

**Natural and  
anthropogenic very  
short-lived species**

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# The contribution of natural and anthropogenic very short-lived species to stratospheric bromine

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## Abstract

We have used a global three-dimensional chemical transport model to quantify the impact of the very short-lived species (VSLs)  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ ,  $\text{CH}_2\text{BrCl}$  and  $\text{C}_2\text{H}_5\text{Br}$  on the bromine budget of the stratosphere. Atmospheric observations of these gases allow constraints on surface mixing ratios that, when incorporated into our model, contribute  $\sim 4.9\text{--}5.2$  parts per trillion (ppt) of inorganic bromine ( $\text{Br}_y$ ) to the stratosphere. Of this total,  $\sim 76\%$  comes from naturally-emitted  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$ . The remaining species individually contribute modest amounts. However, their accumulated total accounts for up to  $\sim 1.2$  ppt of the supply and thus should not be ignored. We have compared modelled tropical profiles of a range of VSLs with observations from the recent 2009 NSF HIPPO-1 aircraft campaign. Modelled profiles agree reasonably well with observations from the surface to the lower tropical tropopause layer.

We have also considered the poorly studied anthropogenic VSLs,  $\text{C}_2\text{H}_5\text{Br}$ ,  $\text{CH}_2\text{BrCH}_2\text{Br}$ ,  $n\text{-C}_3\text{H}_7\text{Br}$  and  $i\text{-C}_3\text{H}_7\text{Br}$ . We find the local atmospheric lifetime of these species in the tropical tropopause layer are  $\sim 183$ ,  $603$ ,  $39$  and  $49$  days, respectively. These species, particularly  $\text{C}_2\text{H}_5\text{Br}$  and  $\text{CH}_2\text{BrCH}_2\text{Br}$ , would thus be important carriers of bromine to the stratosphere if emissions were to increase substantially. Our model shows  $\sim 70\text{--}73\%$  and  $\sim 80\text{--}85\%$  of bromine from these species in the tropical boundary layer can reach the lower stratosphere.

## 1 Introduction

The bromine (Br) budget of the stratosphere is largely controlled by anthropogenic emissions of long-lived source gases (SGs) such as halons (e.g.  $\text{CBrF}_3$ ) and methyl bromide ( $\text{CH}_3\text{Br}$ ). These SGs are sufficiently long-lived that tropospheric gradients are small. In recent years, it has been suggested that very short-lived species (VSLs) of predominately natural origin may provide an additional source of stratospheric

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inorganic bromine ( $\text{Br}_y^{\text{VLS}}$ ) (e.g., Sturges et al., 2000; Dorf et al., 2008). The magnitude of this supply is thought to be 6(3–8) ppt, representing ~ 25 % of total stratospheric bromine (Montzka and Reimann et al., 2010).

Natural emissions of VLS are predominately from marine macro-algae/phytoplankton and show large variability in space and time (e.g., Carpenter et al., 1999). From the tropical marine boundary layer (MBL), troposphere-stratosphere transport can be rapid (hours) in deep convective updrafts. The Western Pacific is a strong convective source region for air entering the tropical tropopause layer (TTL) (e.g., Aschmann et al., 2009). Rapid convective transport allows short-lived SGs to escape oxidation in the troposphere and detrain in the lowermost stratosphere (LMS). Once photolysed, reactive inorganic products (e.g.,  $\text{BrO}$ ) take part in catalytic ozone ( $\text{O}_3$ ) depleting cycles (e.g.,  $\text{BrO} + \text{ClO}$ ) (e.g., Sinnhuber et al., 2002). The most important natural VLS are bromoform ( $\text{CHBr}_3$ ) and dibromomethane ( $\text{CH}_2\text{Br}_2$ ) due to their relatively large emissions and for  $\text{CH}_2\text{Br}_2$  in particular its long local lifetime (e.g., Hossaini et al., 2010). To date, most model work has focused on quantifying the stratospheric  $\text{Br}_y$  supply from these VLS (e.g., Hossaini et al., 2010; Liang et al., 2010). These studies estimate a supply of ~ 2.4 and 5 ppt, respectively. The larger latter value is likely due to the explicit modelling of wet deposition (i.e. removal in precipitation) of soluble  $\text{Br}_y$ . The assumed uniform 10-day lifetime of  $\text{Br}_y$ , employed in Hossaini et al. (2010), is likely an underestimate (in some regions) and thus results in too much scavenging of soluble products (e.g., Aschmann et al., 2011). Other model studies have considered dibromochloromethane ( $\text{CHBr}_2\text{Cl}$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ) and bromochloromethane ( $\text{CH}_2\text{BrCl}$ ) in addition (e.g., Warwick et al., 2006; Schofield et al., 2011). Warwick et al. (2006) reported a total  $\text{Br}_y^{\text{VLS}}$  contribution of 6–7 ppt from these species. Variation in the calculated contribution of VLS is expected due to different treatment of emissions and transport processes (Hoyle et al., 2010; Feng et al., 2011).

Some VLS have a predominately anthropogenic source; e.g. n-propyl bromide (n- $\text{C}_3\text{H}_7\text{Br}$ , nPB), i-propyl bromide (i- $\text{C}_3\text{H}_7\text{Br}$ , iPB), ethyl bromide ( $\text{C}_2\text{H}_5\text{Br}$ ) and ethylene dibromide ( $\text{CH}_2\text{BrCH}_2\text{Br}$ , EDB).  $\text{C}_2\text{H}_5\text{Br}$  is used in chemical synthesis, as

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a refrigerant and as a flame retardant. Observations show surface mixing ratios of < 0.3 ppt (Low et al., 2003) and 0.09–0.49 ppt (Carpenter et al., 1999). EDB is used as a fumigant and has been observed at ~ 5 ppt and 1 ppt in urban areas (Pratt et al., 2000) and the South Pole (Khalil and Rasmussen, 1985), respectively.

