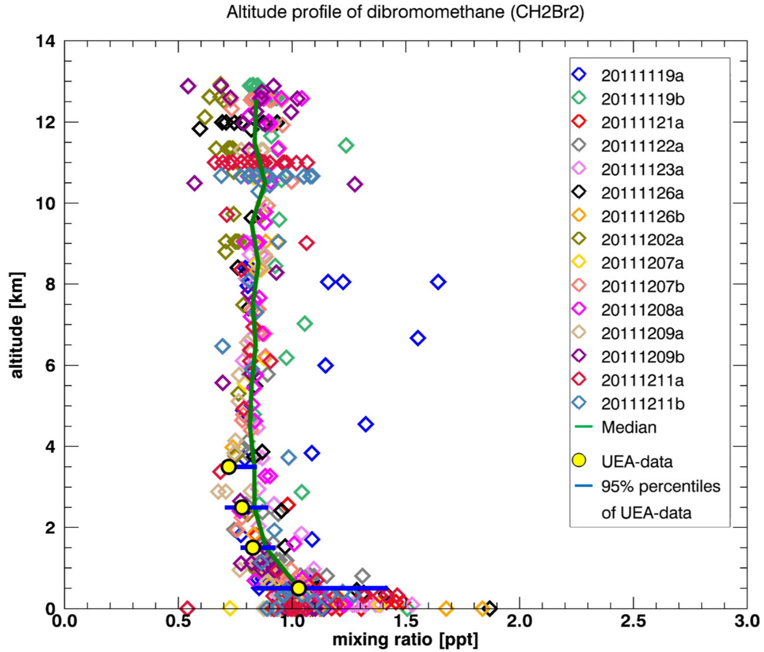

Fig. 2. Illustration of the mixing ratio of CH_2Br_2 vs. the flight altitude in which the particular air sample was taken. The color coding indicate the different flights and the corresponding numbering is the date of the flight in the format year (YYYY), month (MM), day (DD) and a letter, whether it is the first **(a)** or the second **(b)** flight of a day. The green line marks the median of the GHOST-MS data binned in 1 km altitude intervals. The yellow filled circles are the median of the WASP data for the same intervals and the blue bars show the related 95 % percentiles. For better visualization, no error bars for the individual points of the GHOST-MS measurements are shown. The measurement uncertainty for the particular substance is listed in Table 2.

