Bridging the gap between bromocarbon oceanic emissions and upper air concentrations

S. Tegtmeier¹, K. Krüger¹, B. Quack¹, I. Pisso², A. Stohl³, and X. Yang⁴,⁵

¹IFM-GEOMAR, Kiel, Germany
²Research Institute for Global Change, JAMSTEC, Yokohama, Japan
³Norwegian Institute for Air Research (NILU), Kjeller, Norway
⁴National Centre for Atmospheric Science (NCAS), Cambridge, UK
⁵University of Cambridge, Department of Chemistry, Cambridge, UK

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Correspondence to: S. Tegtmeier (stegtmeier@geomar.de)
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Abstract

Oceanic emissions of halogenated very short-lived substances (VSLS) are expected to contribute significantly to the stratospheric halogen loading and therefore to ozone depletion. Estimates of the amount of VSLS transported into the stratosphere are highly uncertain and based on sporadic observations around the tropical tropopause layer (TTL) and on modeling studies which use prescribed emission scenarios to reproduce observed atmospheric concentrations. Actual measurements of VSLS emissions at the ocean surface have not been linked to the stratospheric halogen loading until now. Here we use observations of oceanic VSLS emissions in the western Pacific and an atmospheric Lagrangian transport model to estimate the direct contribution of bromoform (CHBr$_3$), and dibromomethane (CH$_2$Br$_2$) to the stratospheric bromine loading. Our emission-based estimates of VSLS profiles provide the first link between observed oceanic emissions and in situ TTL measurements. The emission-based and observed profiles of CHBr$_3$ show good agreement, confirming the importance of the western Pacific as a source region. However, CH$_2$Br$_2$ emission-based estimates are considerably smaller than current upper air observations as a result of relatively low western Pacific emissions. We estimate the relative importance of the highly variable emission rates and the surface to stratosphere transport for the contribution of the two bromocarbons to the stratospheric bromine budget. Our results show that stratospheric entrainment of bromine in form of VSLS or their degradation products is highly variable and that this variability is primarily linked to the variability of the observed sea-to-air flux. Together, both bromocarbons contribute to the stratospheric bromine budget with 0.4 pptv on average and 2.3 pptv for cases of maximum emissions.
1 Introduction

Organic brominated compounds, emitted at the surface through natural and anthropogenic processes, are the primary source of stratospheric bromine. While brominated substances are transported through troposphere and stratosphere, inorganic bromine \((\text{Br}_y)\) is released via photolysis or reaction with OH. Once released the reactive bromine species are known to participate in catalytic ozone destruction in the stratosphere (McElroy et al., 1986; Solomon et al., 1995; Garcia and Solomon, 1994) and may also have a significant impact on tropospheric ozone (von Glasow et al., 2004; Yang et al., 2005). However, the contributions of individual bromine sources to the stratospheric \(\text{Br}_y\) budget as well as the abundance of tropospheric bromine are still highly uncertain.

Long-lived bromocarbons with chemical lifetimes of years are well mixed in the troposphere and transported into the stratosphere without any significant chemical loss. In contrast, very short-lived substances (VSLS) have chemical lifetimes of less than 6 months (e.g., Ko and Poulet et al., 2003) and are often oxidized or photolyzed in the troposphere. In case the VSLS reach the stratosphere before being photochemically destroyed they provide an in-situ source of stratospheric \(\text{Br}_y\) upon their degradation. The cross-tropopause transport of VSLS is referred to as source gas injection (SGI). In case the VSLS are destroyed in the troposphere inorganic bromine is produced which is soluble and can be removed from the troposphere by wet deposition. If however, the inorganic product gases are transported into the stratosphere before being washed out, a process referred to as product gas injection (PGI), they will add to the stratospheric \(\text{Br}_y\) budget. The dehydration of air masses during troposphere-to-stratosphere transport is not completely understood so far and therefore estimates of the wet deposition of \(\text{Br}_y\) are highly uncertain (Montzka and Reimann et al., 2011). Overall, the rate of SGI and PGI depends strongly on the efficiency of troposphere-to-stratosphere transport compared to the degradation of source gases (through photochemical loss) and product gases (through wet deposition). As a result, estimating the contribution of
bromine containing VSLS to stratospheric Br\(_y\) is by far more complicated than doing so for the long-lived bromocarbons.