In general these *minor* VSLS are poorly studied and observations are sparse. Laube et al. (2008) have suggested unidentified peaks in their chromatogram from air sampled at 15.2 km point towards the presence of C<sub>2</sub>H<sub>5</sub>Br, nPB and EDB. These species are estimated to currently contribute < 0.2 ppt of organic bromine in the TTL region (Montzka and Reimann et al., 2010). Quantifying the present-day contribution of these unregulated anthropogenic VSLS on stratospheric Br<sub>y</sub> is important. In this study we have used a global model constrained by observations to

1. Evaluate modelled distribution of bromine-containing VSLS with new observations from the 2009 NSF HIAPER Pole-to-Pole (HIPPO-1) campaign (Wofsy et al., 2011) and ongoing National Oceanic and Atmospheric Administration (NOAA) measurement programs.
2. Calculate the local atmospheric lifetimes of poorly studied C<sub>2</sub>H<sub>5</sub>Br, CH<sub>2</sub>BrCH<sub>2</sub>Br, n-C<sub>3</sub>H<sub>7</sub>Br and i-C<sub>3</sub>H<sub>7</sub>Br.
3. Estimate Br<sub>y</sub><sup>VSLS</sup> in the tropical lower stratosphere. Given convection is an uncertainty in a global model, we examine the sensitivity of Br<sub>y</sub><sup>VSLS</sup> to two treatments of convection.

Section 2 describes the model, improvements on our previous model set up (Hossaini et al., 2010) and experiments performed. Results are presented in Sect. 3 along with a description of the NSF HIPPO-1 data. Conclusions and recommendations for future work are discussed in Sect. 4.

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## 2 Model description

TOMCAT/SLIMCAT is a three-dimensional (3-D) chemical transport model (CTM) described in detail by Chipperfield (2006). For this study we ran the CTM with 38 hybrid  $\sigma$ - $p$  vertical levels extending from the surface to  $\sim 35$  km and with a resolution of  $5.6^\circ \times 5.6^\circ$ . The offline model is forced by analysed winds taken from the European Centre for Medium-Range Weather Forecasts (ECMWF) Era-Interim reanalysis. The CTM includes an *online* parameterisation of cumulus convection based on the Tiedtke (1989) mass flux scheme (Stockwell and Chipperfield, 1998). This CTM set up is described in Hossaini et al. (2010) and has been shown to simulate the transport/chemistry of short-lived tracers reasonably well.

We have made two improvements compared to Hossaini et al. (2010). First, as model convection is an uncertainty, we also now include an additional approach to the Tiedtke (1989) mass flux scheme. Here the CTM can be forced with Era-Interim archived convective updraft/downdraft mass fluxes and detrainment rates (Feng et al., 2011). Second, we model the wet deposition of soluble  $\text{Br}_y$  in both large-scale dynamic and also convective precipitation (Giannakopoulos et al., 1999). The fraction of  $\text{Br}_y$  available for wet deposition is altitude-dependent. Here we partition  $\text{Br}_y$  among non-soluble products (e.g.  $\text{BrO}$ ) and soluble  $\text{HBr}$  using a  $\text{HBr}:\text{Br}_y$  ratio from a previous full chemistry TOMCAT integration (Breider et al., 2010).

In this study we include 9 bromine-containing VLSL SG tracers and the long-lived species, methyl bromide ( $\text{CH}_3\text{Br}$ ), Halon-1211 (H1211), Halon-1301 (H1301) and Halon-2402 (H2402, Table 1). The CTM here also includes methyl iodide ( $\text{CH}_3\text{I}$ ) and an idealised tracer with a 6 h lifetime (i6hr). These shorter lived species are useful for assessing troposphere-stratosphere transport in modelled convection. The model surface mixing ratio of most SGs are constrained by HIPPO-1 observations in the tropical regions. For  $\text{CHBrCl}_2$  and  $\text{CH}_2\text{BrCl}$  the model is constrained by the estimated MBL mixing ratios, based on a compilation of observations, provided in Law and Sturges et al. (2007). Observations of EDB, nPB and iPB are sparse. For these gases, the

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model surface mixing ratio cannot be constrained by observations and thus have an arbitrary value at the surface. Therefore, these gases are not considered in the calculated  $Br_y^{VLS}$ .

There is significant uncertainty in the surface emissions of natural and anthropogenic VLS. There is likely to be considerable spatial variation in the location of emission (e.g., Law and Sturges et al., 2007). For simplicity, and to overcome some of this uncertainty, in the model runs presented here we do not specify emissions but instead we overwrite the surface volume mixing ratio (vmr) of the halogenated source gases. The surface vmr is constant with latitude and longitude within the tropics and is scaled so that the model gives good agreement with observation in the free troposphere, where available. This approximation is better for longer-lived species which will be mixed by transport processes and are the species which are potentially more important for transport to the stratosphere.

Loss of SG occurs via oxidation by OH and photolysis. Rate constants and absorption cross sections are taken from Sander et al. (2006) where available. SG degradation is assumed to release  $Br_y$  immediately (i.e.  $CHBr_3 + OH \rightarrow 3 \times Br_y$ ). This assumption, which ignores any organic product gases (e.g.  $CBr_2O$ ), has been shown to be good for  $CHBr_3$  and  $CH_2Br_2$  (Hossaini et al., 2010). Henry's law constants needed for calculating the wet deposition of soluble  $Br_y$  products are taken from Law and Sturges et al. (2007).

We have performed 2 model simulations; run  $S_{diagnosed}$  where we diagnose convective transport and run  $S_{archived}$  where convective transport is forced with archived mass fluxes. Both simulations were initialised on 1 January 2005 and run for 3 yr.