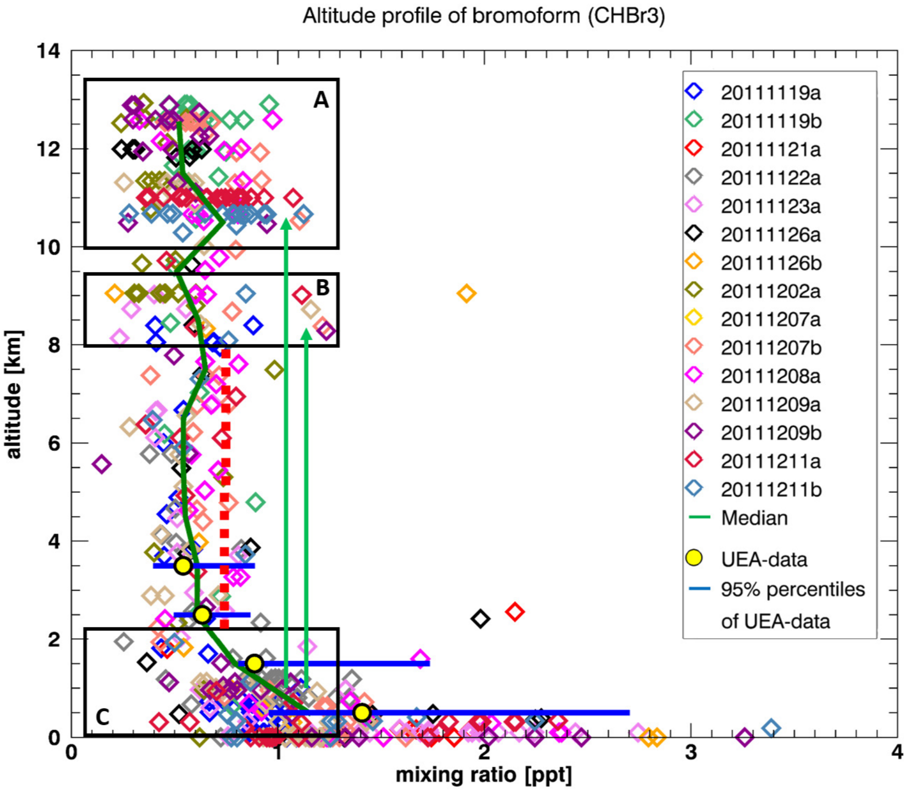

Fig. 3. As Fig. 2, for $CHBr_3$. The boxes marked with A and B show regions in the upper troposphere (10–13 km and 8–9.5 km), where during some flights higher mixing rations than in the free troposphere (2–8 km) occur. The red dotted line shows the mean value of CHBr3 plus 1 σ atmospheric variability in the free troposphere (see also Table 4). The green arrows show possible transport pathways for air masses with higher mixing ratios from the planetary boundary layer (box C) into the upper regions of the atmosphere (boxes B and C).

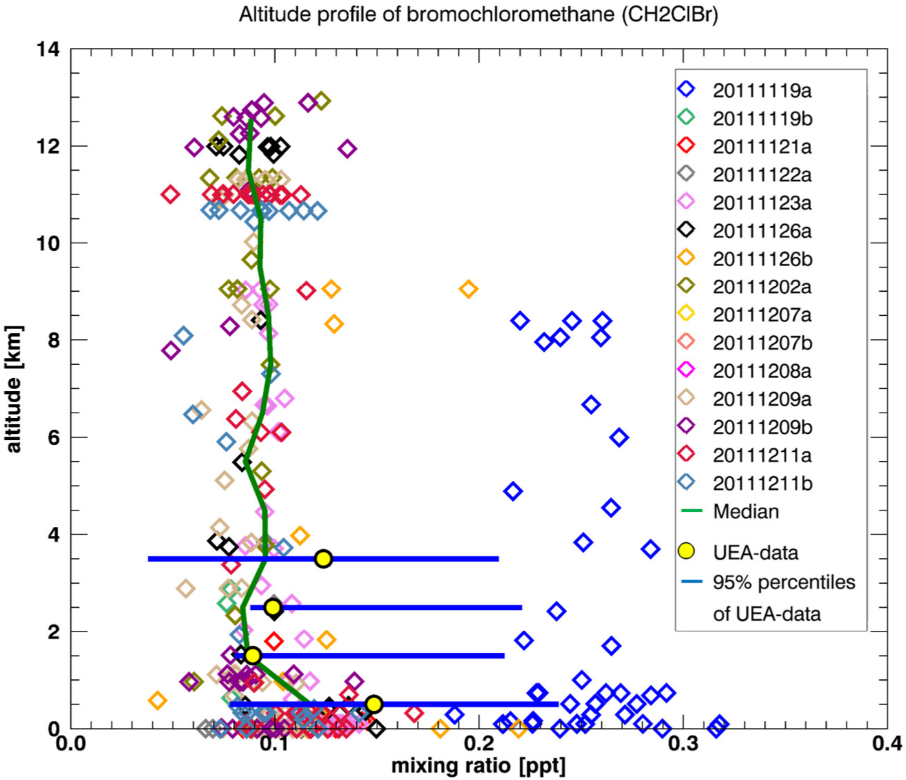

Fig. 4. As Fig. 2, for CH_2ClBr.