Measurements of VSLS are scarce and current estimates of their contribution to stratospheric Br\(_y\) range from 1.5 to 8 pptv based on balloon-borne measurements (Dorf et al., 2008), ground-based observations of column BrO (Sinnhuber et al., 2002, and references therein), and satellite BrO measurements (Sinnhuber et al., 2005; Livesey et al., 2006; Sioris et al., 2006; McLinden et al., 2010). In addition to the estimates based on in situ and satellite observations several recent modeling studies are available which focus on bromoform (CHBr\(_3\)) and dibromomethane (CH\(_2\)Br\(_2\)), the two most abundant short-lived bromocarbons (Law and Sturges et al., 2007). Their contribution to stratospheric Br\(_y\) is estimated to be ~2–5 pptv (Kerkweg et al., 2008; Gettelman et al., 2009; Aschmann et al., 2009; Bossaini et al., 2010; Liang et al., 2010) which is less than suggested by observations. A modeling study from Warwick et al. (2006) taking into account all five major short-lived bromocarbons yields estimates of 6–7 pptv. The model studies either used prescribed removal timescales for Br\(_y\) in the Tropical Tropopause Layer (TTL) or explicitly calculate the Br\(_y\) removal based on dehydration processes in the model. There are large differences in the effect of washout predicted by models which together with the lack of observations of bromine PG in the TTL result in a wide range of CHBr\(_3\) and CH\(_2\)Br\(_2\) PGI from 0.4 to 3.9 ppt. The upper limit of SGI and PGI estimates obtained from observations and models would imply a relatively large impact of stratospheric inorganic bromine produced from VSLS (Br\(_y^{\text{VSLS}}\)) on mid-latitude ozone depletion (Salawitch et al., 2005). Therefore the extent to which VSLS contribute to the stratospheric Br\(_y\) budget remains a key question of ongoing research.

CHBr\(_3\) and CH\(_2\)Br\(_2\) are expected to account for a large fraction of stratospheric Br\(_y^{\text{VSLS}}\). The uncertainty in the contribution of the two VSLS to stratospheric Br\(_y\) originates partially from the uncertainty in the efficiency of SGI and PGI and partially from strongly variable sources. CHBr\(_3\) is mainly produced in the ocean by marine life forms such as macro algae, ice algae and phytoplankton (e.g., Carpenter and Liss, 2000; Quack and Wallace, 2003), while CH\(_2\)Br\(_2\) is a by-product during the CHBr\(_3\) forma-
The oceanic production and thereafter the ocean-to-atmosphere flux of CHBr$_3$ is spatially and temporal highly variable with tropical, subtropical and shelf waters being identified as potentially important source regions (Quack et al., 2004; Butler et al., 2007; Quack et al., 2007). Observational estimates of local oceanic emissions of the two VSLS are based on measurements of surface water and atmospheric concentration data. In general, only data of limited spatial and temporal coverage are available. As a result, current estimates of oceanic emissions of CHBr$_3$ and also of CH$_2$Br$_2$ are a major source of uncertainty in atmospheric modeling studies which often rely on uniformly mixed background mixing ratios and might miss the influence of strongly localized sources. This would be particularly problematic in case of a correlation between emission strength and efficiency of transport into the TTL, resulting in systematic over- or underestimates of PGI and SGI when using averaged emission fluxes. Due to the large regional differences in the CHBr$_3$ emission rates and its short tropospheric lifetime of 15–30 days (Hossaini et al., 2010) compared to atmospheric transport time scales the tropospheric CHBr$_3$ distribution is highly variable in time and space. CH$_2$Br$_2$ has a longer tropospheric lifetime (50–400 days) than CHBr$_3$, however, not long enough to be well mixed in the troposphere. CHBr$_3$ and CH$_2$Br$_2$ measurements in the upper troposphere and TTL region are available from a few aircraft and balloon campaigns (Schaufler et al., 1998; Schaufler et al., 1999; Sinnhuber and Folkins, 2006; Law and Sturges et al., 2007; Laube et al., 2008) and show a large spread. A current challenge is to relate the variability of observed VSLS sea-to-air fluxes to the variability of measured VSLS in the upper troposphere and TTL region.

In this study we use sea-to-air fluxes of CHBr$_3$ and CH$_2$Br$_2$ obtained from ship-based measurements to estimate their SGI and PGI into the stratosphere. The measurements were done during the TransBrom Sonne cruise in the tropical western Pacific in 2009 as described in Sect. 2.1. The transport calculations are carried out with the Lagrangian particle dispersion model FLEXPART which is introduced in Sect. 2.2. Results of the transport calculations including estimates of the amount of VSLS and their degrada-
tion products transported into the TTL are presented in Sect. 3. Simulated CHBr₃ and CH₂Br₂ vertical profiles are compared with aircraft observations. Analyzing how emission rates and convective activity influence SGI and PGI will help to understand the relative importance of these two processes for the stratospheric Brᵧ budget.

2 Data and model

2.1 Sonne TransBrom campaign

Atmospheric and oceanic CHBr₃ and CH₂Br₂ were measured during the TransBrom cruise with the R/V Sonne from Tomakomai, Japan, 9 October 2009 to Townsville, Australia, 23 October 2009 (Krüger and Quack, 2012). The time of the ship cruise was within the season of high typhoon occurrence in the tropical western Pacific, a region which is in general characterized by the globally highest convective activity (“warm pool”) throughout the year. The cruise track crossed the typhoon Melor in the northern extratropics and the two tropical depressions Nepartak and Lupit. The transit route from Japan to Australia followed almost exactly the 146° E meridian from 44° N to 18° S through extratropical and tropical regions. The TTL had a latitudinal extension from at least 36° N to 18° S during the time of the ship cruise.

