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Bromoform and dibromomethane in the tropics: a 3-D model study of chemistry and transport

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Abstract

We have developed a detailed chemical scheme for the degradation of the short-lived source gases bromoform (CHBr_3) and dibromomethane (CH_2Br_2) and implemented it in the TOMCAT/SLIMCAT three-dimensional (3-D) chemical transport model (CTM).

- 5 The CTM has been used to predict the distribution of the two source gases (SGs) and 11 of their organic product gases (PGs). These first global calculations of the organic PGs show that their abundance is small. The longest lived organic PGs are CBr_2O and CHBrO , but their peak tropospheric abundance relative to the surface vmr of the SGs is less than 5%. We calculate their mean local tropospheric lifetimes in the tropics to be
10 ~7 and ~2 days (due to photolysis), respectively. Therefore, the assumption in previous modelling studies that SG degradation leads immediately to inorganic bromine seems reasonable.

We have compared observed tropical SG profiles from a number of aircraft campaigns with various model experiments. In the tropical tropopause layer (TTL) we find
15 that the CTM run using p levels and vertical winds from analysed divergence overestimates the abundance of CH_2Br_2 , and to a lesser extent CHBr_3 , although the data is sparse and comparisons are not conclusive. Better agreement in the TTL is obtained in the run using θ levels and vertical motion from diabatic heating rates. Trajectory estimates of residence times in the two model versions confirm the more realistic transport
20 in the θ -level version. In the p -level model even when we switch off convection we still find significant amounts of the SGs considered may reach the cold point; the stratospheric source gas injection is only reduced by ~16% for CHBr_3 and ~2% for CH_2Br_2 without convection.

Overall, the relative importance of the SG pathway and the PG pathway for transport of bromine to the stratosphere has been assessed. Assuming a 10-day washout
25 lifetime of Br_y we find the delivery of total Br from CHBr_3 to be 0.72 pptv with ~53% of this coming from SGI. Similarly, for CH_2Br_2 we find a total Br value of 1.69 pptv with ~94% coming from SGI. We infer that these species contribute ~2.4 pptv of inorganic

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1 Introduction

Bromine-containing very short-lived species (VSLs) are known to provide an additional supply of inorganic bromine (Br_y) to the stratosphere. Emissions of such species are predominately of natural oceanic origin and have been shown to exhibit large variability, particularly in tropical coastal regions, that harbour substantial macroalgae (e.g. Quack and Wallace, 2003; Carpenter et al., 2009). It is also at tropical latitudes that deep convection allows the rapid ascent of such species from the marine boundary layer to the tropical tropopause layer (TTL). The rate of transport of these species, to and through, the TTL is currently poorly understood.

Current estimates of the contribution of inorganic bromine derived from VSLs ($\text{Br}_y^{\text{VSLs}}$) to the stratospheric Br_y budget range from 3 to 8 ppt (Law and Sturges et al., 2007), with a more recent value of approximately 5 pptv derived by Dorf et al. (2008). Quantifying this additional source of bromine is important due its role in catalytic ozone depletion in the stratosphere. In addition, it is expected that reactive $\text{Br}_y^{\text{VSLs}}$ will impact tropospheric composition (e.g. Von Glasow et al., 2004).

Two distinct pathways having been identified leading to the arrival of $\text{Br}_y^{\text{VSLs}}$ in the stratosphere; namely source gas injection (SGI) and product gas injection (PGI) (e.g. Ko and Poulet et al., 2003). SGI refers to the transport of a source gas (SG, e.g. bromoform, CHBr_3) to the stratosphere, where upon degradation will provide an in-situ source of Br_y . In contrast, PGI is the cross-tropopause transport of bromo-organic intermediates (e.g. CBr_2O) and also inorganic products (e.g. HBr , BrO , Br), produced from SG degradation in the troposphere. The efficiency of both SGI and PGI depends largely upon the photochemical loss of source gases (mainly via reaction with OH or photolysis) and rate of removal of degradation products (via wet deposition) versus the timescale for troposphere-stratosphere transport. For this reason, it is of interest to investigate the impact of convection on this additional source of bromine, $\text{Br}_y^{\text{VSLs}}$, in

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model experiments.

Previous model work has concentrated on quantifying $\text{Br}_y^{\text{VSLs}}$ from the more abundant very short-lived source gases such as CHBr_3 . From a 2D model study, Dvortsov et al. (1999) concluded that CHBr_3 contributes around 1 pptv additional Br_y to the lower stratosphere (LS). Similarly, Nielsen and Douglass (2001) also derived a value of 1 pptv from 3-D simulations with ~50% of this from SGI. In both of these studies the lifetime of Br_y following source gas degradation was assumed to be 10 days. More recently, Sinnhuber and Folkins (2006) used a 2-D mechanistic model of the tropical atmosphere to estimate that CHBr_3 contributes between 0.8–2.1 pptv bromine via both SGI and PGI to the lower stratosphere with assumed Br_y lifetimes of 10–100 days. From this study, the contribution from SGI was approximately 0.5 pptv. The most recent model study, Kerkweg et al. (2008), confirmed earlier suggestions that CHBr_3 contributes “substantial amounts” of Br_y to the lower stratosphere and that $\text{Br}_y^{\text{VSLs}}$ should not be neglected in stratospheric modelling.