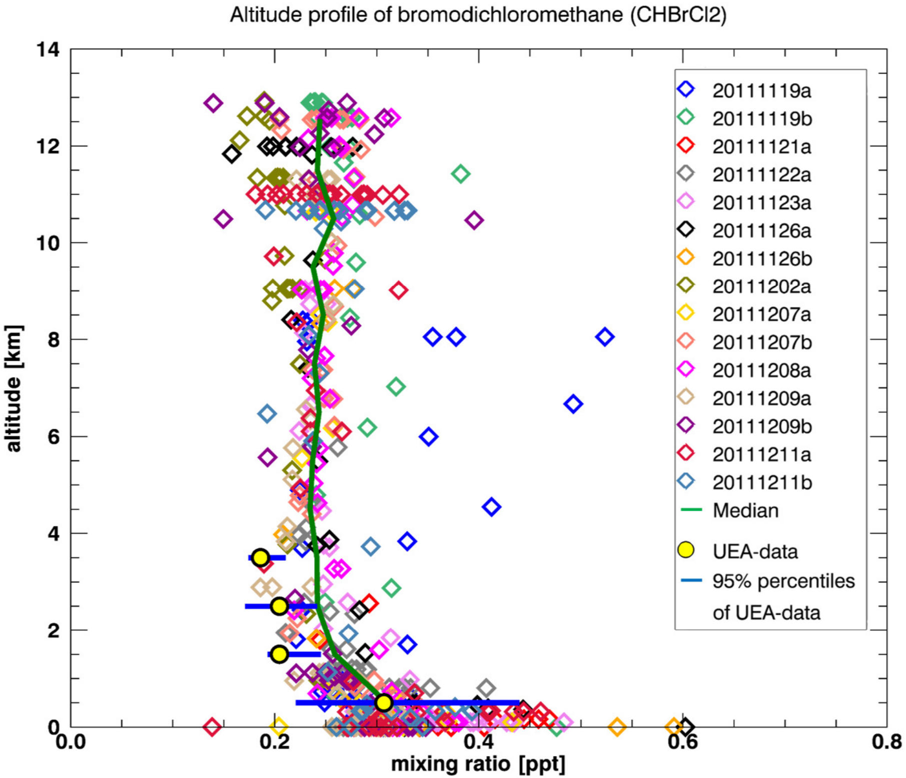

Fig. 5. As Fig. 2, for $CHBrCl_2$.

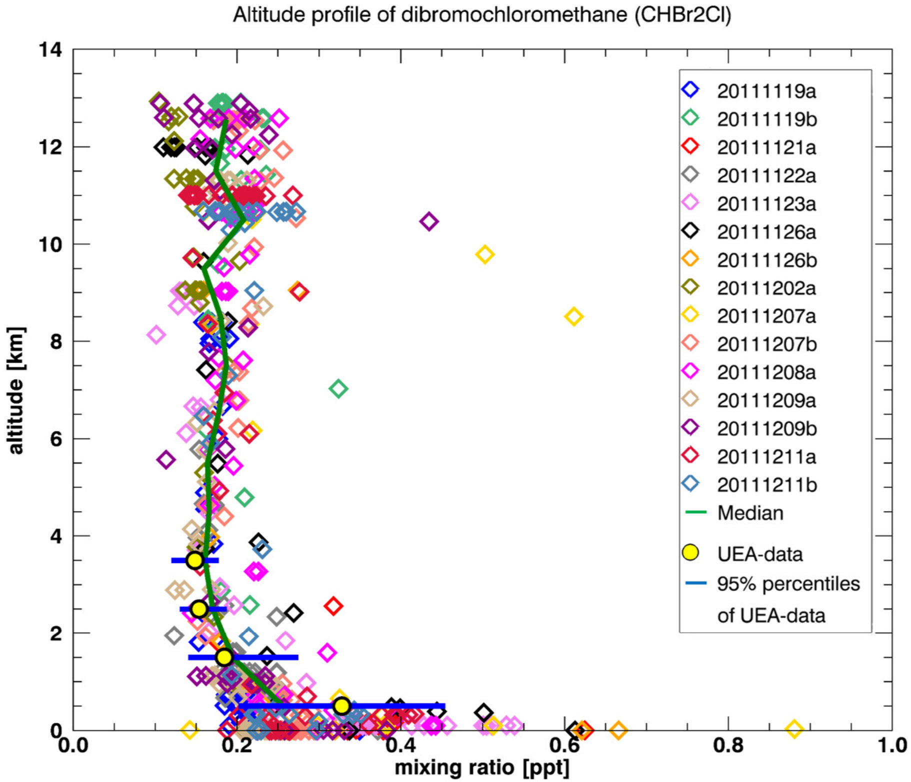

Fig. 6. As Fig. 2, for $CHBr_2Cl$.