Surface air samples were collected every 3 hours during the cruise section from 32.6° N to 18.7° S in pressurized stainless steel canisters. The air samples were analyzed subsequently for CHBr₃, CH₂Br₂ and other VSLS at the Rosenstiel School of Marine and Atmospheric Sciences (RSMAS) in Miami by the group of Elliot Atlas following the method from Schauffler et al. (1999). Surface water samples were collected simultaneously by a submersible pump at 5m depth and analyzed on board using a purge-and-trap GC/MS analytical system. A detailed description of the system can be found in Quack et al. (2004). The instantaneous sea-to-air flux of CHBr₃ and CH₂Br₂ was calculated from the measured sea surface concentration and local atmospheric mixing ratios, Henry’s law constant from Moore et al. (2005) and the instantaneous
wind speed. The flux calculations are based on the transfer coefficient parameterization of Nightingale et al. (2000), which were adapted to CHBr$_3$ and CH$_2$Br$_2$ (Quack and Wallace, 2003).

### 2.2 FLEXPART trajectories

The atmospheric transport of CHBr$_3$ and CH$_2$Br$_2$ from the oceanic surface into the upper troposphere and TTL is simulated with the Lagrangian particle dispersion model FLEXPART (Stohl et al., 2005). This model has been used extensively in studies of long-range and mesoscale transport (e.g., Spichtinger et al., 2001; Stohl et al., 2003; Forster et al., 2004). Validation of FLEXPART is based on comparisons with measurement data from three large-scale tracer experiments (Stohl et al., 1998) and on intercontinental air pollution transport studies (e.g. Stohl and Trickl, 1999; Forster et al., 2001; Spichtinger et al., 2001). FLEXPART is an off-line model driven by meteorological fields from the ECMWF (European Centre for Medium-Range Weather Forecasts) numerical weather prediction model. It includes parameterizations for moist convection (Forster et al., 2007), turbulence in the boundary layer and free troposphere (Stohl and Thompson, 1999), dry deposition and in-cloud as well as below-cloud scavenging, and the simulation of chemical decay.

In order to describe the transport and dispersion of CHBr$_3$, we simulate trajectories of a multitude of air parcels, each carrying a mass fraction of the VSLS tracer. For each data point of the observed sea-to-air flux a separate FLEXPART run is launched where 10 000 air parcels were released over one hour from a 0.0002° × 0.0002° grid box (~500 m$^2$) at the ocean surface centered at the measurement location. The total amount of CHBr$_3$ emitted from this grid box over one hour is calculated based on the observation-derived flux and uniformly distributed over the 10 000 air parcels. The FLEXPART runs are driven by the ECMWF reanalysis product ERA-Interim (Dee et al., 2011) given at a horizontal resolution of 1° × 1° on 60 model levels. Transport, dispersion and convection of the air parcels are calculated from the 6-hourly fields of horizontal and vertical wind, temperature, specific humidity, convective and large...
scale precipitation and others. The input data is retrieved from the ECMWF archives using a pre-processor which calculates the vertical wind in hybrid coordinates mass-consistently from spectral data.

Figure 1 illustrates a FLEXPART run for one case study based on the emitted CHBr$_3$ flux observed during the TransBrom Sonne campaign at 19° N, 148° E on 14 October 2009 at 11 a.m. UTC. The spatial distribution of all 10,000 air parcels on 24 October 2009, 10 days after their release from the measurement location, is displayed. A large fraction of the air parcels is spread out over the maritime continent, Southeast Asia, India, and the tropical Indian Ocean all the way from the west coast of Australia to the east coast of Africa. A smaller fraction of air parcels has been transported eastwards from the release location and is now distributed along two narrow latitude bands at roughly 30° N and 30° S across the tropical Pacific. Overall, a large number of air parcels have reached altitudes above 10 km which illustrates the strong impact of deep convection on the vertical transport observed for this case study. Each air parcel carries an assigned mass of the CHBr$_3$ tracer which is reduced at a rate corresponding to its chemical lifetime.