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### 3 Results and discussion

#### 3.1 Modelled tracer profiles

The modelled source gas profiles of  $\text{CH}_3\text{Br}$ , H1211, H1301, H2402,  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{C}_2\text{H}_5\text{Br}$  and  $\text{CH}_3\text{I}$  are shown in Fig. 1. We compare with aircraft observations in the tropics ( $\pm 20^\circ$ ) from the recent NSF HIPPO-1 campaign (January 2009, <http://hippo.ornl.gov/>). Whole air samples, collected in stainless steel and glass flasks, from 5 flights were analysed using gas chromatography/mass spectrometry in two different laboratories; the University of Miami and NOAA (Schauffler et al., 1999). Mixing ratios reported by the Miami laboratory were multiplied by factors of 0.90, 0.94, 0.98, 0.94, 0.81 and 1.01 for  $\text{CH}_3\text{Br}$ , H1301, H1211, H2402,  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$ , respectively, to be consistent with the NOAA laboratory calibration scale.

We also consider January 2009 monthly mean surface observations from an ongoing NOAA program at three sites in the Pacific Basin; American Samoa (SMO), Mauna Loa (MLO) and Cape Kumukahi (KUM). Aircraft observations up to  $\sim 6.5$  km a.s.l. over Raratonga are also considered. These additional observations are consistent in space/time with the observations from HIPPO. For this comparison, the model is averaged over the flight days and also in space. The TTL base is defined as the level of main convective outflow ( $\sim 12$  km) and the top as the cold-point tropopause (CPT,  $\sim 17$  km). The *upper TTL* is defined as beyond the level of zero radiative heating, where slow radiatively-driven ascent dominates over convective mixing (Law and Sturges et al., 2007).

Both runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$  show good agreement with observations. Model profiles of  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  give good agreement when constrained by 1–1.2 ppt at the surface. This is consistent with previous aircraft comparisons (Hossaini et al., 2010). The profiles indicate  $\sim 0.5$  and 0.8 ppt of  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  in the lower TTL, respectively. This is consistent with the lower TTL (12–14 km) mean mixing ratio and range of 0.61(0.3–1.1) ppt and 0.92(0.77–1.15) ppt reported by Montzka and Reimann et al. (2010) and based on a compilation of previous observations. The HIPPO-1

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observations show  $\text{CHBr}_2\text{Cl}$  mixing ratios of 0.1–0.2 ppt in the lower TTL. This is again consistent with previously observed mixing ratios of 0.1(0.06–0.15) ppt (Montzka and Reimann et al., 2010). The anthropogenic short-lived species,  $\text{C}_2\text{H}_5\text{Br}$ , was also detected in the TTL ( $\sim 0.4$  ppt). nPB was below the detection limit of  $\sim 0.5$  ppt.

Overall, run  $S_{\text{archived}}$  shows more tracer transported to the upper TTL. This can be expected given the archived mass fluxes show strong convection in the tropics (e.g., Hoyle et al., 2010; Feng et al., 2011). However, the averaged profiles in Fig. 1 show only small differences between runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$ , particularly for the relatively longer-lived gases for which vertical transport in convective cells is less important. The differences between the two model runs is discussed further in Sect. 3.2.

### 3.2 Archived versus diagnosed convection

The implementation of 6-hourly ECMWF archived convective mass fluxes in the TOM-CAT CTM is described in Feng et al. (2011). Here we use observations of short-lived halogen species in the mid-upper troposphere to examine the performance of these fluxes compared to fluxes diagnosed within the model. The archived convective updraft mass flux shows non-zero values at 100 hPa ( $\sim 16.5$  km). The diagnosed convection typically does not extend above 200 hPa ( $\sim 12.5$  km) and this does not capture deep convective events (Feng et al., 2011). To investigate the differences between runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$  further, we also consider  $\text{CH}_3\text{I}$ ; a trace gas with a local lifetime of  $\sim 7$  days and thus shorter lived than any of the bromine-containing VSLs previously discussed (Law and Sturges et al., 2007). Figure 2 shows modelled profiles of  $\text{CH}_3\text{I}$  in the tropics from both runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$  versus observations made on board the DC8 aircraft during the 2007 NASA TC4 campaign (see Hossaini et al. (2010) for campaign description).

In Fig. 2, the difference between the two convective set ups is more pronounced than for the longer-lived bromine-containing VSLs. With an assumed uniform surface mixing ratio of 1 ppt in the tropics, both runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$  give reasonable agreement with the observations. A surface mixing ratio of 1 ppt is within the estimated

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range of 0.3–1.9 ppt for the marine boundary layer reported by Montzka and Reimann et al. (2010). Run  $S_{\text{archived}}$  shows significantly more  $\text{CH}_3\text{I}$  in the TTL. This appears to provide a better fit to observations, particularly for flights on the 5/8 August 2007 (see Fig. 2).

The zonally averaged mixing ratio of the idealised tracer with a 6 h lifetime (i6hr),  $\text{CH}_3\text{I}$ ,  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$  at the approximate base of the TTL ( $\sim 200$  mb) and the tropical cold point tropopause (CPT,  $\sim 100$  mb) is shown in Fig. 3. Run  $S_{\text{archived}}$  transports more tracer to higher altitudes in all seasons with the the largest difference between runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$  being for the relatively shortest lived species (e.g. i6hr,  $\text{CH}_3\text{I}$ ). For  $\text{CH}_3\text{I}$ , CPT mixing ratios are within with the estimated range of 0.02–0.18 ppt reported by Law and Sturges et al. (2007) for the tropical upper troposphere. The CPT  $\text{CH}_3\text{I}$  mixing ratios from  $S_{\text{diagnosed}}$  are up to  $\sim 6\times$  lower. For  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$ , both the TTL and CPT mixing ratios are less sensitive to the choice of convection scheme.

Figure 4 shows the annual mean mixing ratio of i6hr at the CPT for runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$ . Clearly, stronger convection with run  $S_{\text{archived}}$  leads to a larger modelled mixing ratio at this level. Here, the strongest convection occurs over the Western Pacific, indicating a strong source region for the troposphere-stratosphere of VSLs – consistent with Aschmann et al. (2009). For studying the troposphere-stratosphere transport of relatively shorter lived gases (including species whose lifetime is equal to or less than that of  $\text{CH}_3\text{I}$ ), the choice of convection scheme is clearly important.

