Quantifying the vertical transport of CHBr₃ and CH₂Br₂ over the western Pacific

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Abstract. We use the GEOS-Chem global 3-D atmospheric chemistry transport model to interpret atmospheric observations of bromoform (CHBr₃) and dibromomethane (CH₂Br₂) collected during the CAST and CONTRAST aircraft measurement campaigns over the western Pacific, January–February 2014. We use a new linearized, tagged version of CHBr₃ and CH₂Br₂, allowing us to study the influence of emissions from specific geographical regions on observed atmospheric variations. The model describes 32 %–37 % of CHBr₃ and 15 %–45 % of CH₂Br₂ observed variability during CAST and CONTRAST, reflecting model errors in vertical transport. The model has a mean positive bias of 30 % that is larger near the surface, reflecting errors in the poorly constrained prior emission estimates. We find using the model that observed variability of CHBr₃ and CH₂Br₂ is driven by open ocean emissions where there is deep convection. Atmospheric variability above 6 km includes a significant contribution from coastal oceans, but it is still dominated by emissions from the open ocean and by older air masses that originate upwind. In the absence of reliable ocean emission estimates, we use a new physical age-of-air simulation to determine the relative abundance of halogens delivered by CHBr₃ and CH₂Br₂ to the tropical transition layer (TTL). We find that 76 % (92 %) of air masses that originate from the ocean reach the TTL within two (three) atmospheric e-folding lifetimes of CHBr₃ and almost all of them reach the TTL within one e-folding lifetime of CH₂Br₂. Over the duration of CAST and CONTRAST, and over our study region, oceans delivered a mean (range) CHBr₃ and CH₂Br₂ mole fraction of 0.46 (0.13–0.72) and 0.88 (0.71–1.01) pptv, respectively, to the TTL, and a mean (range) Br₃ mole fraction of 3.14 (1.81–4.18) pptv from source gases to the upper troposphere.

1 Introduction

Halogenated very short-lived substances (VSLSSs) are gases that have a tropospheric e-folding lifetime of < 6 months. This lifetime is shorter than the characteristic timescale associated with atmospheric transport of material from the surface to the tropopause. Natural sources of VSLSSs represent a progressively larger fraction of the inorganic halogen budget in the stratosphere that drives halogen-catalysed ozone loss, as anthropogenic halogenated compounds continue to decline in accordance with international agreements. Quantifying the magnitude of and variation in these natural VSLS fluxes to the stratosphere is therefore a research priority for environmental science. VSLSs include a wide range of gases such as bromoform
(CHBr$_3$), dibromomethane (CH$_2$Br$_2$), bromochloromethane (CH$_2$BrCl), dibromochloromethane (CHBr$_2$Cl), and bromodichloromethane (CHBr$_2$Cl). Here we focus on CHBr$_3$ and CH$_2$Br$_2$, which collectively represent > 80% of the organic bromine in the marine boundary layer and upper troposphere and are dominated by marine sources (WMO, 2007). We use aircraft observations of CHBr$_3$ and CH$_2$Br$_2$ collected over the western Pacific in January and February 2014 to quantify the regional flux of these compounds to the stratosphere.

The main sources of CHBr$_3$ and CH$_2$Br$_2$ include phytoplankton, particularly diatoms, and various species of seaweed (Carpenter and Liss, 2000; Quack and Wallace, 2003; Carpenter et al., 2014). The magnitude and distribution of these emissions reflect supersaturation of the compounds and nutrient-rich upwelling waters (Quack et al., 2007). Tropical, subtropical, and shelf waters are important sources of CHBr$_3$ and CH$_2$Br$_2$ with high spatial and temporal variability (Ziska et al., 2013). Current emission inventories, informed by sparse ship-borne data, have large uncertainties (Warwick et al., 2006; Liang et al., 2010; Ordóñez et al., 2012; Tegtmeier et al., 2012; Hossaini et al., 2013; Ziska et al., 2013). The atmospheric lifetime of CHBr$_3$ is ∼24 days, determined primarily by photolysis and to a lesser extent by OH oxidation. CH$_2$Br$_2$ has an atmospheric lifetime of ∼123 days determined by OH oxidation (Ko and Poulet, 2003).

Vertical ascent of CHBr$_3$ and CH$_2$Br$_2$ and their oxidation products to the upper troposphere–lower stratosphere (UTLS) represent a source of bromine that acts as a catalyst for ozone loss in the stratosphere. Balloon-borne and satellite observations estimate that brominated VSLSs and their degradation products contribute 2–8 ppt to stratospheric Br$_x$ (Sinnhuber et al., 2002, 2005; Sioris et al., 2006; Dorf et al., 2008; McLinden et al., 2010; Salawitch et al., 2010). Model estimates range between 2 and 7 ppt for this contribution (Aschmann et al., 2009; Hossaini et al., 2010; Liang et al., 2010; Ordóñez et al., 2012; Fernandez et al., 2014).

This contribution mainly originates from areas of deep convection over the tropical Indian ocean, over the western Pacific, and off the Pacific coast of Mexico (Gettelman et al., 2002; Fueglistaler et al., 2004; Aschmann et al., 2009; Ashfold et al., 2012; Hossaini et al., 2012). The stratospheric community has categorized two methods of delivering VSLSs to the stratosphere: (1) source gas injection (SGI), which describes the direct transport of the emitted halogenated compounds (e.g. CHBr$_3$ and CH$_2$Br$_2$), and (2) product gas injection (PGI), which refers to the transport of the degradation products of these emitted compounds. Previous model-based calculations (Hossaini et al., 2012; Tegtmeier et al., 2012; Aschmann and Sinnhuber, 2013; Liang et al., 2014) have estimated that 15%–75% of the stratospheric inorganic bromine budget from VSLSs is delivered by SGI, with uncertainty of the total Br$_x$ reflecting uncertainty of wet deposition of PGI product gases in the UTLS (Sinnhuber and Folkins, 2006; Liang et al., 2014).