2.3 Wet deposition of Br$_y$

The degradation of CHBr$_3$ and CH$_2$Br$_2$ along each trajectory is simulated by prescribing an altitude dependent chemical lifetime, ranging from 16 (50) days at the ocean surface to 29 (400) days in the TTL for CHBr$_3$ (CH$_2$Br$_2$) (Hossaini et al., 2010). The fraction of photochemically destroyed CHBr$_3$ and CH$_2$Br$_2$ contributes to the inorganic product gases which are grouped together as Br$_y$ and are transported together with the VSLS source gases along the trajectory. The assumption of instantaneous conversion between organic intermediate product gases and Br$_y$ has been shown to be reasonable (Hossaini et al., 2010). Br$_y$ can be removed from the troposphere by wet deposition which is initiated in FLEXPART if the relative humidity exceeds a certain threshold. The resultant washout is modeled via the cloud scavenging ratio calculated with the help of the effective Henry coefficient. Within the family of inorganic bromine, HOBr and
HBr can be washed out while the remaining species Br, BrO, BrONO₂, and Br₂ are not soluble. HOBr and HBr have different solubility properties which are described by different Henry coefficients. In order to determine which fractions of Brᵣ are in the form of HBr and HOBr and which fraction is not soluble we apply the Brᵣ partitioning modeled with the Chemical Transport Model (CTM) p-TOMCAT (Yang et al., 2010). The model uses analyzed wind-fields together with complex chemical schemes to simulate the tracer distribution in the troposphere and lower stratosphere. The 3-dimensional Brᵣ field from p-TOMCAT and its partitioning into HOBr, HBr, Br, BrO, BrONO₂, and Br₂ are given every 30 min for October 2009. The partitioning of the Brᵣ field into the individual members of the Brᵣ family varies strongly with location and time and is applied to every air parcel according to its location each time before the wet deposition is initiated. Wet deposition is then calculated individually for each member of the Brᵣ family in order to realistically simulate the Brᵣ removal along the trajectories.

2.4 Ozone Depletion Potential

The Ozone Depletion Potential (ODP), a measure of a substance’s destructive effects to the ozone layer relative to the reference substance CFC-11 (CCl₃F) is estimated for CHBr₃ and CH₂Br₂. The ODPS are determined by the fraction of VSLS which reach the stratosphere and their subsequent residence time in the stratosphere, during which ozone depletion can occur. The ODPS for CHBr₃ and CH₂Br₂ are calculated as a function of location and time of emission following a previously developed trajectory-based method (Pisso et al., 2010). Owing to the different timescales and processes in the troposphere and stratosphere, the estimates are based on separate ensembles of trajectories calculated for air masses emitted in the western Pacific in October 2009. The tropospheric trajectories are used to quantify the fraction of VSLS reaching the stratosphere while stratospheric trajectories are run for longer time periods in order to determine stratospheric residence time. Results from the two trajectory ensembles are combined in order to estimate the VSLS ODP as a function of emission location. Uncertainties of the method are associated with tropospheric chemistry and transport,
but also with the representation of stratospheric chemistry (ozone depletion by heterogeneous reactions) and transport (large scale circulation). A depletion efficiency factor of 60 is used for Br (Law and Sturges et al., 2007; Montzka and Reimann et al., 2011). The average stratospheric residence time for active chlorine is assumed to be 60 months.

2.5 VSLS vertical profiles

The VSLS vertical profiles represent the VSLS mixing ratios averaged over all air parcels which have been originally emitted at one measurement site above a certain atmospheric level. The profiles are estimated from the overall amount of VSLS entrained above an atmospheric level together with the overall amount of air entrained above this level. In order to account for the fact that our VSLS emission grid box is very small while the air entrained above a certain level originates from all over the globe we scale the amount of air so that it is proportional to the size and duration of the emission grid box. Note, that since we cannot account for mixing with air masses from other regions the profiles are not assumed to be real atmospheric profiles but rather display profiles one would expect if one would assume emission and atmospheric transport properties as observed in the western Pacific globally. In other words our estimated profiles describe the relative contribution of western Pacific emissions to atmospheric VSLS mixing ratios. Uncertainties in our estimates of VSLS abundance in the upper TTL are associated with uncertainties in the convective parameterization, the vertical transport driven by the vertical wind fields and the prescribed lifetime of the species. Testing the model sensitivity shows that our results are mainly constrained by the accurate representation of convection (which has been validated with tracer experiments and $^{222}$Rn measurements in Forster et al., 2007), with small variations in the prescribed lifetime leading only to small differences in the derived VSLS profiles. Applying transport timescales based on vertical heating rates instead of vertical wind fields in the TTL between 15 and 17 km also results in only minor differences.
3 Results