### 3.3 Source gas local lifetimes

We have calculated the local lifetimes ( $\tau_{\text{local}}$ ) of source gases in the model using:

$$\tau_{\text{local}}^{-1} = \tau_{\text{OH}}^{-1} + \tau_{\text{hv}}^{-1}$$

Here  $\tau_{\text{OH}}$  and  $\tau_{\text{hv}}$  are the lifetimes with respect to OH oxidation and photolysis, respectively. The annual tropical mean lifetimes of  $\text{C}_2\text{H}_5\text{Br}$ , EDB, nPB and iPB are shown in Fig. 5.

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For these species OH oxidation is the dominant sink in the troposphere. For C<sub>2</sub>H<sub>5</sub>Br, the simulated local lifetime is ~ 18 days at the surface and up to ~ 183 days in the TTL. Similarly for EDB, the local lifetime is ~ 30 and up to ~ 603 days at the surface and in the TTL, respectively. The long local lifetime in the cold TTL is due to the strong temperature dependence of the OH sink reaction. Once in the TTL, C<sub>2</sub>H<sub>5</sub>Br and EDB are thus potentially important carriers of bromine to the stratosphere.

It is clear that local lifetimes of VSLS can vary substantially with altitude. The simulated local lifetime of nPB is ~ 6 days at the surface and up to to 38 days in the TTL. Similarly for iPB, we find local lifetimes of 8 (surface) and 49 days (TTL). For these species with relatively shorter lifetimes at the surface, rapid convective transport to the TTL is likely required for their SGI contribution to be significant. The tropospheric mean local lifetimes of VSLS have also been calculated. These values are shown in Table 2.

Our simulated local lifetimes in the TTL vary from those quoted in the recent World Meteorological Organisation (WMO) Assessment Report (Montzka and Reimann et al., 2010). The reason for this is that the WMO values are based on OH loss rates calculated using a uniform tropospheric OH concentration ( $1 \times 10^6$  molecules cm<sup>-3</sup>) and for a temperature of 275 K, i.e. representative of the surface. The simulated local lifetimes here are derived using a spatially/temporally varying OH field (and photolysis) and can be quoted as a function of temperature/altitude. A direct comparison of the two is therefore not appropriate, but if a gas is sufficiently long-lived to be transported away from the surface then the WMO lifetimes may not be applicable.

### 3.4 Modelled total bromine

The modelled source gas injection (SGI), product gas injection (PGI) and total bromine (SGI + PGI) for VSLS, CH<sub>3</sub>Br and the halons is shown in Table 2. SGI is the organic bromine resulting from direct transport of a source gas to the lower stratosphere (i.e. for CH<sub>2</sub>Br<sub>2</sub>, 2 × the SG mixing ratio at the tropopause). Similarly, PGI is the contribution from the inorganic products, formed following SG degradation.

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The total bromine contribution from *major* VLS CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> is ~2.09 and 1.69 ppt (tropical mean), respectively from simulation S<sub>diagnosed</sub>. The contribution is larger (2.32 and 1.74 ppt) from simulation S<sub>archived</sub>. The larger SGI values from simulation S<sub>archived</sub> are due to deeper model convection from the ECMWF Era-Interim fields. This allows more rapid tracer transport to the cold TTL where the SG lifetime is relatively longer. However, run S<sub>archived</sub> also experiences more spatially widespread convection and thus also precipitation. This increases the likelihood of wet deposition of soluble Br<sub>y</sub> in certain regions. Physical atmospheric removal of Br<sub>y</sub> in the TTL is also possible from adsorption on to ice. However, according to recent model work, this process (not considered here) represents only a small sink (Aschmann et al., 2011).

Our modelled Br<sub>y</sub><sup>VLS</sup> from CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> alone (~4 ppt) is slightly lower than the 5 ppt reported by Liang et al. (2010) but larger than the our previously reported 2.4 ppt (Hossaini et al., 2010). This is due to the explicit modelling of wet deposition, resulting in a larger contribution from the PGI route in our present work. For CHBr<sub>3</sub>, we find here 0.97 ppt of Br<sub>y</sub> reaches the tropical lower stratosphere via the PGI route. This is ~3× larger than the 0.3 ppt reported in Hossaini et al. (2010).

The *minor* VLS individually provide a modest amount of total bromine to the lower stratosphere. The largest contributor, CH<sub>2</sub>BrCl, provides about one fifth that of CHBr<sub>3</sub>. However, their accumulated total (~1.2 ppt from S<sub>archived</sub>) is significant and is likely a lower limit due to nPB, iPB and EDB not considered in the calculation.

The contribution of VLS and also the long-lived species to total stratospheric bromine is shown in Fig. 6. The model (S<sub>archived</sub>) shows ~21 ppt of total bromine in the stratosphere. We find a total Br<sub>y</sub><sup>VLS</sup> supply of ~4.9–5.2 ppt for runs S<sub>diagnosed</sub> and S<sub>archived</sub>, respectively. This range is consistent with the inferred Br<sub>y</sub><sup>VLS</sup> supply of 5.2(±2.5) ppt (Dorf et al., 2008). Of the VLS with a solely anthropogenic source, we have only considered C<sub>2</sub>H<sub>5</sub>Br in our calculated value of Br<sub>y</sub><sup>VLS</sup>. Our result may therefore represent a lower limit due to EDB, nPB and iPB not being included in the calculation. Montzka and Reimann et al. (2010) estimate that minor anthropogenic VLS including C<sub>2</sub>H<sub>5</sub>Br, EDB and nPB species contribute < 0.2 ppt via the SGI pathway. Our

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model shows  $C_2H_5Br$  and EDB are sufficiently long-lived to be potentially important carriers of bromine to the stratosphere. Simulations show, regardless of the surface vmr,  $\sim 70$ – $73\%$  and  $80$ – $85\%$  of total surface bromine from  $C_2H_5Br$  and EDB in the tropics can reach the lower stratosphere.