The tropical tropopause layer (TTL) represents a gradual transition from the troposphere to the stratosphere (Zhou et al., 2004; Fueglistaler et al., 2009; Pan et al., 2014). It extends over a few kilometres within the upper troposphere between where the atmospheric lapse rate is at a minimum (∼12–13 km) and the cold point tropopause (∼17 km) (Gettelman and Forster, 2002). The TTL is the dominant transport pathway for SGI and PGI gases to the lower stratosphere. TTL temperatures vary zonally, with the smallest values between 130 and 180ºE throughout the year, corresponding to the tropical warm pool over the western Pacific where convective activity is largest (Gettelman et al., 2002). Estimates of SGI within this region are highly dependent on the strength and spatial variability of source regions, and how they couple with atmospheric transport mechanisms.

We use data from two coordinated aircraft campaigns over the western Pacific during 2014, the Coordinated Airborne Studies in the Tropics (CAST, Harris et al., 2016) and the CONvective Transport of Active Species in the Tropics (CONTRAST, Pan et al., 2016), to study the emission, vertical transport, and chemical transformation of halogenated gases. The CAST and CONTRAST campaigns measured a suite of trace gases and aerosols centred on the Micronesian region in the western Pacific, including Guam, Chuuk, and Palau during January and February 2014. We interpret aircraft measurements of CHBr$_3$ and CH$_2$Br$_2$ mole fraction using the GEOS-Chem atmospheric chemistry transport model.

In the next section we describe CAST and CONTRAST and the data we used. Section 3 describes the GEOS-Chem model and how it is used to interpret the airborne data. In Sect. 4 we evaluate the model and describe our results. We conclude the paper in Sect. 5.

2 Observational data

2.1 CAST and CONTRAST CHBr$_3$ and CH$_2$Br$_2$ mole fraction data

We use CHBr$_3$ and CH$_2$Br$_2$ mole fractions from the CAST and CONTRAST aircraft campaigns (Harris et al., 2016; Pan et al., 2016). Here for the sake of brevity we provide only brief details about the CHBr$_3$ and CH$_2$Br$_2$ data and refer the reader to Andrews et al. (2016) for a more comprehensive description of the data collection and analysis procedures used during the campaigns.

Figure 1 shows the spatial distribution of whole air samples (WASs) collected during CAST and CONTRAST. For CAST, WAS canisters were filled aboard the Facility for Airborne Atmospheric Measurements (FAAM) BAe-146 aircraft. These canisters were analysed for CHBr$_3$ and CH$_2$Br$_2$ and other trace compounds within 72 h of collection. The WAS instrument was calibrated using the National Oceanic and Atmospheric Administration (NOAA) 2003 scale for CHBr$_3$ and the NOAA 2004 scale for
CHBr₃ and CH₂Br₂. For CONTRAST, a similar WAS system was employed to collect CHBr₃ and CH₂Br₂ measurements on the NSF/NCAR Gulfstream-V HIAPER (High-performance Instrumented Airborne Platform for Environmental Research) aircraft. A working standard was used to regularly calibrate the samples, and that working standard was calibrated using a series of dilutions of high concentration standards that are linked to National Institute of Standards and Technology standards. The mean absolute percentage error for CHBr₃ and CH₂Br₂ measurements between 0 and 8 km is 7.7% and 2.2%, respectively, representing the combined error between the two WAS systems and two accompanying GC/MS instruments.

Table 1 shows mean measurement statistics of CHBr₃ and CH₂Br₂ for the CAST and CONTRAST campaigns. CHBr₃ is generally more variable than CH₂Br₂ throughout the study region, reflecting its shorter atmospheric lifetime, so that sampling differences between CAST and CONTRAST will introduce larger differences for this gas. CAST measurements of CHBr₃ are typically lower than for CONTRAST, but CAST recorded the highest and lowest CHBr₃ mole fractions at 0–2 and 6–8 km, respectively. We define the TTL from 13 km (Pan et al., 2014) to the local tropopause determined from the GEOS5–FP-analysed meteorological fields, as described below. CONTRAST measured a minimum CHBr₃ value indistinguishable from zero just below the TTL at 10–13 km. Measurements of CH₂Br₂ are generally consistent between CAST and CONTRAST at all altitudes. There is only a small vertical gradient for CH₂Br₂ above 2 km with a mean value of ~0.91 pptv. CONTRAST measured the lowest value of 0.21 pptv just below the TTL. Within the TTL, CONTRAST reports mean (maximum) values of 0.42 pptv (0.85 pptv) and 0.84 pptv (1.05 pptv) for CHBr₃ and CH₂Br₂, respectively, providing some evidence of rapid convection of surface emissions to the upper troposphere.

2.2 NOAA ground-based CHBr₃ and CH₂Br₂ measurements

Table 2 summarizes the independent surface measurements of CHBr₃ and CH₂Br₂ collected by the NOAA Earth System Research Laboratory (ERSL), which we have used to evaluate the GEOS-Chem atmospheric chemistry model simulation on a global scale. This evaluation was undertaken to report on model performance and is not used to provide additional data over the western Pacific.