3.1 Case study of CHBr₃ transport

Four case studies of modeled CHBr₃ transport which are characterized by highly variable emission and transport properties are analyzed. The first case study is based on an example of a relatively low CHBr₃ sea-to-air flux of 110.6 pmol m⁻² h⁻¹ observed at 30° N, 145° E on 10 October 2009. The black line in Fig. 2a shows the vertical distribution of CHBr₃ 10 days after the release event which has been obtained by adding up the amount of trace gas contained in all tropical (30° N – 30° S) air parcels. The vertical distribution of CHBr₃ peaks between 2 and 8 km and only a very small fraction of the air masses has been transported into the TTL. Figure 2b shows the vertical distribution of CHBr₃ over a one month time period starting at the date of the release event on October 10. Most air masses remain in the region below 10 km over the entire month due to the lack of deep convection. The second case study, displayed in Fig. 2c, is based on the CHBr₃ sea-to-air flux observed at 19° N, 148° E on 14 October 2009 which was also very low with 133.4 pmol m⁻² h⁻¹. Air mass transport for this example has been discussed in the previous section including the presentation of the spatial distribution of all air parcels 10 days after the release. The slowly decreasing concentrations of CHBr₃ over time are caused by the chemical decay of the tracer. Also mixing into the extratropics will decrease the total amount of tropical CHBr₃. However Fig. 1 indicated that this process is weak and most air masses remain between 30° N and 30° S. The total amount of CHBr₃ entrained above a certain level is calculated as the sum of CHBr₃ carried by all the trajectories which cross that level. For case study 2 the total amount of CHBr₃ entrained above 17 km is 5.9 nmol. Compared to case study 1 this example shows quite the opposite behavior with strong upward transport of CHBr₃ over a very short time period of only hours to days right after the release event which is evident from the tracer distribution. The strong convective activity lifting the majority of the air masses is very likely related to the tropical depression observed close to the measurement location.
A direct comparison of the vertical distribution of CHBr$_3$ 10 days after the release event between the two case studies can be seen in Fig. 2a illustrating the highly variable vertical distribution of CHBr$_3$ as a result of the impact of deep convection. Case study 3 is based on the sea-to-air flux observed at 3° S, 154° E on 19 October 2009, while case study 4 describes the flux observed at 18° S, 145° E on 23 October 2009. Both case studies are chosen since they describe so-called hot-spots of emissions with very high fluxes of 2875.71 and 4551.7 pmol m$^{-2}$ h$^{-1}$, respectively. The subsequent transport of the large amounts of CHBr$_3$ develops very differently for the two events with case study 3 displaying strong convective events influencing transport up to 14/15 km during the first 10 days (Fig. 2e), while case study 4 shows the strongest impact of convection below 10 km (Fig. 2f). A comparison 10 days after the release event reveals that for case study 4 most of the CHBr$_3$ is still between 0 and 3 km, while case study 3 results in most of the CHBr$_3$ between 9 and 15 km (Fig. 2d). The four case studies demonstrate that we find a high variability in emission strength and transport intensity which will be analyzed systematically in the following paragraph.

3.2 SGI and PGI during the Sonne-Transbrom cruise

Modeling of transport, chemical decay and wet deposition of CHBr$_3$, CH$_2$Br$_2$ and Br$_y$ as described in Sect. 2 has been carried out for all observations of sea-to-air fluxes obtained during the TransBrom Sonne campaign. For each of the 103 observed CHBr$_3$ and 64 CH$_2$Br$_2$ fluxes a FLEXPART simulation analogous to the examples illustrated above was performed. Figure 3a and b show the oceanic emission rates (black lines) of the two major bromocarbons as observed during the ship campaign in the western Pacific. The oceanic emissions of both trace gases are characterized by a strong variability along the cruise track, linked to wind speed variations and differences in the compounds saturation state. Currently available global estimates of oceanic emissions of CHBr$_3$ and CH$_2$Br$_2$ can differ approximately by a factor four and are highly uncertain (Montzka and Reimann et al., 2011). The mean emission rates observed in the western Pacific in October 2009 for CHBr$_3$ of 536.7 pmol m$^{-2}$ h$^{-1}$ are approximately in
the middle of the range of global mean values (Carpenter and Liss, 2000; Quack and Wallace, 2003), whereas the mean rates for CH$_2$Br$_2$ of 163.5 pmol m$^{-2}$ h$^{-1}$ are only slightly larger than the lowest global estimate (Yokouchi et al., 2005).