The impact of $\text{Br}_y^{\text{VSLs}}$ in the stratosphere has been studied with multi-annual simulations by Feng et al. (2007) using the SLIMCAT 3-D chemical transport model (CTM). Salawitch et al. (2005) also performed a similar 2-D model study. Both studies report an ~10 DU decrease in the ozone column with an additional 6 pptv of $\text{Br}_y^{\text{VSLs}}$ in the lower stratosphere. The impact of this additional bromine depends on the aerosol loading; the bromine causes a larger decrease in ozone when the aerosol loading is high and ClO is elevated.

The model studies discussed above have not directly considered the bromo-organic products (i.e. product gases, PGs) formed following source gas degradation. This omission is addressed in this study which evaluates the contribution of CHBr_3 and CH_2Br_2 to the stratospheric Br budget, along with the relative contribution of SGI and PGI. Furthermore, results include novel estimates of the major and minor PGs formed following CHBr_3 and CH_2Br_2 removal. Vertical source gas profiles are compared to measurements made during several aircraft campaigns in the tropical troposphere and near-tropopause regions. To date, there have been no measurements of organic PGs

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in the tropical atmosphere. We provide the first model estimates of the local lifetimes and abundances of these species in the tropical atmosphere.

Section 2 describes the derived chemical scheme for degradation of CHBr_3 and CH_2Br_2 . Kinetic and mechanistic assumptions are also discussed. Section 3 contains
5 a description of the basic CTM setup, along with details of sensitivity runs carried out. Section 4 presents the model results. Conclusions and recommendations for future research are discussed in Sect. 5.

2 Chemistry scheme

Here we outline our chemical scheme to describe the tropospheric degradation of bromoform and dibromomethane. Reasonable mechanistic and kinetic assumptions have
10 been made and are discussed. Kinetic data either is taken from Sander et al. (2006) (hereafter “JPL”) or the Leeds Master Chemical Mechanism (hereafter “MCM”, see <http://mcm.leeds.ac.uk/MCM/>). A summary of reactions and kinetic data used within the scheme is given in Tables 1 and 2 for CHBr_3 and CH_2Br_2 , respectively.

15 2.1 Bromoform

The degradation of CHBr_3 has been examined in previous theoretical studies (e.g. McGivern et al., 2002, 2004). Its local tropospheric lifetime is ~ 26 days with photolysis being the dominant loss process (e.g. Ko and Poulet et al., 2003). Our bromoform scheme considers 7 organic species: CHBr_3 , CBr_3O_2 , CHBr_2O_2 , CBr_3OOH ,
20 CHBr_2OOH , CBr_2O and CHBrO and is summarised in Fig. 1. The following subsections discuss the details of this scheme.

2.1.1 Removal of CHBr_3 source gas

The scheme assumes removal of CHBr_3 occurs via reaction with OH/Cl radicals and also, more rapidly, by photolysis (Reactions R1–R3). The rates of reaction with OH

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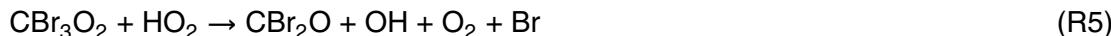


and Cl (k_1 , k_2) are calculated using the JPL recommended temperature-dependent expressions. The rate of photolysis (j_3) is calculated using JPL absorption cross section data along with a parameterisation for their temperature-dependence (Moortgat et al., 1993). The quantum yield for Br atoms following Reaction (R3) is assumed to be unity. It is also assumed that the immediate products of Reactions (R1–R3) (CBr_3 and CHBr_2) will be rapidly oxidised under tropospheric conditions.



10 2.1.2 Removal of peroxy species

The two peroxy radicals formed in Reactions (R1–R3) are assumed to be removed via reaction with NO and HO_2 (Reactions R4–R9). Self-reaction of these species is deemed slow and is therefore not considered here. The $\text{CBr}_3\text{O}_2 + \text{NO}$ Reaction (R4) is assumed to produce CBr_2O , an expected major product of bromoform degradation (Ko and Poulet et al., 2003). Excited intermediates, such as $\text{CBr}_3\text{OOONO}^*$ (not considered here), are expected to fragment rapidly to form CBr_3O , which itself would undergo a rapid decomposition to CBr_2O (e.g. McGivern et al., 2002). The rate constant for Reaction (R4) (k_4) is calculated using the recommended JPL expression for the analogous species CCl_3O_2 . Similarly, rate constants for the $\text{CBr}_3\text{O}_2 + \text{HO}_2$ reactions (k_5 , k_6) are assumed equal (i.e. equal branching ratio of products) and taken from the MCM. These reactions produce CBr_2O and the minor hydroperoxide product CBr_3OOH , respectively.



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The reaction of $\text{CHBr}_2\text{O}_2 + \text{NO}$ (Reaction R7) is assumed to produce a second major product of bromoform degradation, namely formyl bromide (CHBrO). As for R4 it is likely that R7 would proceed via an excited intermediate (not considered here as sufficiently short-lived) such as $\text{CHBr}_2\text{OOH}^*$. The rate constant for this reaction (k_7) is assumed equal to the analogous species CHCl_2O_2 and taken from the MCM. This is also the case for the $\text{CHBr}_2\text{O}_2 + \text{HO}_2$ reactions (Reactions R8, R9) which produce CHBrO and the minor hydroperoxide, CHBr_2OOH respectively.