We have also quantified tropospheric loss of the major long-lived SG,  $CH_3Br$ . We find  $\sim 0.7$  ppt of source gas is removed in the troposphere from  $S_{diagnosed}$ ;  $9\%$  of the assumed  $7.5$  ppt surface boundary condition. This is consistent with the estimated  $CH_3Br$  gradients of  $0$ – $15\%$  reported by Schauffler et al. (1999). The PGI route still allows  $\sim 0.33$  ppt of the resulting  $Br_y$  to enter the stratosphere. Therefore,  $\sim 0.4$  ppt of bromine is physically removed from the atmosphere ( $\sim 5\%$  of the surface boundary condition). This result implies that estimates of  $Br_y^{VLSL}$  that ignore tropospheric gradients of  $CH_3Br$  may have a low bias of  $0.4$  ppt or so (though this may be compensated for by omission of minor VLSL). This result is likely sensitive to the model OH field and also treatment of wet deposition; both of which carry some uncertainty. Tropospheric loss of the long-lived halons in the model was found to be negligible.

## 4 Conclusions

We have used a 3-D offline CTM and improved our previous estimate of the contribution of VLSL on the stratospheric bromine budget. We have considered 9 VLSL, methyl bromide and also four halons source gases. Modelled profiles of these gases give good agreement with tropical observations from the recent 2009 HIPPO-1 aircraft campaign. Both model and observations reiterate that a significant amount of total stratospheric bromine may arise from naturally-emitted VLSL. The observations did not detect significant levels of anthropogenic-VLSL. However, ethyl bromide ( $C_2H_5Br$ ) was detected at  $\sim 0.4$  ppt in the TTL. Anthropogenic VLSL likely contribute only a small amount of bromine to the present day stratosphere. However, observations of these species are limited and more data is needed to support this conclusion.

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Both ethyl bromide and ethylene dibromide (EDB) are long-lived in the tropical tropopause layer and thus are potentially efficient carriers of bromine to the stratosphere. The simulated local atmospheric lifetime of these anthropogenic gases are up to ~ 183 and 603 days in the TTL, respectively. Other anthropogenic gases considered, n-propyl bromide and i-propyl bromide are shorter-lived. The maximum simulated local lifetimes in the TTL are ~ 39 and 49 days.

Our model shows the contribution of the VSLs  $\text{CHBr}_3$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CHBr}_2\text{Cl}$ ,  $\text{CHBrCl}_2$ ,  $\text{CH}_2\text{BrCl}$  and  $\text{C}_2\text{H}_5\text{Br}$  to stratospheric  $\text{Br}_y$  is 4.9–5.2 ppt for the present day, consistent with balloon-borne estimates. This may represent a lower limit as three anthropogenic gases, EDB, n-propyl bromide and iso-propyl bromide are not included in the calculation. Approximately 76 % of this supply comes from  $\text{CHBr}_3$  and  $\text{CH}_2\text{Br}_2$ . To date, most model work has focused on these species. Our study shows *minor* VSLs (e.g.  $\text{CHBr}_2\text{Cl}$ ,  $\text{CH}_2\text{BrCl}$ ) individually contribute modest amounts. However, their overall total is significant and comparable to that of one of the *major* VSLs (e.g.  $\text{CH}_2\text{Br}_2$ ). Omission of these *minor* species in model simulations may result in an underestimate of stratospheric  $\text{Br}_y$  by ~ 1.2 ppt. More observations of these gases, particularly in the upper TTL, are required to further constrain estimates of their contribution to stratospheric  $\text{Br}_y$ .

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**Table 1.** Model Br-containing source gases and assumed surface volume mixing ratio (vmr/ppt).

| Source gas               | Formula                                       | Source | Surface vmr         |
|--------------------------|---|--------|---------------------|
| Methyl bromide           | CH <sub>3</sub> Br                            | N(A)   | 7.50 <sup>a</sup>   |
| Halon 1211 (H1211)       | CF <sub>2</sub> BrCl                          | A      | 4.23 <sup>a</sup>   |
| Halon 1301 (H1301)       | CBrF <sub>3</sub>                             | A      | 3.15 <sup>a</sup>   |
| Halon 2402 (H2402)       | C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub> | A      | 0.46 <sup>a</sup>   |
| Bromoform                | CHBr <sub>3</sub>                             | N(A)   | 1.20 <sup>a,b</sup> |
| Dibromomethane           | CH <sub>2</sub> Br <sub>2</sub>               | N      | 1.0 <sup>a,b</sup>  |
| Dibromochloromethane     | CHBr <sub>2</sub> Cl                          | N(A)   | 0.20 <sup>a</sup>   |
| Bromodichloromethane     | CHBrCl <sub>2</sub>                           | N(A)   | 0.33 <sup>c</sup>   |
| Bromochloromethane       | CH <sub>2</sub> BrCl                          | N      | 0.47 <sup>c</sup>   |
| Ethyl bromide            | C <sub>2</sub> H <sub>5</sub> Br              | A      | 0.30 <sup>a</sup>   |
| Ethylene dibromide (EDB) | CH <sub>2</sub> BrCH <sub>2</sub> Br          | A      | –                   |
| n-propyl bromide (nPB)   | n-C <sub>3</sub> H <sub>7</sub> Br            | A      | –                   |
| i-propyl bromide (iPB)   | i-C <sub>3</sub> H <sub>7</sub> Br            | A      | –                   |

<sup>a</sup> Best fit to HIPPO observations (this work).

<sup>b</sup> Best fit to observations (Hossaini et al., 2010).

<sup>c</sup> Estimated tropical MBL mixing ratio (Law and Sturges et al., 2007).

Source data both natural (N) and/or anthropogenic (A) taken from Law and Sturges et al. (2007).