These measurements are part of the ongoing NOAA/ESRL global monitoring program (https://www.esrl.noaa.gov/gmd/, last access: 4 September 2018). CHBr₃ and CH₂Br₂ measurements are obtained approximately weekly using paired steel flasks, which are then analysed by GC/MS. Further details about their sampling are given in Montzka et al. (2011). In Appendix A, we evaluate the model using mean monthly statistics at each site from 1 January 2005 to 31 December 2011.

3 The GEOS-Chem global 3-D atmospheric chemistry transport model

To interpret CAST and CONTRAST data we use v9.02 of the GEOS-Chem global 3-D atmospheric chemistry transport model (www.geos-chem.org, last access: 4 September 2018), driven by GEOS5–FP-analysed meteorological fields provided by the Global Modelling and Assimilation Office (GMAO) at NASA Goddard Space Flight Centre. For our experiments we degrade the native meteorological fields to a model horizontal spatial resolution of 2° latitude × 2.5° long-
Table 1. Mean measurement statistics for CHBr$_3$ and CH$_2$Br$_2$ mole fraction data as a function of altitude for CAST and CONTRAST aircraft campaigns. $\bar{x}$, $\sigma$, and $n$ denote the mean value, the standard deviation, and the number of data points used to determine the statistics.

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>CAST CHBr$_3$</th>
<th>CONTRAST CHBr$_3$</th>
<th>CAST CH$_2$Br$_2$</th>
<th>CONTRAST CH$_2$Br$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\bar{x}$</td>
<td>$\sigma$ &amp; range</td>
<td>$n$</td>
<td>$\bar{x}$</td>
</tr>
<tr>
<td>0–2</td>
<td>0.95</td>
<td>0.45</td>
<td>0.42–3.00</td>
<td>502</td>
</tr>
<tr>
<td>2–4</td>
<td>0.61</td>
<td>0.16</td>
<td>0.29–0.98</td>
<td>147</td>
</tr>
<tr>
<td>4–6</td>
<td>0.44</td>
<td>0.17</td>
<td>0.03–0.79</td>
<td>59</td>
</tr>
<tr>
<td>6–8</td>
<td>0.38</td>
<td>0.25</td>
<td>0.02–0.81</td>
<td>53</td>
</tr>
<tr>
<td>8–10</td>
<td>0.48</td>
<td>0.34</td>
<td>0.14–0.82</td>
<td>2</td>
</tr>
<tr>
<td>10–13</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>TTL</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2. Location and code of NOAA/ESRL ground-based stations.

<table>
<thead>
<tr>
<th>Station</th>
<th>Name</th>
<th>Latitude</th>
<th>Longitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALT</td>
<td>Alert, NW Territories, Canada</td>
<td>82.5° N</td>
<td>62.3° W</td>
</tr>
<tr>
<td>SUM</td>
<td>Summit, Greenland</td>
<td>72.6° N</td>
<td>38.4° W</td>
</tr>
<tr>
<td>BRW</td>
<td>Pt. Barrow, Alaska, USA</td>
<td>71.3° N</td>
<td>156.6° W</td>
</tr>
<tr>
<td>MHD</td>
<td>Mace Head, Ireland</td>
<td>53.0° N</td>
<td>10.0° W</td>
</tr>
<tr>
<td>LEF</td>
<td>Wisconsin, USA</td>
<td>45.6° N</td>
<td>90.2° W</td>
</tr>
<tr>
<td>HFM</td>
<td>Massachusetts, USA</td>
<td>42.5° N</td>
<td>72.2° W</td>
</tr>
<tr>
<td>THD</td>
<td>Trinidad Head, USA</td>
<td>41.0° N</td>
<td>124.0° W</td>
</tr>
<tr>
<td>NWR</td>
<td>Niwot Ridge, Colorado, USA</td>
<td>40.1° N</td>
<td>105.6° W</td>
</tr>
<tr>
<td>KUM</td>
<td>Cape Kumukahi, Hawaii, USA</td>
<td>19.5° N</td>
<td>154.8° W</td>
</tr>
<tr>
<td>MLO</td>
<td>Mauna Loa, Hawaii, USA</td>
<td>19.5° N</td>
<td>155.6° W</td>
</tr>
<tr>
<td>SMO</td>
<td>Cape Matatula, American Samoa</td>
<td>14.3° S</td>
<td>170.6° W</td>
</tr>
<tr>
<td>CGO</td>
<td>Cape Grim, Tasmania, Australia</td>
<td>40.7° S</td>
<td>177.8° E</td>
</tr>
<tr>
<td>PSA</td>
<td>Palmer Station, Antarctica</td>
<td>64.6° S</td>
<td>64.0° W</td>
</tr>
<tr>
<td>SPO</td>
<td>South Pole</td>
<td>90.0° N</td>
<td>–</td>
</tr>
</tbody>
</table>

...gitude described on 47 vertical levels, with a top pressure of 0.01 hPa. Dynamic tropopause height and convective mass flux (CMF) from the meteorological fields are given on a 1-hourly and 3-hourly averaging period, respectively.

Below we describe two new GEOS-Chem simulations that we developed to interpret observed variations in CHBr$_3$ and CH$_2$Br$_2$ during CAST and CONTRAST airborne campaigns: (1) a tagged simulation of CHBr$_3$ and CH$_2$Br$_2$ to better understand source attribution, and (2) an age-of-air simulation to improve understanding of the vertical transport of these short-lived halogenated compounds. For both simulations, we sample the model at the time and location of CAST and CONTRAST observations.