2.1.3 Removal of minor end products

Removal of the two hydroperoxide species produced in Reactions (R6) and (R9) is assumed to be achieved via reaction with OH (Reactions R10, R12) and also by photolysis (Reactions R11, R13). Rate constants for the OH reactions are assumed equal

to that of the analogous chlorine-containing species, CCl_3OOH and CHCl_2OOH , from the MCM. The photolysis rates are calculated using the absorption cross sections of methylhydroperoxide (CH_3OOH). Reaction of these hydroperoxides with OH leads to the reformation of the respective peroxy radical (initially formed in Reactions R1 and R3).



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2.1.4 Removal of major end products and Br_y

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- Removal of the major products of bromoform degradation, CBr₂O and CHBrO, is assumed to occur via photolysis (Reactions R14, R15). For CBr₂O + $h\nu$ we assume a yield of two Br atoms, with other photolysis pathways, such as that leading to HBr production, not considered. Similarly, for CHBrO + $h\nu$ it is assumed the quantum yield for Br atoms is unity. Photolysis rates for both reactions are calculated using the recommended JPL cross section data.



- In the current scheme all inorganic bromine species produced are grouped together as Br_y without any further partitioning. Depending on the model run (see Sect. 3.2), Br_y is removed in the troposphere by washout given a specified assumed lifetime.



2.2 Dibromomethane

- The degradation of CH₂Br₂ has also been examined in previous theoretical studies (e.g. McGivern et al., 2002, 2004). The local tropospheric lifetime is quoted as ~120 days with reaction with OH being the dominant loss process (Ko and Poulet et al., 2003). Our scheme considers six organic species, CH₂Br₂, CHBr₂O₂, CH₂BrO₂, CHBrO, CHBr₂OOH and CH₂BrOOH. The major products of CH₂Br₂ degradation are expected to be CHBrO and Br_y with CHBr₂OOH being a minor product.

2.2.1 Removal of CH₂Br₂ source gas

Our scheme assumes removal of CH₂Br₂ is achieved via reaction with OH/Cl radicals and also, less rapidly, by photolysis (Reactions R17–19). The rates of reaction

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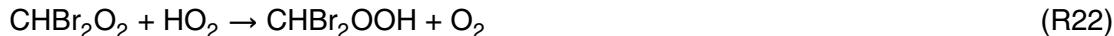


with OH and Cl (k_{17} , k_{18}) are calculated using the JPL temperature-dependent expressions. The rate of photolysis (j_{19}) is calculated using JPL absorption cross section data at 295–298 K. The quantum yield for Br atoms is assumed to be unity. As for the CHBr₃ scheme, it is assumed that following H abstraction and photolysis, the immediate products of source gas degradation (CHBr₂, CH₂Br) will be rapidly oxidised under tropospheric conditions forming associated peroxy radicals.

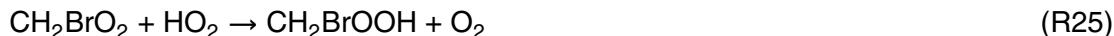


10 2.2.2 Removal of peroxy species

The two peroxy radicals formed in Reactions (R17–R19) are assumed to be removed via reaction with NO and HO₂. Loss of CHBr₂O₂ via these Reactions (R20–22) is treated as that described in Sect. 2.1.2 for the bromoform scheme.



The CH₂BrO₂+NO Reaction (R23) is assumed to produce NO₂ and Br_y. The rate constant for this reaction (k_{23}) is calculated using the recommended JPL expression. For reactions with HO₂ (Reactions R24, R25), rate constants are taken from the MCM. The products of these reactions are Br_y and the hydroperoxide CH₂BrOOH, respectively.



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2.2.3 Removal of end products

- Removal of CHBrO (Reaction R26), produced in Reactions (R20) and (R21), is achieved via photolysis as discussed in Sect. 2.1.3. Similarly removal of CHBr₂OOH (Reaction R27, R28) produced in Reactions (R22) is analogous to removal in Reactions (R12) and (R13) (i.e. by reaction with OH and by photolysis respectively). Removal of CH₂BrOOH, produced in Reaction (R25), has yet to be considered and is also assumed to be removed via reaction with OH (Reaction R29) and also by photolysis (Reaction R30). The rate constant for the OH reaction (k_{29}) is taken from the MCM and the reaction products are expected to be the peroxy species CH₂BrO₂ and water.
- 5 The photolysis rate (j_{30}) is calculated using the cross sections of CH₃OOH.
- 10



3 Model and experiments

3.1 TOMCAT/SLIMCAT 3-D CTM

- 15 TOMCAT is an off-line 3-D CTM described in detail by Chipperfield (2006). The model has performed well in previous tropospheric studies and has been shown to simulate key chemistry and transport reasonably (e.g. Arnold et al., 2005). The model uses the Prather (1986) conservation of second-order moments advection scheme, a parameterisation of convection (Stockwell and Chipperfield, 1998) and also a parameterisation
- 20 of boundary layer mixing (Holtslag and Boville, 1993). The CTM in TOMCAT mode uses a hybrid $\sigma-p$ vertical coordinate and diagnoses the large-scale vertical motion from divergence. The CTM has an option (“SLIMCAT”) for running with isentropic (θ) levels in the upper troposphere and stratosphere with the vertical motion calculated from heating rates. The SLIMCAT model only considers transport by large-scale advection; there

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is no parameterisation of convection and boundary layer mixing. The CTM includes a scheme to calculate trajectories (e.g. Monge-Sanz et al., 2007).