**Table 2.** 2007 tropical mean source gas injection (SGI), product gas injection (PGI) and total bromine (SGI + PGI) loading from VSLS, CH<sub>3</sub>Br and the halons in the lower stratosphere. Results are from simulations S<sub>diagnosed</sub> and S<sub>archived</sub>.

| Species <sup>a</sup>                  | SGI (ppt)         |                   | PGI (ppt)         |                   | Total <sup>b</sup> |                   |
|---------------------------------------|-------------------|-------------------|-------------------|-------------------|--------------------|-------------------|
|                                       | S <sub>diag</sub> | S <sub>arch</sub> | S <sub>diag</sub> | S <sub>arch</sub> | S <sub>diag</sub>  | S <sub>arch</sub> |
| CH <sub>3</sub> Br                    | 6.77              | 6.90              | 0.33              | 0.29              | 7.11 [95]          | 7.19 [96]         |
| H1211                                 | 3.94              | 3.98              | 0.21              | 0.19              | 4.15 [98]          | 4.17 [99]         |
| H1301                                 | 3.09              | 3.09              | 0.04              | 0.04              | 3.13 [99]          | 3.13 [99]         |
| H2402                                 | 0.86              | 0.87              | 0.04              | 0.04              | 0.90 [98]          | 0.91 [99]         |
| CHBr <sub>3</sub> {21}                | 1.06              | 1.41              | 1.03              | 0.91              | 2.09 [58]          | 2.32 [64]         |
| CH <sub>2</sub> Br <sub>2</sub> {212} | 1.49              | 1.58              | 0.20              | 0.16              | 1.69 [85]          | 1.74 [87]         |
| CHBr <sub>2</sub> Cl {42}             | 0.19              | 0.22              | 0.10              | 0.08              | 0.29 [73]          | 0.30 [75]         |
| CHBrCl <sub>2</sub> {35}              | 0.14              | 0.17              | 0.09              | 0.07              | 0.23 [70]          | 0.24 [73]         |
| CH <sub>2</sub> BrCl {274}            | 0.37              | 0.39              | 0.04              | 0.03              | 0.41 [87]          | 0.42 [89]         |
| C <sub>2</sub> H <sub>5</sub> Br {72} | 0.17              | 0.19              | 0.04              | 0.03              | 0.21 [70]          | 0.22 [73]         |
| EDB {200}                             | –                 | –                 | –                 | –                 | – [80]             | – [85]            |
| nPB {17}                              | –                 | –                 | –                 | –                 | – [40]             | – [50]            |
| iPB {21}                              | –                 | –                 | –                 | –                 | – [50]             | – [60]            |
| <b>∑ VSLS</b>                         | <b>3.42</b>       | <b>3.96</b>       | <b>1.50</b>       | <b>1.28</b>       | <b>4.92</b>        | <b>5.24</b>       |
| <b>∑ ALL</b>                          | <b>18.08</b>      | <b>18.80</b>      | <b>2.12</b>       | <b>1.84</b>       | <b>20.21</b>       | <b>20.64</b>      |

<sup>a</sup> Values in curly brackets ( { } ) give the mean species-weighted tropical tropospheric lifetime (days).

<sup>b</sup> Values in square brackets ( [ ] ) give the fraction of total boundary layer bromine reaching the lower stratosphere (%).

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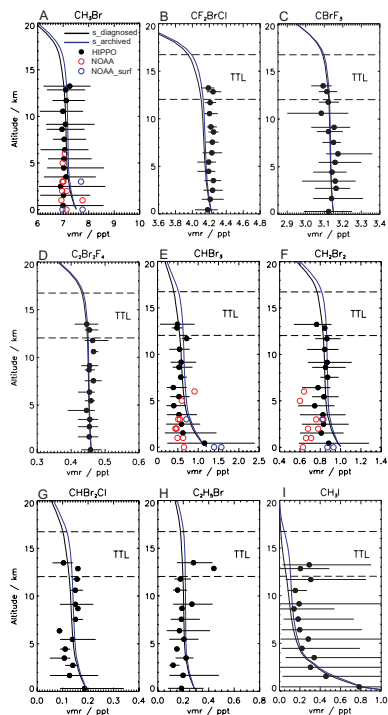
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**Fig. 1.** Mean observed and modelled tropical ( $\pm 20^\circ$ ) mixing ratio (ppt) of **(a)**  $\text{CH}_3\text{Br}$ , **(b)**  $\text{CF}_2\text{BrCl}$  (H1211), **(c)**  $\text{CBrF}_3$  (H1301), **(d)**  $\text{C}_2\text{Br}_2\text{F}_4$  (H2402), **(e)**  $\text{CHBr}_3$ , **(f)**  $\text{CH}_2\text{Br}_2$ , **(g)**  $\text{CHBr}_2\text{Cl}$ , **(h)**  $\text{C}_2\text{H}_5\text{Br}$  and **(i)**  $\text{CH}_3\text{I}$ . Observations (filled circles) taken from the NSF HIPPO-1 campaign (January 2009). Horizontal bars denote min-max variability of observations at given level. Open circles denote observations during January 2009 from three NOAA surface sites (blue points from SMO,  $14.3^\circ\text{S}$ ,  $170.6^\circ\text{W}$ , 77 m a.s.l.; MLO,  $19.5^\circ\text{N}$ ,  $155.6^\circ\text{W}$ , 3397 m a.s.l.; KUM,  $19.5^\circ\text{N}$ ,  $154.8^\circ\text{W}$ , 3 m a.s.l.) or from vertical profiles (red points sampled over Raratonga,  $21^\circ\text{S}$ ,  $159.8^\circ\text{W}$ ).