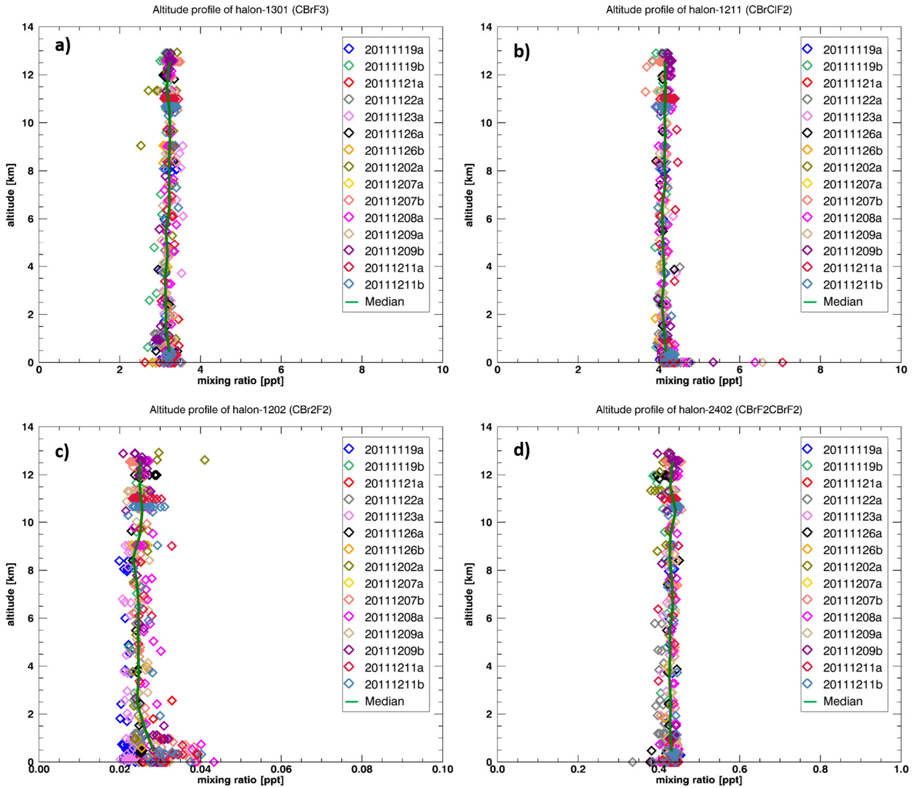

Fig. 7. As Fig. 2, for H-1301 **(a)**, H-1211 **(b)**, H-1202 **(c)** and H-2402 **(d)**.