3.2 Simulations

In all simulations described here (see Table 3) the resolution of the model was
5 $5.6^\circ \times 5.6^\circ$ with 38 (or 31) vertical levels (~ 1 km deep in mid troposphere) extending from the surface to ~ 35 km. The model was forced using the European Centre for Medium-Range Weather Forecasts (ECMWF) 6-hourly analyses. The model was initialised on 1/1/2006 and run for 2 years. Year 1 was treated as model spin-up and year 2 output (2007) was saved every 3.75 days for analysis.

10 For the “base run” (run *B*), the TOMCAT model included specified oxidant fields along with the CHBr_3 and CH_2Br_2 degradation schemes described in Sect. 2. Monthly mean diurnal mean fields of the concentration of fixed species (e.g. OH, NO, HO_2) were read from a previous TOMCAT full chemistry run for 2005. The background concentration of atomic chlorine, which was not calculated in the tropospheric full chemistry run, was set to 1×10^4 molecules cm^{-3} . The model chemical scheme used a climatological tropical ozone profile for photolysis calculations (Chipperfield, 1999)

15 Figure 3 shows example tropical zonal mean profiles of temperature and the primary oxidant OH. The mixing ratio of CHBr_3 and CH_2Br_2 source gases were fixed uniformly in space and time at 1.2 pptv in the bottom two layers of the model in the tropical regions ($\pm 20^\circ$). This value seems reasonable for a typical surface mixing ratio of these SGs and furthermore provides the best fit to observed profiles (see Sect. 4). In this study we are interested in the relative mixing ratios of bromine species in the TTL compared to the surface and we do not need to introduce the complication of specifying uncertain emission fluxes. All other advected tracers were initialised at zero at the start of the simulation. The lifetime of Br_y was assumed to be infinite for run *B*. A number of sensitivity runs were also performed. Run *S_{NOCONV}* differed from run *B* in that model convection was switched off (note, mixing in the PBL remained switched on). Runs *S₁₀*, *S₂₀* and *S₄₀* differed from run *B* in that the lifetime of Br_y was set to 10, 20

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and 40 days below the cold-point tropopause (CPT), respectively. Run $S_{2\text{OH}}$ differed from the base in that model [OH] was doubled. Run S_{L31} differed in that the model employed coarser vertical resolution (factor of 2) above ~ 300 hPa and therefore had only 31 levels. Finally, a SLIMCAT simulation (run S_{SLIMCAT}) was also carried out in which artificial mixing in the tropical troposphere was assumed by fixing both CHBr_3 and CH_2Br_2 SGs in the lower 8 levels of the $\sigma - \theta$ model (surface to ~ 10 km).

4 Results and discussion

4.1 Source gas injection

Figure 4 shows the mean modelled loss rates (due to reaction with OH and photolysis)

and the local photochemical lifetimes for CHBr_3 and CH_2Br_2 in the tropics. Results from this analysis are also summarised in Table 4. For CHBr_3 , the dominant loss process is photolysis. The calculated local lifetime of CHBr_3 (τ_{local}) ranges between ~ 25 – 30 days in the TTL and has a surface value of ~ 15 days. This is generally consistent with previous model calculations (e.g. Warwick et al., 2006; Sinnhuber and Folkens, 2006). For CH_2Br_2 , in the mid-troposphere loss is dominated by reaction with OH with photolysis being slow. At the CPT, the two loss channels are roughly equal. The local lifetime of CH_2Br_2 ranges from ~ 50 days at the surface to a maximum of ~ 520 days in the TTL. This is somewhat large given the working definition of a VSLs as a species whose lifetime is less than 6 months (Law and Sturges et al., 2007).

Figure 5 shows the tropical zonal mean profiles for the source gases CHBr_3 and CH_2Br_2 from the base run B and sensitivity runs S_{NOCONV} (no convection), $S_{2\text{OH}}$ ($2\times[\text{OH}]$) and S_{SLIMCAT} . The location of the CPT and the approximate base of the TTL is shown for reference. Note that we define the base of the TTL as the level of maximum convective outflow (approximately 12 km) and the top of the TTL as the cold-point (e.g. Law and Sturges et al., 2007). The results here show that with the full TOMCAT model transport (run B) the mean CHBr_3 mixing ratio at the CPT