3.1 Tagged CHBr$_3$ and CH$_2$Br$_2$ simulation

The purpose of this simulation is to relate observed atmospheric variations to surface emissions from individual sources and/or geographical regions. To achieve this we use pre-computed monthly 3-D fields of OH and photolysis rates for CHBr$_3$ and CH$_2$Br$_2$ from the full-chemistry version of GEOS-Chem, allowing us to linearize the chemistry so that we can isolate the contributions from individual sources and geographical regions.

The structure of the model framework follows closely other tagged simulations within GEOS-Chem (e.g. Jones et al., 2003; Palmer et al., 2003; Finch et al., 2014; Mackie et al., 2016). We use the following temperature-dependent (temperature is denoted by $T$) reaction rate constants that describe oxidation of CHBr$_3$ and CH$_2$Br$_2$ by OH (Sander et al., 2011): for CHBr$_3$, $k(T) = 1.35 \times 10^{-12} \exp(-600/T) \text{cm}^{-3} \text{molec}^{-1} \text{s}^{-1}$; and for CH$_2$Br$_2$, $k(T) = 2.00 \times 10^{-12} \exp(-840/T) \text{cm}^{-3} \text{molec}^{-1} \text{s}^{-1}$.

Figure 2 shows the magnitude and spatial distribution of our prior emissions of CHBr$_3$ and CH$_2$Br$_2$ (Liang et al., 2010). These emission estimates were derived from airborne measurements in the troposphere and lower stratosphere over the western Pacific and North America. Liang et al. (2010) has global annual totals of 425 Gg Br yr$^{-1}$ for CHBr$_3$ and 57 Gg Br yr$^{-1}$ for CH$_2$Br$_2$. These emissions integrated over the geographical region and duration of the campaign are 3 and 0.4 Gg Br yr$^{-1}$ for CHBr$_3$ and CH$_2$Br$_2$, respectively. We temporally distribute emissions every 30 min without any diurnal variation. We found that other commonly used emission inventories for CHBr$_3$ and CH$_2$Br$_2$ (e.g. Ordóñez et al., 2012 and Ziska et al., 2013) were not noticeably better than Liang et al. (2010) at describing the CAST and CONTRAST data (not shown). We chose to use Liang et al. (2010) because it has a consistent bias for CHBr$_3$ and CH$_2$Br$_2$.

Figure 3 shows the ocean (open and coastal) tagged tracer regions we use in the GEOS-Chem model. These geographical definitions are informed by the NOAA ETOPO2v2 Global Relief map (National Geographic Data Center, NOAA, 2006), which combines topography and ocean depth data at 2 min spatial resolution: heights between 0 and $-200$ m are defined as coastal oceans, and heights below $-200$ m are open ocean. Each 2 min cell that falls within a model grid box is assigned a coastal or open ocean. Each model grid box can then be described as fractional contributions ($R_i$) to the open and coastal ocean tagged regions. We have explicitly included elevated coastal emissions from the inventory in the coastal tracer. We assign individual tracers...
For model evaluation, we sample at the time and location of each observation. For the NOAA data described above, we calculate monthly mean statistics from 1 January 2005 to 31 December 2011.

3.2 Physical age-of-air model calculation

We use the age-of-air simulation to understand how short-lived halogenated compounds are transported to the TTL, independent of emission inventories. The method uses only knowledge of the distribution of emissions, and not the magnitude, so we can investigate the influence of the emissions source region with respect to respective CHBr3 and CH2Br2 atmospheric e-folding lifetimes. We use the GEOS-Chem model to determine the physical age of air A, building on previous studies (Finch et al., 2014), and we use a consistent set of geographical regions in our tagged CHBr3 and CH2Br2 simulations (Fig. 3).
For each model tracer we define a surface boundary volume mixing ratio \( B \) that linearly increases with time \( t \) so that smaller values correspond to older physical ages:

\[
B = f \times t, \tag{1}
\]

where \( f \) is a constant \( (1 \times 10^{-15} \text{ s}^{-1}) \), \( B \) describes a volume mixing ratio of each tracer dependent on their time of emission. Fractional contributions of tracers are calculated based on \( R_x \), where the finalized \( B (B_{\text{final}}) \) in the surface boundary condition is calculated using the following:

\[
B_{\text{final}} = (B \times R_x) + (1 - R_x \times X), \tag{2}
\]

where \( X \) denotes the mixing ratio of tracers within the grid box. As time progresses, smaller volume mixing ratios represent older air that has spent more time away from the surface boundary.

We initialize this model in July 2013 and run for 6 months until the start of January 2014 so that at least one \( e \)-folding lifetime of CH\(_2\)Br\(_2\) has been achieved. We then sample the resulting 3-D field of model tracer mixing ratios \( (X) \), at the time and location of CAST and CONTRAST measurements. The physical age of a tracer \( A \) since it last came into contact with a ocean surface is given by the following:

\[
A = t - X/f. \tag{3}
\]

We account for atmospheric dispersion by using the GEOS-Chem model, but we do not consider any chemical losses.

To explicitly evaluate marine convection in GEOS-Chem we also developed a short-lived tagged tracer simulation with an \( e \)-folding lifetime of 4 days, comparable to that of methyl iodide \( (\text{CH}_3\text{I}) \) in the tropics (Carpenter et al., 2014). We emit the tracer with an equilibrium mole fraction of 1 pptv over all oceanic regions described in Fig. 3. We initialize the model on 1 January 2014 with an empty 3-D atmospheric field and run for 2 months until 1 March 2014. Model output is archived every 2 h and the model is sampled along the aircraft flight tracks. By comparing our model with \( \text{CH}_3\text{I} \) observations, we find that GEOS-Chem captures mean marine convective flow over the study region. We also find that the model captures fast, infrequent, large-scale convective transport that results in upper tropospheric ages of 3–5 days, but does not capture small-scale variations due to rapid convection. Appendix B includes a more detailed report on the results.