The cold point in the vertical temperature profile at around 17 km is of special importance for SGI and PGI. Above this level no significant washout is expected and VSLS product gases and source gases reaching this altitude can be assumed to contribute to the stratospheric halogen loading irrespective of their remaining chemical lifetime. The amount of VSLS product gases entrained above 17 km is calculated as the sum of CHBr$_3$ or CH$_2$Br$_2$, respectively, carried by all the computational particles which cross this level. For each observed oceanic VSLS emission along the cruise track we determine the fraction of the originally emitted amount of CHBr$_3$ and CH$_2$Br$_2$ entrained above the 17 km surface. On average, these fractions range from 15 % for CH$_2$Br$_2$ to 4 % for CHBr$_3$, indicating decreasing efficiency of vertical transport with decreasing lifetime. The time series of the entrained VSLS fractions as a function of latitude along the cruise track is displayed in Fig. 3a and b for CHBr$_3$ and CH$_2$Br$_2$, respectively (colored dots). Rapid vertical uplift in deep convection provides the major pathway for VSLS from the surface to the TTL. The variability of convection occurrence has a stronger impact on the shorter lived gas CHBr$_3$ as evident from its highly variable entrained VSLS fractions. We find the largest CHBr$_3$ entrainment of up to 10 % during the first part of the cruise at around 20° N related to the strong vertical uplift observed during the developing typhoon Lupit (Krüger and Quack, 2011). During the second part of the cruise vertical transport is less intense and therefore the fractional entrainment is lower reaching values between 2 and 5 %. For CH$_2$Br$_2$ the fractional entrainment is overall larger and shows less variability compared to CHBr$_3$ as a result of the longer lifetime. Together, the VSLS emissions and the transport efficiency (expressed as the entrained VSLS fractions) determine the total amount of VSLS entrained above the 17 km surface (colored lines in Fig. 3a and b). The hot spot emissions during the second part of the cruise result in strongest VSLS entrainment although the vertical transport intensity is larger during the first part of the cruise. If events of strong vertical transport would coin-
cide with strong VSLS emissions one could expect very large amounts of VSLS being transported into the stratosphere. However, strong localized oceanic sources related to coastal regions determine the peak emissions and therefore no direct link between emission strength and wind variations or vertical transport intensity exists. For both bromocarbons the total entrainment is highly correlated with the surface emissions ($r > 0.95$) but not correlated with the transport efficiency.

The contribution of VSLS to the stratospheric bromine loading depends on SGI as discussed above and also on PGI where inorganic bromine resulting from the degradation of CHBr$_3$ and CH$_2$Br$_2$ is entrained into the stratosphere. Similar to what has been done for the VSLS source gases the Br$_2$ entrainment above the cold point has been estimated. Considerably more Br$_2$ originating from the degradation of CHBr$_3$ than from the degradation of CH$_2$Br$_2$ is entrained into the stratosphere (Fig. 3c). This is due to stronger CHBr$_3$ fluxes and the fact that CHBr$_3$ contains one more bromine atom than CH$_2$Br$_2$. Additionally, for CH$_2$Br$_2$ a larger fraction is entrained already as source gas and therefore less bromine is left for potential product gases. Maximum amounts of PGs are transported into the stratosphere for peak emission events similar to what has been noted for the SGI. Overall SGI and PGI of bromocarbons emitted in the western Pacific are determined by the intensity of surface emissions and show the same strong variability. This holds for a region of intense vertical transport where transport efficiency shows less variability than the sea-to-air flux. On average more source gas particles are entrained than product gas particles. The ratio of SGI and PGI is 1.2 on average and shows some variability ranging from 0.5 to 2. Note that the ratio is calculated for SGI and PGI in mol and that one particle of the source gas CHBr$_3$ results in three particles of product gas. Therefore although SGI and PGI show similar size when compared in mol the relative importance of SGI is 3.6 times larger than the one of PGI.

In order to determine the potential impact of CHBr$_3$ and CH$_2$Br$_2$ on stratospheric ozone, the ODP, a measure of a substance’s destructive effects to the ozone layer relative to the reference substance CFC-11 has been estimated. The ODPs (Fig. 3d) are considerably larger than estimates obtained from previous global model studies.
(Brioude et al., 2010; Wuebbles et al., 2011). While in these studies mean ODP values were obtained as averages over longer time periods and large regions, we present the first pointwise ODPs calculated individually for emission measurements. ODPs are a function of chemical and transport properties relevant for the VSLS but do not take into account the strength of the emission. As a result the relative ozone-destroying capabilities for VSLS (expressed as ODPs) can be large when transport from the boundary into the stratosphere is efficient while the actual contribution of VSLS to the stratospheric Br-loading is small due to weak VSLS emissions. In general our estimated ODPs show a large variability where episodic injections estimated for a highly convective region can be orders of magnitude higher than the global mean. However, cases of maximum ODP (or maximum vertical transport) do not coincide with peak emissions of VSLS. Our results indicate that mean ODP values for VSLS obtained by coarse global models mask a large variance over space and time. This can lead to an inaccurate estimation of the VSLS contribution to stratospheric ozone depletion.