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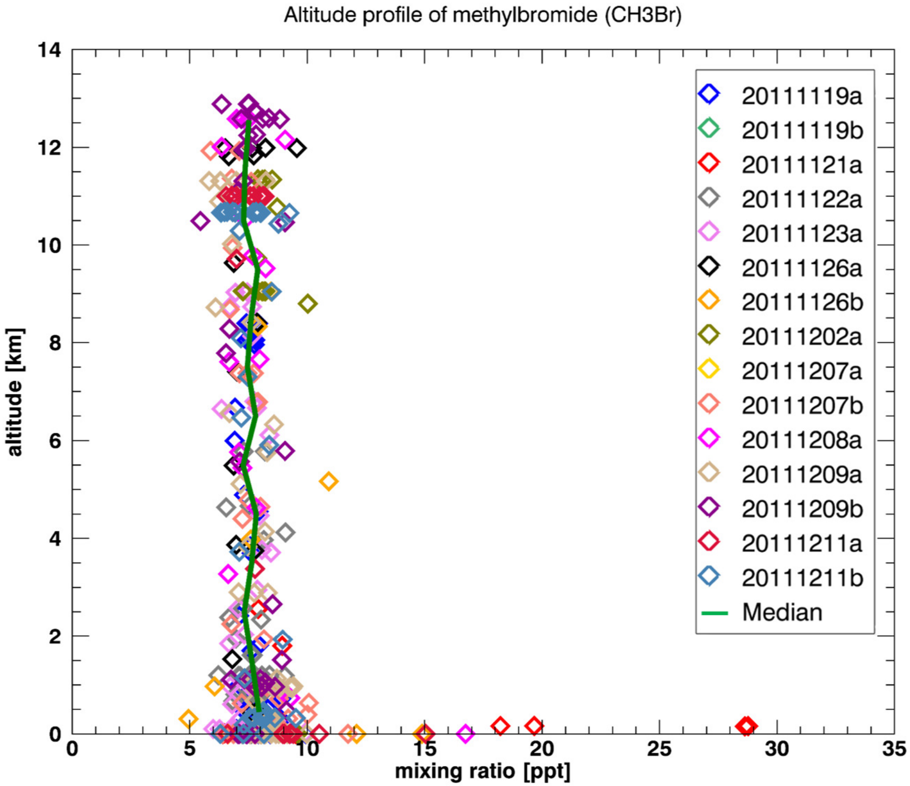

Fig. 8. As Fig. 2, for CH_3Br.

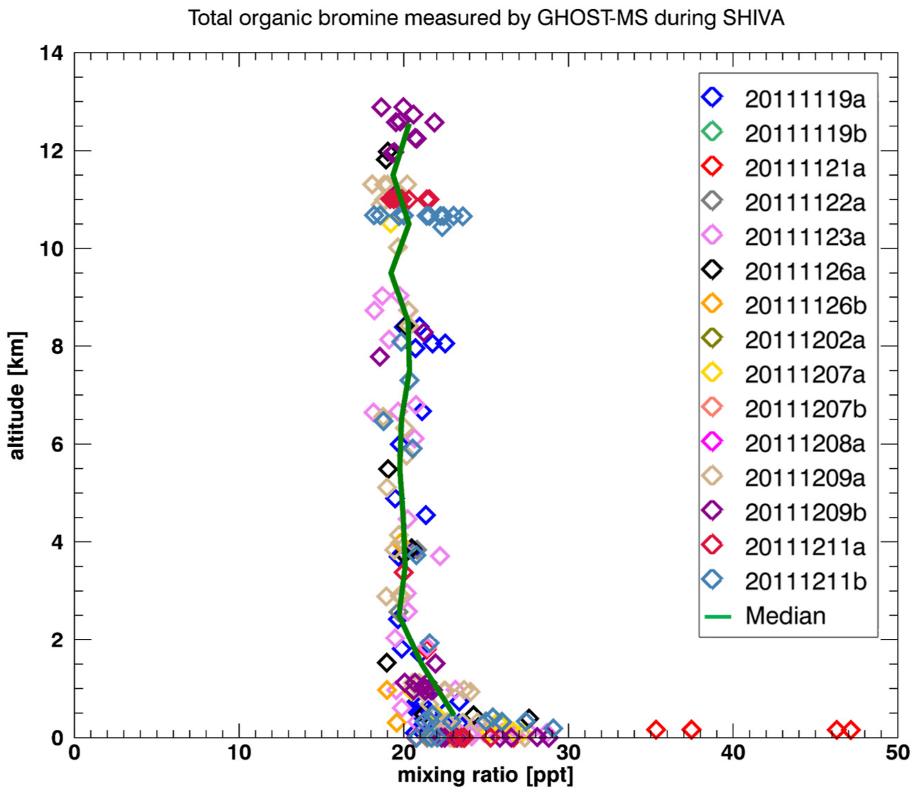

Fig. 9. As Fig. 2, for the total organic bromine. For the calculation, only datapoints are used, where data for every substance is available.