4 Results

4.1 Model evaluation

We evaluate our tagged model of atmospheric CHBr\(_3\) and CH\(_2\)Br\(_2\) using NOAA surface data, and CAST and CONTRAST aircraft data during January and February 2014.

Model evaluation using the NOAA data is described in Appendix A. In brief, the model generally has a positive bias but reproduces 30%–60% of the seasonal variation (Pearson correlation coefficients in Table 3), depending on geographical location. Model errors in reproducing the observed seasonal cycle reflect errors in production and loss rates. The model generally has less skill at reproducing observations collected at coastal sites close to emission sources.

Figure 4 shows that CAST and CONTRAST observed and model vertical profiles CHBr\(_3\) and CH\(_2\)Br\(_2\) have an inverted “S” shape (Harris et al., 2016; Pan et al., 2016). This suggests that GEOS-Chem has skill in describing the broad-scale atmospheric transport over the study region. From Pearson correlation coefficients, we find that GEOS-Chem reproduces more than 30% of the observed variability of CHBr\(_3\) from CAST and CONTRAST and between 15% (CAST) and 45% (CONTRAST) of the observed variability of CH\(_2\)Br\(_2\). Larger differences in the correlations for CH\(_2\)Br\(_2\) is likely due to differences in the sampled air masses that have originated far upwind. Figure 4 also shows that GEOS-Chem has a positive model bias of 30% for both campaigns, which we calculate using \( 100/N \Sigma (\text{mod}_i - \text{obs}_i)/\left( \max(\text{mod}_i, \text{obs}_i) \right) \). The relative model error is reasonably constant with altitude for CHBr\(_3\) and CH\(_2\)Br\(_2\), suggesting that this bias is representative of prior surface emissions. Consequently, we remove this bias from subsequent calculations. We attribute the variations about the mean bias to errors due to model atmospheric transport.

4.2 Tagged-VSLS model output

Figures 5 and 6 show a strong region of convection south of Chuuk and along the Equator that transports CHBr\(_3\) and CH\(_2\)Br\(_2\) directly from open oceanic emission sources to the mid-troposphere. Above the mid-troposphere (10 km) convective mass fluxes get smaller and advection plays a more important role in distributing the gases. This results in an inverted “S” shape in the vertical profiles of CHBr\(_3\) and CH\(_2\)Br\(_2\), as discussed above. There is also a strong convection region west of Papua New Guinea and the north of Australia, which transports coastal emissions to the mid-troposphere and upper troposphere.

Model mean mole fractions of CHBr\(_3\) are \( \approx 1.4 \text{ ppt} \) throughout the boundary layer (0–2 km), determined by open ocean emissions, but fall off rapidly as a function of altitude due to chemical losses. At the TTL over the study domain and during the campaign period, mean CHBr\(_3\) mole fractions range 0.4–0.6 ppt mainly due to open ocean emissions. Coastal emissions are typically much larger than open ocean emissions but they play a much smaller role in observed variations throughout the troposphere, except over the strong convective regions over Papua New Guinea and the north of Australia. Prevailing easterly transport of gases over the region is dominated by the vast area of open ocean sources that appear to weaken the magnitude of spatially limited coastal
emissions (Andrews et al., 2016; Pan et al., 2016). The vertical and spatial distributions of CH$_2$Br$_2$ mole fractions are consistent with CHBr$_3$, although they deplete less rapidly with altitude by virtue of its longer atmospheric lifetime. At the TTL, averaged over the campaign study, CH$_2$Br$_2$ mole fractions range 0.1–0.3 ppt mainly due to smaller magnitude of ocean emissions compared to CHBr$_3$. Coastal sources contribute up to 0.1 ppt of CH$_2$Br$_2$ in the TTL, with the remaining originating from an open ocean source.

Figure 7 shows that ocean emissions provide the largest fractional contribution to CHBr$_3$ during CAST, typically more than 80% throughout the low to mid troposphere, with the remainder originating from emissions prior to the campaigns. This is dominated by open ocean emissions that range between 50% and 70% of the total tracer. Coastal ocean emissions represent a smaller contribution to CHBr$_3$ at lower altitudes, but increase their influence above 6 km in the CONTRAST data with contributions from geographical regions immediately outside the study region that reach a maximum of 60% of the total CHBr$_3$ tracer in the TTL. This results in an inverted “S” shape observed over the vertical profile, which is described above. Island land masses generally represent only a minor contribution to the vertical profile at our model resolution, and we have excluded them from further analysis.

The ocean, in particular the open ocean, represents the largest contributions to total CH$_2$Br$_2$ over the campaign period. They typically represent 20% of the total CH$_2$Br$_2$ and reach a maximum of 28% in the TTL for the CONTRAST measurements. Maximum contributions of coastal emission sources peak at 15% of total CH$_2$Br$_2$ tracer in the TTL, much less than for CHBr$_3$. The remaining contributions are representative of emissions prior to the campaign period.

Different CHBr$_3$ and CH$_2$Br$_2$ emission scenarios (Ordóñez et al., 2012; Ziska et al., 2013) vary with spatial distribution and magnitude of coastal and open ocean emissions, leading to uncertainties of atmospheric mixing ratios (Hossaini et al., 2013, 2016). This would have implications for results presented here, as source region mixing ratios will vary depending on the emission scenario used. We developed the age-of-air calculation to ascertain the influence of ocean emission regions independent of emission scenarios.