3.3 Comparison with SGI and PGI based on tropical Atlantic emissions

It is of interest to compare VSLS emissions and their subsequent atmospheric transport for different oceanic regions. Therefore observations of VSLS emissions during the R/V Meteor cruise #55 in the tropical Atlantic in October/November 2002 (Quack et al., 2004) are used to calculate SGI and PGI for CHBr₃. Figure 4 shows the mean emission for CHBr₃ observed during the Meteor #55 and Sonne TransBrom cruises. Emissions during both campaigns are on average of very similar magnitude and in the middle range of global mean emission estimates. The sea-to-air flux observed during the Meteor #55 cruise is strongly localized (Quack et al., 2004) as it is also the case for TransBrom, and includes intense emissions in tropical open ocean regions. Additionally, mean CH₂Br₂ emissions for the Sonne TransBrom cruise are displayed which are quite low compared to global mean estimates and compared to CHBr₃ emissions during the same cruise. (Note, that CH₂Br₂ sea-to-air fluxes were not observed during the Meteor cruise #55.) For all three cases mean SGI and PGI values are shown...
in Fig. 4. SGI estimated for CHBr$_3$ emissions in the tropical Atlantic is relatively low with 1.1% of all emitted source gases being transported into the tropical stratosphere while in the western Pacific 3.8% of all emitted source gases are entrained. This difference results from the stronger convective activity in the western Pacific which acts as the main mechanism for the fast vertical uplift of air masses. For PGI similar results are found with stronger entrainment for western Pacific emissions compared to tropical Atlantic emissions. However, for PGI the difference is less pronounced than for SGI indicating that although variability of vertical transport leads to a more efficient SGI and PGI in the western Pacific in the first place, the variability of wet deposition acts to reduce this difference and decreases the PGI more in the western Pacific than in the tropical Atlantic. Overall, the main difference between CHBr$_3$ entrainment in the western Pacific and in the tropical Atlantic results from differences in the efficiency of the vertical transport from the boundary layer in the emission region into the stratosphere. However, variability of PGI and SGI within one campaign comes mainly from the variability of the emission strength and only in the second place from the variability of the vertical transport (not shown here). For CH$_2$Br$_2$ SGI is quite efficient and more than 10% of the emitted SG are injected into the stratosphere. However, PGI is very low as already discussed for the time series displayed in Fig. 3.

3.4 PG and SG profiles

Based on observed VSLS emissions in the western Pacific and subsequent modeling of atmospheric transport we estimate VSLS vertical profiles in the TTL. In Fig. 5 our emission-based estimates are compared to atmospheric VSLS profiles based on globally available upper air measurements (Montzka and Reimann et al., 2011). This comparison provides a new aspect to the current state of VSLS modeling where an agreement between upper air measurements and model results is obtained by adjusting oceanic emission scenarios instead of using the emission rates as an independent source of information. The emission-based atmospheric VSLS profiles depend on the accurate representation of vertical transport within the model simulation. The
profiles are estimated based on the emission and transport properties of the western Pacific region and do not take into account mixing with air masses from other regions. The measurement-based atmospheric VSLS profiles are estimated from available aircraft and balloon campaigns (Montzka and Reimann et al., 2011) and depend on their observational coverage. Emission-based and measurement-based profiles are not coincident in time and space and can therefore only be compared in a qualitative way. For CHBr$_3$ emission-based estimates and observations show a good agreement (Fig. 5a). The fact that the relative fraction of upper-air CHBr$_3$ resulting from western Pacific emission and transport properties is in good agreement with measurement-based global profiles is consistent with the western Pacific emissions being in the middle range of global emission estimates. The mean profiles are of similar magnitude above 15 km with observations being slightly larger. The maximum CHBr$_3$ abundances derived from observations (0.31 ppt at 17 km) are slightly smaller than the ones derived from the emission-based estimates (0.36 ppt at 17 km) indicating that localized strong sources found at the ocean surface can lead to higher mixing ratios in the upper atmosphere than observed so far. On average CHBr$_3$ emitted in the western Pacific can lead to atmospheric abundances of 0.07 ppt CHBr$_3$ at 17 km if not mixed with other air masses. This is smaller than global estimates derived from modeling studies which range between 0.1 ppt and 0.15 ppt (Warwick et al., 2006; Aschmann et al., 2009; Hossaini et al., 2010). For CH$_2$Br$_2$, the emission-based estimates are much smaller than the atmospheric observations (Fig. 5b). This difference is very likely caused by the low emissions observed in the western Pacific during TransBrom, indicating that emissions from other oceanic regions are more important for the stratospheric budget. Also shown are CHBr$_3$ estimates based on emissions in the tropical Atlantic observed during the Meteor #55 campaign (Fig. 5c). As opposed to the western Pacific estimates the modeled CHBr$_3$ abundances are considerably smaller than the observed ones. The modeled CHBr$_3$ drops down to zero above 15 km indicating that there is only very little convectively driven transport reaching the upper TTL on short timescales. Figure 5d shows total Br profiles summarizing VSLS transport calculations for emissions from the
western Pacific. Total Br is derived from source gas and product gas abundances individually for CHBr$_3$ and CH$_2$Br$_2$. Estimates of total Br amount to 0.26 ppt for CHBr$_3$ (with 80% from SGI and 20% from PGI) and 0.12 ppt for CH$_2$Br$_2$ (with more than 90% from SGI). The contribution of both VSLS to stratospheric Br$_y$ is about 0.38 ppt on average (with approximately 80% from SGI). The major fraction of total Br results from CHBr$_3$ and its degradation products and only a small part originates from CH$_2$Br$_2$. This relatively low importance of CH$_2$Br$_2$ results from the low emissions observed in the western Pacific in October 2009 and can be quite different for other oceanic regions. Globally the contribution of CH$_2$Br$_2$ to stratospheric Br$_y$ is expected to be of equal or greater importance compared to CHBr$_3$.