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(~17 km) is ~0.126 pptv resulting in an SGI contribution of ~0.38 pptv of Br_y to the lower stratosphere. This is in general agreement with the SGI value of 0.5 pptv predicted by Sinnhuber and Folkins (2006). Similarly for CH₂Br₂, run *B* predicts a mean of 0.797 pptv of SG at the tropopause, resulting in a value for SGI of ~1.59 pptv; i.e. over 5 4× that of bromoform. Without convection (run S_{NOCONV}) the SGI values reduce to 0.32 pptv and 1.57 pptv, i.e. ~84% and ~98% of run *B* values for CHBr₃ and CH₂Br₂, respectively. These results suggest that SGI via both species is not overly sensitive to model parameterised convection, particularly at the CPT. For CHBr₃, this apparently contradicts the findings of Nielsen and Douglass (2001) who report a treatment 10 of convection is required in their model simulations in order for CHBr₃ to reach the tropical lower stratosphere. Similarly, Warwick et al. (2006) report from a 3-D model study CHBr₃ to be highly dependent on convection in the tropical upper troposphere. Without further details on the experiments performed in these other studies we cannot 15 comment further on the differences. In our experiments, although we switch off convection we still include the parameterisation of mixing in the PBL which causes mixing of surface-emitted tracers in the bottom few km. If we also switch off PBL mixing then we see CHBr₃ especially largely confined to the lowest model level (~100 m) and a large decrease in UT values. It may be that the studies of Nielsen and Douglass (2001) and Warwick et al. (2006) also included transport due to this process in their definition of 20 convection. Given that turbulent mixing in the PBL can transport tracers to the lower free troposphere, then the lifetimes of CHBr₃ and CH₂Br₂ would indicate that resolved vertical advection by the analysed winds could still cause some transport to the UT.

There is uncertainty in the modelled OH profile in the UT and so a sensitivity run was performed to investigate the impact of a large ($\times 2$) change in [OH] on the modelled SG 25 profiles. From the run $S_{2\text{OH}}$ profile in Fig. 5 it is clear the abundance of CH₂Br₂ and associated SGI is more sensitive to changes in OH concentration than that of CHBr₃. This is expected given the dominance of the CH₂Br₂+OH reaction over photolysis, relative to that of CHBr₃+OH. For the SLIMCAT run S_{SLIMCAT} , SG profiles have been scaled to approximately mimic that of the base run in the mid-troposphere. It can be

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seen that SLIMCAT predicts a lower abundance of both SGs in the TTL and near-tropopause regions.

TOMCAT model runs with ECMWF winds have been reported previously to exhibit too rapid vertical motion in the lower stratosphere region (e.g. Chipperfield, 2006; 5 Monge-Sanz et al., 2007). The problem is more obvious with ERA-40 winds than that with the more recent ECMWF datasets and is mainly related to the noisy analysed wind fields. This is known to affect all CTMs using wind velocities or divergence to obtain the vertical motion (e.g. Scheele et al., 2005; Wohltman and Rex, 2008). SLIMCAT runs are not affected by the same problem as, in this case, above 350 K vertical motion 10 is computed from diagnosed heating rates. For this reason, the spurious vertical transport present in TOMCAT runs due to analysis noise is eliminated from SLIMCAT runs. In addition, SLIMCAT uses isentropic levels in the stratosphere which helps to separate vertical and horizontal motion and has also proven to provide more realistic transport in the LS than TOMCAT (e.g. Chipperfield, 2006).

15 Krueger et al. (2008) performed a Lagrangian model study in the TTL region using ECMWF operational winds and found that the use of the ECMWF vertical wind field resulted in significantly faster motion than the use of computed heating rates. A study by Wohltman and Rex (2008) with ECMWF winds has also shown improvements in the vertical velocities when obtained from diagnosed heating rates with respect to the 20 vertical velocity field from the analyses (although we do not use the vertical velocity from the analyses).

The trajectory calculation inside the TOMCAT/SLIMCAT CTM has been used to estimate the mean tracer vertical transport in the TTL in runs *B* and S_{SLIMCAT} . Trajectories were initialised at 80 hPa (run *B*) and 380 K (run S_{SLIMCAT}) and advected backwards in 25 time using the vertical winds from the analysed divergence field and diagnosed heating rates respectively. The mean vertical motion, calculated from the trajectory displacement, was 0.64 mm/s in run *B* and 0.324 mm/s in run S_{SLIMCAT} . Analysis of HCFC and HFC data from the WB-57 indicates a transit time from 360 K to 380 K of about 3–4 months (E. Atlas, personal communication, 2009). Analysis of CO₂ data (Park et

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al., 2009) shows a similar transit time, which corresponds to a range in vertical transport, between the lower boundary of the TTL and the tropopause, of 0.5–0.14 mm/s. Krueger et al. (2008) find residence times in the winter TTL (2001/02) of 36 days using operational ECMWF with diagnosed heating rates, and only 20 days when using the corresponding ECMWF vertical winds. Our calculations show a residence time in the 360–380 K region of 20 days based on the TOMCAT run and 52 days based on the SLIMCAT run for the period November–December 2005. Therefore, the vertical motion in the θ -coordinate model run is more realistic, which leads to overall better agreement with the observations (see below). The residence times in the TTL calculated here are within the range, 20–80 days, as published (WMO, 2007).