### 4.3 Physical age of air

Figure 8 shows that the air masses over the open ocean study domain are responsible for the youngest air throughout the troposphere. Coastal ocean contributions are only present in the younger age profile up to 4 km. At progressively higher altitudes the probability distribution shifts towards older ages, as expected, corresponding to longer periods from the point of contact with the surface. However, at 10–13 km we see a noticeable shift towards younger ages, reflecting the peak of the convective outflow of surface air. Within the TTL, mean age increases to a value greater than the e-folding lifetime of atmospheric CHBr$_3$. However, we find, using our CH$_3$I–like tracer (mean lifetime of approximately 4 days), that air masses can be transported to the TTL within 3–5 days but these are infrequent events and so are not easily observed (Appendix B).

Assuming an indicative e-folding atmospheric lifetime $\tau$ of 24 days for CHBr$_3$ and 123 days for CH$_2$Br$_2$, we calculate that the majority of air over the ocean has an age within $3\tau_{CHBr_3}$ and $1\tau_{CH_2Br_2}$. We find that 76% (92%) of oceanic emissions reach the TTL within $2\tau_{CHBr_3}$ ($3\tau_{CHBr_3}$), with 64% (88%) of open ocean emissions and 9% (50%) of coastal emissions being transported in the same time frames.
Figure 4. Comparison of model and observed (a, c, e) CHBr₃ (pptv) and (b, d, f) CH₂Br₂ (pptv) mole fraction data for CAST (denoted by blue) and CONTRAST (denoted by red). Panels (a, b) describe the comparison between model (dotted line) and observed (solid line) values as a box-and-whiskers plot on 2 km altitude bins. Panels (c, d) describe the model and data comparison as a scatter plot. Pearson correlations (r²) and percentage biases are shown inset. Black, red, and blue dashed lines denote the 1 : 1 line, and the best fit linear models for CONTRAST and CAST, respectively. Panels (e, f) show the relative model error, described as a box-and-whiskers plot on 2 km altitude bins. The vertical dashed line denotes the zero error line.

The corresponding statistics for CH₂Br₂ are 99 % of air over the ocean reaches the TTL within 1τCH₂Br₂, and 99 % (97 %) of air emitted from the open (coastal) ocean.

Figure 9 shows that the atmospheric sampling adopted by the CAST and CONTRAST campaigns captures a similar distribution of physical ages discussed above. CAST represents a profile dominated within the boundary layer, with CONTRAST more representative of age profiles outside of the boundary layer that reflects its more extensive horizontal and vertical sampling domain. Despite intensive measurements around coastal land masses of the region, CAST did not capture coastal emissions very well. This is reflective of a model resolution that is too coarse to capture such localized effects on a sub-model grid scale.
Figure 5. Model mole fractions (pptv) of CHBr$_3$ over the study domain as a function of altitude, averaged between 18 January 2014 and 28 February 2014, from the total (column 1), open (column 2), and coastal ocean (column 3) tagged tracers. The corresponding mean model convective mass flux (kg m$^{-2}$ s$^{-1}$) is shown in column 4. Tagged tracers are averaged from 2 h fields and convective mass fluxes are averaged from daily fields.

Figure 10 shows mixing ratios of CHBr$_3$ decreasing with altitude, but remaining fairly constant with increasing age within each altitude range. Coastal emissions are associated with the highest surface emissions but they are also subjected to slow ascent rates and consequently greater photochemical losses. In contrast, open ocean emissions are lower than coastal emissions but are convected more rapidly and subject to less chemical loss. Consequently, CHBr$_3$ appears to be insensitive to age. From our analysis, we found that CHBr$_3$ values are determined mainly by younger air masses from the open ocean (Fig. 8). Within the TTL, higher median mole fractions are associated with the highest model convective mass flux in each age bin. The peak frequency for the mean age of air in the TTL is 48–72 days, corresponding to 3$\tau_{\text{CHBr}_3}$. 

www.atmos-chem-phys.net/18/13135/2018/ Atmos. Chem. Phys., 18, 13135–13153, 2018
and median values of 0.5 pptv CHBr$_3$ from oceanic emission sources, and 0.6 pptv in high convective systems. However, less than 0.5 % (2 %) of air being transported to the TTL within 24–48 (48–72) days of emission are associated with high convection events. Weaker, mean convection plays an important role in more consistently transporting large mole fractions to the free troposphere, which are then transported more slowly to the TTL.

To estimate the mean observed transport of CHBr$_3$ and CH$_2$Br$_2$ to the TTL we remove the calculated model bias (Sect. 4.1), assuming this bias reflects errors in surface emissions. Figure 11 shows the resulting corrected mean vertical profiles. We calculate the uncertainties using the upper and lower limits of the bias correction, which are based on CHBr$_3$ and CH$_2$Br$_2$ data that are ±2 mean absolute deviations from the observed mean mole fractions. For CHBr$_3$ and CH$_2$Br$_2$ we find biases that range −8 %–80 % and 19 %–43 %, respectively, which we then apply to the model values throughout the atmosphere over the campaign period. We find that the resulting mean model values underestimate observed CHBr$_3$ and CH$_2$Br$_2$ between 9 and 12 km, above the main region of convective outflow, with the observations in-
Figure 7. The percentage contributions from total ocean, open oceans, and coastal oceans to total (a) CHBr$_3$ and (b) CH$_2$Br$_2$ described as a box-and-whiskers plot on 1 km altitude bins.