4 Summary

The strength and novelty of our study results from modeling upper air VSLS abundances based on observations of highly localized oceanic emissions. SGI and PGI estimated from local sea-to-air flux observations are characterized by a large variability where episodic injections can be orders of magnitude higher than the global mean. Our results indicate that mean values of VSLS SGI and PGI obtained by coarse global models mask a large variance over space and time. This can lead to an inaccurate estimation of the VSLS contribution to stratospheric ozone depletion. Especially if the intensity of vertical transport and the VSLS sea-to-air flux are correlated coarse models could potentially over- or underestimate upper air VSLS abundances. Such a correlation has not been observed for above presented emission and transport in the western Pacific since for both bromocarbons, the peak emissions have been determined by strong localized oceanic sources which are not related to atmospheric transport characteristics. However, in a scenario of relatively uniform oceanic concentrations the emission rates could be determined by the wind speed variations which would enable a correlation between emission strength and vertical transport intensity.

CHBr$_3$ and CH$_2$Br$_2$ emitted in the western Pacific, a region of intense vertical trans-
port, have a large potential to destroy stratospheric ozone as illustrated by their high ODP values. Where and when strong vertical transport and strong emissions coincide, large VSLS entrainment into the stratosphere can be expected. For CHBr$_3$ mean emission-based estimates are consistent with upper air observations while peak emissions lead to larger than so far observed atmospheric abundances. Our results show the importance of the western Pacific as a VSLS entrainment region and illustrate the need for quantifying the spatial and temporal variability of CHBr$_3$ emission rates. For CH$_2$Br$_2$ observed emission in the western Pacific and estimated atmospheric abundances are considerably lower than observations. Both bromocarbons will contribute directly and in form of their product gases to the stratospheric bromine loading. Current observational estimates of the total contribution of all VSLS to the stratospheric bromine budget range around 5 pptv. Our emission-based estimates of CHBr$_3$ and CH$_2$Br$_2$ yield a direct source gas contribution of the two bromocarbons to the stratospheric bromine loading of 0.3 pptv Br on average and 1.7 pptv Br in a maximum case. Together with PGI this results in a total Br entrainment of 0.4 pptv on average and 2.3 pptv for cases of maximum emissions.

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References


Fig. 1. Spatial distribution on 24 October 2009, of air parcels originally released at the surface at 19° N, 148° E on 14 October 2009, i.e. 10 days after their release. The air parcels are color coded by altitude. Air mass transport including convection has been calculated with the Lagrangian particle dispersion model FLEXPART.
Fig. 2. The vertical distribution of tropical CHBr$_3$ [nmol] 10 days after the release event is displayed for four case studies (a and d). Vertical distribution of tropical CHBr$_3$ over a one month time period starting at the date of the release event is shown (b, c, e, and f) with black lines indicating 10 days after the release event. The four case studies are based on observed CHBr$_3$ sea-to-air fluxes at 30° N, 145° E on 10 October 2009 (case 1), at 19° N, 148° E on 14 October 2009 (case 2), at 3° S, 154° E on 19 October 2009 (case 3), and at 18° S, 145° E on 23 October 2009 (case 4).
Fig. 3. Observed emissions of VSLS for one hour over 500 m² (black line), and relative (colored dots) and total (colored line) amount of VSLS entrained above 17 km for CHBr₃ (a) and CH₂Br₂ (b) are shown. For CHBr₃ the four numbers indicate the four case studies discussed in the text. PGI is given based on CHBr₃ and CH₂Br₂ emissions (c). Ozone depletion potential as a function of emission location is displayed for both VSLS (d).
Fig. 4. Average SG emissions of CHBr$_3$ and CH$_2$Br$_2$ observed in the western Pacific during the TransBrom Sonne campaign and in the tropical Atlantic during the Meteor #55 campaign are shown. Total SGI and PGI based on the observed emissions are also displayed.
Fig. 5. VSLS profiles based on atmospheric observations (black lines) and estimated from observed emissions (colored lines) of western Pacific CHBr₃ (a), western Pacific CH₂Br₂ (b), and tropical Atlantic CHBr₃ (c) are shown. Also total Br profiles (PG and SG) based on western Pacific CHBr₃ and CH₂Br₂ emissions are displayed (d). For all profiles lower and upper limits (dashed lines) and mean values (solid lines) are given.