Overall, given the predicted mixing ratios of CHBr_3 and CH_2Br_2 in the near-tropopause region, it seems the latter species may be deemed more significant. Wamsley et al. (1994) reported CH_2Br_2 to have an atmospheric lifetime long enough to reach the stratosphere and CHBr_3 (with shorter lifetime) to contribute negligible amounts to stratospheric Br. The results here are also consistent with Laube et al. (2008) who, based on observations, deduced CH_2Br_2 to be the “dominant” very short-lived SG. Their results, along with Schauffler et al. (1998), find CH_2Br_2 to be present up to ~18.5 km (~0.15 pptv). The results here confirm CH_2Br_2 at this level with run *B* predicting ~0.5 pptv and run S_{SLIMCAT} ~0.16 pptv. The latter seems more reasonable given the observed values discussed above, along with the overestimation of SG in the near-tropopause region by TOMCAT (see below).

Figure 6 shows the modelled profiles of CHBr_3 and CH_2Br_2 versus tropospheric observations from the PEM TROPICS-B (e.g. Colman et al., 2001; http://www-gte.larc.nasa.gov/pem/pemtb_obj.htm) and INTEX-B (<http://www.espo.nasa.gov/intex-b/>) campaigns. The model profiles shown here are averaged over the same spatial domain and for the same months (but for 2007) as the observations. This shows that the model profiles from run *B*, constrained with a surface mixing ratio of 1.2 pptv for both species, fit the observations in the mid troposphere well. Particularly, for CH_2Br_2 , the model is able to reproduce observed mixing ratios and profile shape. Note that the difference

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between runs B and S_{NOCONV} here is small, showing that modelled convection is only playing a small role in this region.

- Figure 7 shows the modelled profiles of CHBr_3 and CH_2Br_2 against tropical observations which extend into the TTL. These are the 2007 NASA TC-4 (<http://www.espo.nasa.gov/tc4/>), the NASA PRE-AVE (http://espoarchive.nasa.gov/archive/arcs/pre_ave/) campaign and the 2006 NASA CR-AVE (<http://www.espo.nasa.gov/ave-costarica2/>) campaigns. For TC-4 DC8 flights targeted recent convective outflow while only a single WB57 flight targeted convection. Again the model profiles are averaged over the same spatial domain and for the same months as the observations.
- For CHBr_3 , the base model B performs reasonably well against the observations in the lower troposphere and near the tropopause. The model is able to reproduce the gradient seen from the surface to ~ 500 hPa and the modelled profile lies within the min-max variability of observations at most levels. Of importance is the model's ability to simulate CHBr_3 in the near-tropopause region. A number of previous model studies have significantly overestimated CHBr_3 in this region when compared with observations (e.g. Warwick et al. 2006; Nielsen and Douglass, 2001). It can be seen that TOMCAT performs well in this regard. However, it seems that TOMCAT may not capture convection effectively shown by the lack of a signature "C-shape" in the profile. Results from TC4, which targeted active convective outflow during most flights, may not be representative of the region as a whole. Similarly for CH_2Br_2 , the modelled profile seems reasonable against observations in the lower troposphere. There is less variability seen here than for CHBr_3 , due to the longer lifetime of CH_2Br_2 . However, in the near-tropopause region, TOMCAT overestimates the abundance of source gas. This will be in part due to the too fast modelled vertical transport through the TTL region in run B (see above). Note that the overestimation of the SGs in the TTL in TOMCAT is not due to the model vertical resolution. The SG profiles are nearly identical in run B and S_{L31} which has the higher vertical resolution (not shown). The vertical transport is controlled by the vertical winds and not by numerical diffusion.

From Fig. 7 it is apparent that run S_{SLIMCAT} , with slower vertical transport in the TTL,

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reproduces observed CH_2Br_2 in the near-tropopause region fairly well and better than the TOMCAT runs. Similarly for PRE-AVE flights, the run *B* profile fits CHBr_3 observations well in the important upper TTL and tropopause regions. A larger difference is seen here between runs with and without convection along with more of a “C-shape” in the modelled profile. This is due to the model being sampled in the months January and February when convection is stronger. The θ -level model in this case seems to underestimate observed CHBr_3 in the TTL, although there are few observations at this level. For CH_2Br_2 , both runs *B* and S_{SLIMCAT} seem reasonable in the near-tropopause region, with the former perhaps fitting the observations better. Unlike comparisons with TC4 and CR-AVE data, run *B* does not show a significant overestimation of CH_2Br_2 . This could be explained by variation in the strength of deep convective uplift between campaigns. Finally, for CR-AVE data, modelled CHBr_3 is overestimated in runs *B* and S_{NOCONV} in the TTL and near-tropopause regions. In these regions run S_{SLIMCAT} performs well. This is also the case for CH_2Br_2 , where the TOMCAT overestimation is greater.