Figure 8. Probability density functions of the age of air $A$ for (blue) total ocean, (green) open oceans, and (black) coastal ocean tracers, described as 2 km altitude regions from the surface to the TTL (13 km to the tropopause) averaged over the whole study domain between 18 January 2014 and 28 February 2014.
Figure 9. As Fig. 8 but sampled along CAST and CONTRAST flight tracks.

Figure 10. Box-and-whiskers plot of model CHBr₃ mole fractions from the entire ocean tracer as a function of 2 km altitude intervals and a nominal 24-day e-folding lifetime (τ). Data are averaged over 18 January–28 February 2014 and over 10° S–30° N, 125–175° E. Blue values correspond to results determined by all available data, and red values correspond to results determined by convective mass fluxes > 95th percentile. Solid lines denote the percentage of occurrence rate over the period and region denoted above. Percentage of occurrence rate refers to how often air masses fall within the specified age range.
We used the GEOS-Chem chemistry transport model to interpret mole fraction measurements of CHBr₃ and CH₂Br₂ over the western Pacific during the CAST and CONTRAST campaigns, January–February 2014. We found that the model reproduced 30 % of CHBr₃ measurements and 15 % (45 %) CAST (CONTRAST) CH₂Br₂, but had a mean positive bias of 30 % for both compounds. CAST mainly sampled the marine boundary layer (70 % of observations) so that biases in prior surface emissions have a greater influence on CAST than CONTRAST, which sampled throughout the troposphere.

To interpret the CAST and CONTRAST measurements of CHBr₃ and CH₂Br₂ we developed two new GEOS-Chem model simulations: (1) a linearized tagged simulation so that we could attribute observed changes to individual sources and geographical regions, and (2) an age-of-air simulation to improve understanding of the vertical transport of these compounds, acknowledging that more conventional photochemical clocks are difficult to use without more accurate boundary conditions provided by surface emission inventories.

We have three main conclusions. First, we found that open ocean emissions of CHBr₃ and CH₂Br₂ are primarily responsible for observed atmospheric mole fractions of these gases over the western Pacific. Emissions from open ocean sources represent up to 70 % of total CHBr₃, with the largest fractional contribution in the lower troposphere. Coastal ocean sources typically contribute 20 % to total atmospheric CHBr₃ but reach a maximum of 60 % in the TTL due to advection of air masses convected from areas outside the study region. Based on this model interpretation, we infer that CAST observations of CHBr₃, which are mainly in the lower troposphere, are dominated by open ocean sources. In contrast, CONTRAST measurements have a mix of sources, including a progressively larger contribution from coastal ocean sources in the upper troposphere. Tropospheric measurements of CH₂Br₂, which has a longer atmospheric lifetime than CHBr₃, are dominated by sources from before the campaign. The open ocean source typically represents only 15 % of the observed variations in CH₂Br₂ emitted during the campaign region throughout the troposphere.

Second, using our age-of-air simulation, we find that the majority of CHBr₃ and CH₂Br₂ mole fractions in the TTL correspond to the youngest air masses being transported from open oceanic sources, with coastal oceans representing older air masses. Within the TTL, the highest CHBr₃ mole fractions are associated with the strongest convective mass flux events, but this represents only 2 % of the air transported to the TTL. Weaker, slower convection processes are responsible for consistently transporting higher mole fractions to the UT and TTL. The majority of air (92 %) is being transported to the TTL within 3TCHBr₃ (48–72 days), corresponding to the majority of weaker convection events.

And third, we estimated the flux of CHBr₃ and CH₂Br₂ to the TTL using model data that have been corrected for bias. We calculated a mean and range of values 0.46 pptv (0.13–0.72 pptv) and 0.88 pptv (0.71–1.01 pptv) for CHBr₃ and CH₂Br₂, respectively. Together, they correspond to a total of 3.14 pptv (1.81–4.18 pptv) Br to the TTL.

5 Discussion and concluding remarks

Data availability. CONTRAST data are publicly available for all researchers and can be obtained at http://data.eol.ucar.edu/master_list/?project=CONTRAST (last access: 11 September 2018). The NOAA surface data are available at http://www.esrl.noaa.gov/gmd/dv/ftpdata.html (last access: 11 September 2018).
Appendix A: Model evaluation using NOAA surface mole fraction measurements

Figure A1 shows that the majority of station sites have a positive model bias with magnitude varying depending on location. Mid-latitude stations (LEF–NWR) have similar bias values of 30%–40% (10%–20%) for CHBr3 (CH2Br2). At the tropical sites, which are comparable with the campaign region, the model bias varies strongly depending on location. This variability will represent the large variability of convective events over the region, as well as the aforementioned errors in model emissions. KUM and MLO both sit on Hawaii, with KUM and SMO being a near-surface coastal station and MLO sitting at an elevated altitude of 3397 m. Model bias calculated for MLO (60%) is much greater than the other two near-surface sites (<10%), however it gives the strongest annual correlation with $r^2$ values of 0.75 (0.55) for CHBr3 (CH2Br2). All coastal sites (with the exception of ALT) near emission sources have low $r^2$ values (<0.4), suggesting the model does not capture local variations in emissions well. This is also representative of the variation in convection events over the tropical region being represented within the model.

Seasonal variations within model bias and correlations of CHBr3 and CH2Br2 are shown in Table 3. The campaign season of DJF is poorly constrained within the model at all sites, with an $r^2 < 0.5$ for both gases. The annual correlation at sites appears to be dominated by other seasons. Within the tropical stations, model bias increases from the annual at KUM to around 20% with no correlation to observed values. MLO and SMO show a similar seasonal bias to the annual, indicating that the effect is local to the KUM station site.