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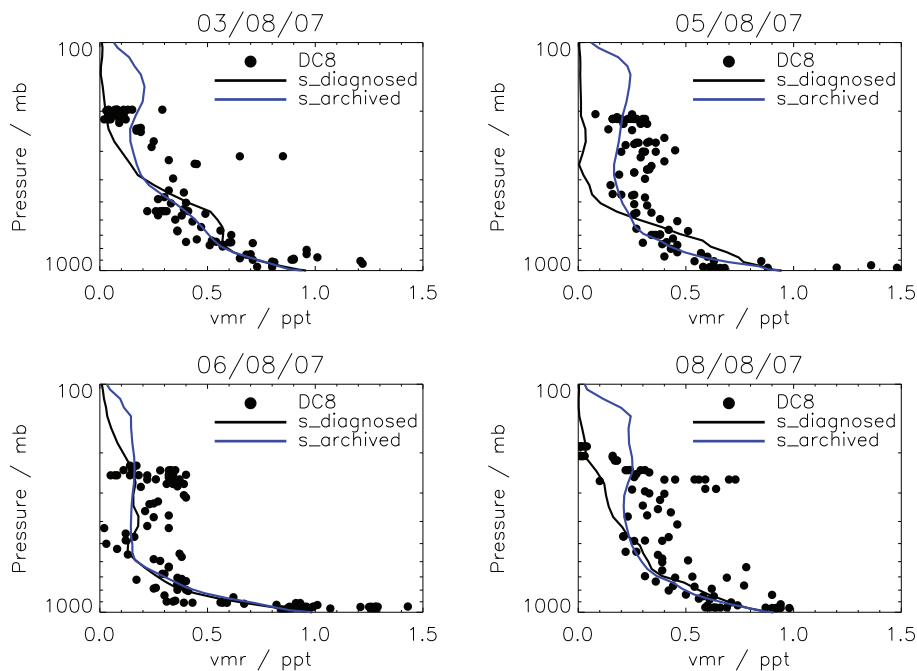
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**Fig. 2.** Comparison of modelled  $\text{CH}_3\text{I}$  profiles with observations made on board 4 DC8 flights during the NASA TC4 campaign (July–August 2007, <http://www.espo.nasa.gov/tc4/>). The CTM profiles are from both runs  $S_{\text{diagnosed}}$  and  $S_{\text{archived}}$ .

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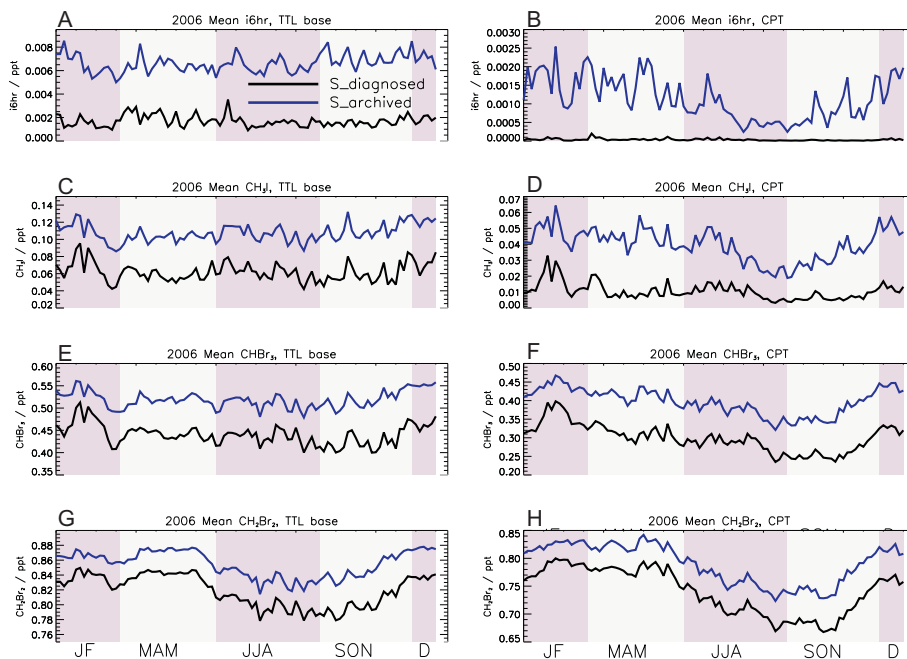
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**Fig. 3.** Zonally averaged volume mixing ratio of **(A,B)**  $i6hr$ , **(C,D)**  $CH_3I$ , **(E,F)**  $CHBr_3$  and **(G,H)**  $CH_2Br_2$  as a function of time (2006) at the TTL base and the tropical cold point tropopause, respectively, for CTM runs  $S_{diagnosed}$  and  $S_{archived}$ .