Figure 8 shows a tracer-tracer plot of CHBr_3 vs. CH_2Br_2 in the 350–80 hPa region from runs *B*, S_{NOCONV} , S_{2OH} and S_{SLIMCAT} . Mean observations from the TC-4 data set (also in this region, see Fig. 7a and b) are included on this figure along with a power line of best fit of all datasets. The origins of the model lines (high SG mixing ratios) are arbitrary and the plot tests the ability of the different model runs to fit both SG profiles simultaneously. The model lines here indicate that with the current model setup (chemistry and transport), both tracers cannot be simulated correctly at the same time. The S_{SLIMCAT} run performs the best as can be seen in the gradient relative to that of the observations. Run S_{SLIMCAT} has the slowest transport through the TTL and allows more loss of CH_2Br_2 relative to CHBr_3 in the lower TTL where loss by OH is faster (Fig. 4).

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4.2 Product gas injection

Figure 9 shows the annual tropical zonal mean abundance of the product gases arising from CHBr_3 and CH_2Br_2 degradation. For bromoform the major degradation products are CBr_2O and CHBrO with CBr_3OOH and CHBr_2OOH being minor products. This is consistent with the suggestions of Ko and Poulet et al. (2003). The mixing ratios of these species in the TTL are very low (<0.03 pptv) for the assumed SG surface vmr. From this we infer that the contribution of these species to PGI and thus total Br from CHBr_3 is negligible. The mixing ratios of the peroxy radicals in the scheme, CBr_3O_2 and CHBr_2O_2 , were found to be near zero throughout the profile (not shown).

Similarly, for dibromomethane the model predicts the major degradation product to be CHBrO and a minor product to be CHBr_2OOH . Again, this is consistent with the suggestions of Ko and Poulet et al. (2003) and the mixing ratios of these species are also near-zero throughout the profile. As for CHBr_3 , it is apparent that the contribution of organic products arising from CH_2Br_2 SG degradation to PGI and thus total bromine, is negligible. Furthermore, although poorly quantified, organic PGs would be expected to be removed from the atmosphere by washout processes due to their solubility. The model work described in this paper has not accounted for this and thus the extremely low near-tropopause mixing ratios reported here for CBr_2O , CHBrO and other PGs could indeed be overestimates. The results here suggest that PGI is dominated by the transport of inorganic products.

Figure 10 shows the calculated loss rates due to photolysis and the resultant lifetime of CBr_2O and CHBrO in the tropics. We find CBr_2O to have a lifetime of ~7days and CHBrO of ~1 day due to photolysis. Overall, these results show that the assumption made in previous model studies of instantaneous conversion between organic bromine product gases and Br_y following SG degradation seems reasonable.

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4.3 Total bromine

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Figures 11 and 12 show the modelled contribution of SGI, PGI and total Br delivered from CHBr_3 and CH_2Br_2 degradation, respectively. Results are shown for sensitivity runs S_{10} , S_{20} and S_{40} (i.e. Br_y lifetime of 10, 20 and 40 days). The base of the TTL and CPT are included for reference. Values of these fields are summarised in Table 5 and are quoted at the location of the CPT (i.e. the approximate contribution to the lower stratosphere). All results here are calculated as an annual zonal mean in the tropics. Assuming a Br_y lifetime of 10 days, our model predicts that CHBr_3 contributes ~0.72 pptv additional bromine to the lower stratosphere. We find the fraction of this value delivered via SGI and PGI to be approximately equal. This is in general agreement with the work of Dvortsov et al. (1999) and Nielsen and Douglass (2001) who report similar values of ~1 pptv. These studies also find the delivery via SGI and inorganic PGI to be approximately equal. Similarly, the results here are in good agreement with the work of Sinnhuber and Folkins (2006) who report total bromine from CHBr_3 reaching the cold point to be 0.8 pptv for the same assumed 10-day Br_y lifetime. In addition, they report a PGI value of 0.3 pptv which is consistent with the 0.35 pptv reported here.

From CH_2Br_2 and with the same 10 day Br_y lifetime, we find a delivery of ~1.69 pptv of bromine to the lower stratosphere, with ~94% from SGI. In this case, the contribution from PGI is small. Despite only two Br atoms per molecule (as opposed to 3 for CHBr_3), the dominance of the SGI pathway is due to the longer local lifetime of CH_2Br_2 , allowing more SG to reach the upper troposphere. The results reported here for CH_2Br_2 may constitute an upper limit given the observed overestimation of SG in the near-tropopause region in TOMCAT. Furthermore, we infer a total Br contribution from both SGs to be ~2.4 pptv to the lower stratosphere. Increasing the assumed Br_y lifetime below the tropopause to 20 and 40 days raises this value to ~2.9 and ~3.6 pptv. The mean lifetime of Br_y in the troposphere and in particular the TTL region is, however, uncertain at present.

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5 Conclusions

We have performed a 3-D model study using the TOMCAT/SLIMCAT CTM in order to quantify, first, the contribution of CHBr_3 and CH_2Br_2 to the stratospheric bromine budget and, second, the relative magnitude of SGI and PGI. A detailed chemical scheme 5 describing the tropospheric degradation of both source gases, along with simplified product gas chemistry, has been developed.

We have thus provided novel estimates of the organic products gases arising from CHBr_3 and CH_2Br_2 degradation. The major degradation products have been found to be CBr_2O and CHBrO whose local lifetimes are calculated at ~ 7 and ~ 2 days respectively. We find their contribution to total bromine negligible and thus infer that assumption of instantaneous production of Br_y following $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ degradation in model studies is reasonable. It is likely that this assumption will also be valid for other short-lived source gases (e.g. CHBr_2Cl , CHBrCl_2) whose degradation products are comparably short-lived. However, attempt at measurements of species such as 15 CBr_2O and CHBrO in the troposphere and TTL would certainly be useful.