Figure A2 shows that the model reproduces the seasonal cycle well at all three sites. The emissions at these sites are not scaled seasonally, but rather the phase is representative of the chemistry at these sites. The shorter-lived CHBr3 profile is dominated by its loss from photolysis, whereas the CH2Br2 cycle is dominated by oxidation with OH. The amplitude of the seasonal cycle is overestimated in CHBr3 at MLO, and to a lesser extent KUM. This can be indicative of local biases within photolysis loss rates and/or emissions. The same effect is not shown within the CH2Br2, suggesting that there is not a similar problem associated with OH fields. This is concurrent with a recent multi-decadal analysis which found that carbon monoxide (Mackie et al., 2016) at higher northern latitudes does not support a major problem with similar monthly 3-D fields of OH.

### Table 3: Seasonal correlation $r^2$ values for CHBr3 and CH2Br2 at all stations

<table>
<thead>
<tr>
<th>Station</th>
<th>CHBr3</th>
<th>CH2Br2</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLO</td>
<td>0.75</td>
<td>0.55</td>
</tr>
<tr>
<td>KUM</td>
<td>0.20</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Figure A1. Mean annual percentage model bias (blue) calculated at NOAA ground station sites (Table 2) for CHBr3 (dots) and CH2Br2 (crosses). The horizontal dashed line denotes zero bias. The right-hand-side y axis describes the ability of the model to reproduce observed variations ($r^2$) (red). The vertical dotted lines define the tropical stations.

Appendix B: Evaluation of model convection

To evaluate model convection over the marine environment during the CAST and CONTRAST campaigns, we developed a short-lived tagged tracer simulation with an e-folding lifetime comparable to CH3I, as described in Sect. 3.

We emitted CH3I at an equilibrium mole fraction of 1 pptv over ocean regions and applied an atmospheric e-folding lifetime of 4 days, similar to that CH3I in the tropics Carpenter et al. (2014). We can then use the model mole fraction to determine the effective mean age-of-air parcels throughout the troposphere, and to compare the qualitative CH3I values to observed CH3I values collected during the CONTRAST campaign.

Figure B1 shows that the model can generally reproduce the quantitative vertical distribution of CH3I: a decrease from the surface source up to an altitude of 10–11 km. Above this, there is a 1–2 km altitude region where values are higher than those in the free troposphere, suggestive of outflow from convection. As expected, the youngest air masses are close to the surface with the ages as young as 5–6 days in the upper troposphere. These ages are indicative of fast convective transport but they are not as young as would be expected from some of the highest observed mole fractions, which are likely due to faster, sub-grid-scale convective transport.

Figure B2 shows that the model captures infrequent fast, large-scale convective transport over the study domain, with ages as young as 3–4 days reaching the upper troposphere. One metric to describe the convective transport is the marine convection index (MCI), following Bell et al. (2002): the ratio of mean upper tropospheric CH3I (8–12 km) to lower tropospheric CH3I (0–2.5 km). The CONTRAST observations

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**Figure A1** Mean annual percentage model bias (blue) calculated at NOAA ground station sites (Table 2) for CHBr3 (dots) and CH2Br2 (crosses). The horizontal dashed line denotes zero bias. The right-hand-side y axis describes the ability of the model to reproduce observed variations ($r^2$) (red). The vertical dotted lines define the tropical stations.

**Figure B1** The CONTRAST observations and modelled CH3I for the I (0–2.5 km). The CONTRAST observations and modelled CH3I for the I (8–12 km) to lower troposphere. These ages are indicative of fast convective transport but they are not as young as would be expected from some of the highest observed mole fractions, which are likely due to faster, sub-grid-scale convective transport.

**Figure B2** The model captures infrequent fast, large-scale convective transport over the study domain, with ages as young as 3–4 days reaching the upper troposphere. One metric to describe the convective transport is the marine convection index (MCI), following Bell et al. (2002): the ratio of mean upper tropospheric CH3I (8–12 km) to lower tropospheric CH3I (0–2.5 km). The CONTRAST observations
Figure A2. Observed (green) and model (blue) mole fractions of (a) \( \text{CHBr}_3 \) and (b) \( \text{CH}_2\text{Br}_2 \) at tropical NOAA sites. The seasonal cycle is shown as the climatological monthly mean anomaly calculated by subtracting the annual mean from the climatological monthly mean (pptv). Horizontal bars on observed values denote \( \pm 1\sigma \).

Overall, we find that the model describes the mean convective flow over the region and can capture instances of rapid, large-scale convective transport. Differences in the MCI suggest the significant role of rapid, sub-grid scale vertical transport that is not captured by our coarse model resolution.

Figure B1. Vertical profiles of observed (blue) and synthetic (coloured as a function of age) \( \text{CH}_3\text{I} \) mole fraction data sampled along flight tracks corresponding to AWAS samples collected during CONTRAST as a function of altitude.
Figure B2. Probability distribution of the physical age of CH$_3$I for the 3-D study domain (solid line) and as sampled by the aircraft (dashed line) between 11 and 15 km during CONTRAST, 18 January–28 February 2014. The dotted line indicates $1_{\Delta \text{CH}_3\text{I}}$ of 4 days.
**Author contributions.** RB and PIP designed the computational experiments with RB conducting the calculations with contributions from LF about the tagged models. PIP and RB wrote the paper, with contributions with the other authors.

**Competing interests.** The authors declare that they have no conflict of interest.

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