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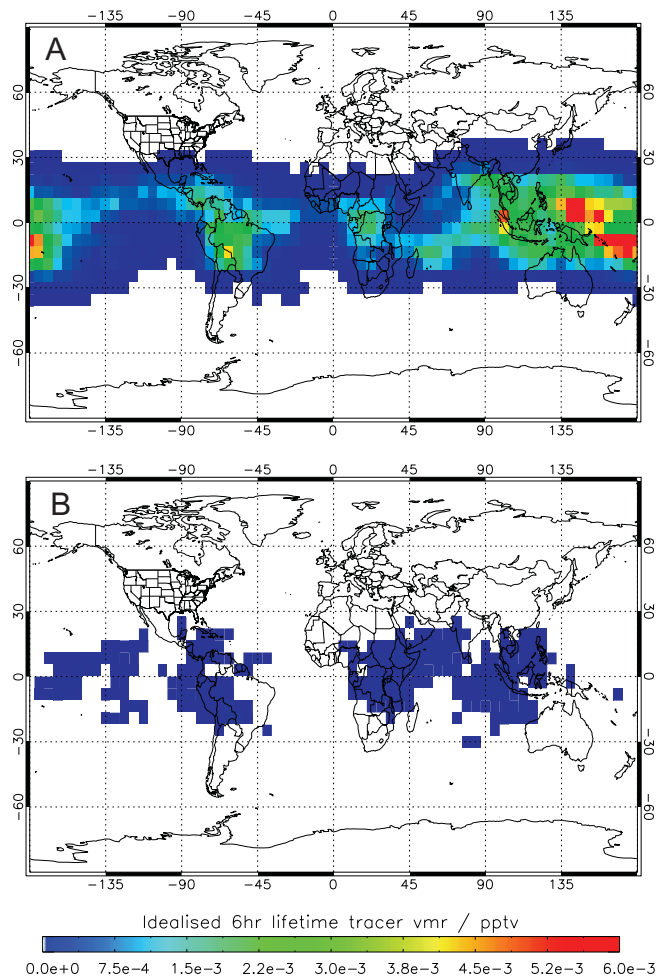
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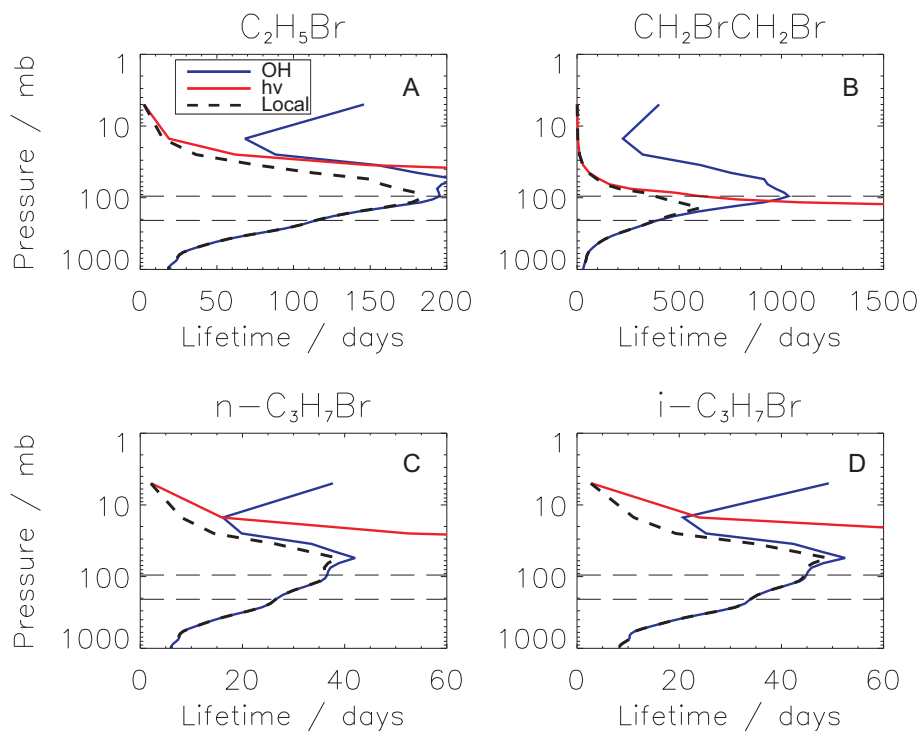
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**Fig. 4.** Modelled annual mean mixing ratio of i6hr at the cold point tropopause from (A)  $S_{\text{archived}}$  and (B)  $S_{\text{Diagnosed}}$ .

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**Fig. 5.** Modelled mean local tropical lifetime (days) with respect to OH oxidation, photolysis and total for **(A)**  $C_2H_5Br$ , **(B)**  $CH_2BrCH_2Br$ , **(C)**  $n-C_3H_7Br$  and **(D)**  $i-C_3H_7Br$ . Horizontal lines denote the approximate TTL.

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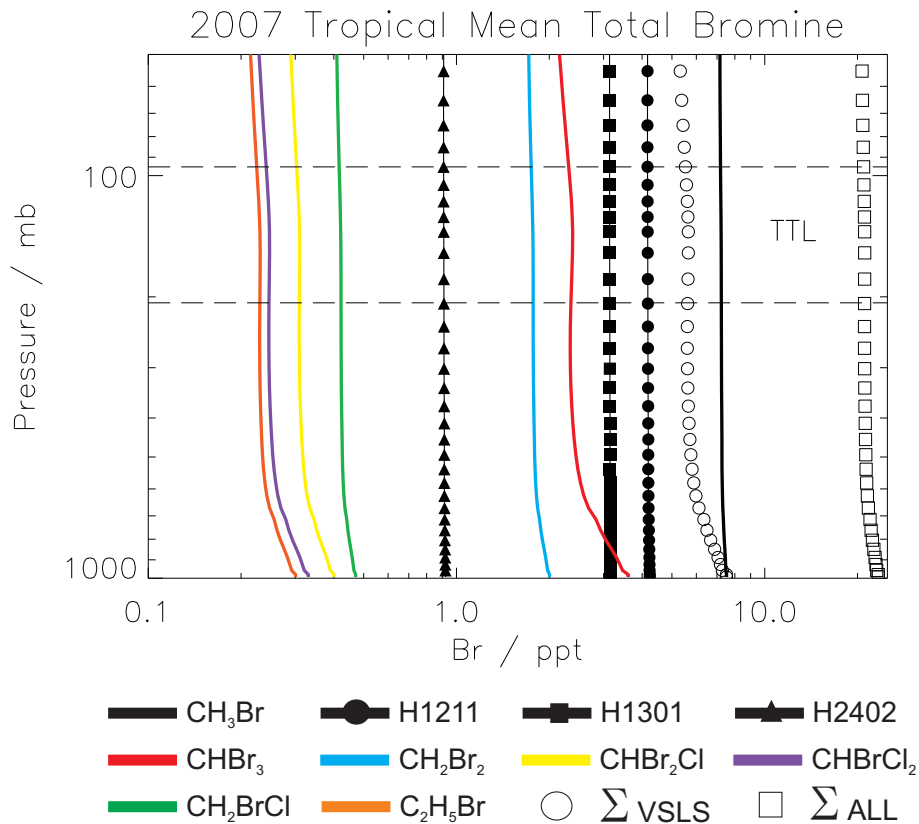
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**Fig. 6.** Modelled tropical mean total bromine (ppt) for 2007 and from simulation  $S_{\text{archived}}$ . Dashed horizontal lines denote the approximate base of the TTL and the cold-point tropopause (CPT).