The TOMCAT/SLIMCAT CTM has been shown to perform reasonably against observations of these SGs in the tropical troposphere-lower stratosphere region. The $\sigma-\theta$ level model (SLIMCAT) tends to agree better than the $\sigma-p$ level model (TOMCAT) due to the more realistic vertical transport in the TTL. The SLIMCAT run also gives the best 20 simultaneous relative comparisons of the profiles of CHBr_3 and CH_2Br_2 . We find a treatment of convection is not required in our TOMCAT simulations to transport significant quantities of SG to the TTL and lower stratosphere. In future work the convective transport parameterisation will be included in SLIMCAT to investigate the impact of this against the background of slower resolved advection.

25 The results presented here have shown CHBr_3 and CH_2Br_2 together could contribute around 2.4 pptv of Br to the lower stratosphere when a Br_y lifetime of 10 days is assumed along with mean surface mixing ratios of 1.2 pptv for both source gases. Assuming the $\text{Br}_y^{\text{VSLs}}$ value of 5 pptv inferred by Dorf et al. (2008), then a shortfall of ~ 2.6

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pptv remains. This may, in part, be supplied from Br-containing SGs such as CH_2BrCl , CHBr_2Cl and CHBrCl_2 (local lifetimes of 150, 69 and 78 days respectively, Law and Sturges et al., 2007). Furthermore, although poorly quantified, it is possible “additional bromine source gases” which remain unknown may contribute (Laube et al., 2008).

5 Our results are generally in agreement with previous model work in that the contribution of bromine-containing VSLs may supply a significant amount of Br_y to the lower stratosphere. Therefore, in future stratospheric simulations it will be important to take this into account.

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Table 1. Summary of bromoform chemistry scheme. **a** Photolysis rates calculated from (where available) recommended absorption cross section data. **b** Paramaterisation for the temperature-dependence of SG absorption cross sections included. **c** Br_y first-order loss due to washout adjusted to give lifetimes of 10, 20, 40 and ∞ days. **d** Rate constant estimated from reactions of analogous chlorine-containing species or generalised expression.

	Reaction	Rate/cm ³ molecule ⁻¹ s ⁻¹	Comment	Ref.
(R1)	CHBr ₃ +OH	$k(T)=1.35E-12.\exp(-600/T)$	–	JPL
(R2)	CHBr ₃ +Cl	$k(T)=4.85E-12.\exp(-850/T)$	–	JPL
(R3)	CHBr ₃ +hv	a, b	Assume quantum yield of 1 for Br	JPL
(R4)	CBr ₃ O ₂ +NO	$k(T)=7.30E-12.\exp(-270/T)$	d	JPL
(R5)	CBr ₃ O ₂ +HO ₂	$k(T)=3.30E-13.\exp(820/T)$	d	MCM
(R6)	CBr ₃ O ₂ +HO ₂	$k(T)=3.30E-13.\exp(820/T)$	As (R5) and equal partitioning of products	MCM
(R7)	CHBr ₂ O ₂ +NO	$k(T)=2.54E-12.\exp(360/T)$	d	MCM
(R8)	CHBr ₂ O ₂ +HO ₂	$k(T)=3.30E-13.\exp(820/T)$	d	MCM
(R9)	CHBr ₂ O ₂ +HO ₂	$k(T)=3.30E-13.\exp(820/T)$	As (R8) and equal partitioning of products	MCM
(R10)	CBr ₃ OOH+OH	$k(T)=1.90E-12.\exp(190/T)$	d	MCM
(R11)	CBr ₃ OOH+hv	a	Assume cross sections of CH ₃ OOH	JPL
(R12)	CHBr ₂ OOH+OH	$k(T)=1.90E-12.\exp(190/T)$	d	MCM
(R13)	CHBr ₂ OOH+hv	a	Assume cross sections of CH ₃ OOH	JPL
(R14)	CBr ₂ O+hv	a	Assume quantum yield of 2 for Br	JPL
(R15)	CHBrO+hv	a	Assume quantum yield of 1 for Br	JPL
(R16)	Br _y washout	c	Variable in model – see text	

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Table 2. As Table 1 but for dibromomethane.

Reaction	Rate/cm ³ molecule ⁻¹ s ⁻¹	Comment	Ref.
(R17) CH ₂ Br ₂ +OH	$k(T)=2.00E-12 \exp(-840/T)$	–	JPL
(R18) CH ₂ Br ₂ +Cl	$k(T)=6.30E-12 \exp(-800/T)$	–	JPL
(R19) CH ₂ Br ₂ +hv	a	Assume quantum yield of 1 for Br	JPL
(R20) CHBr ₂ O ₂ +NO	$k(T)=2.54E-12 \exp(360/T)$	As Table 1 (Reaction R7)	
(R21) CHBr ₂ O ₂ +HO ₂	$k(T)=3.30E-13 \exp(820/T)$	As Table 1 (Reaction R8)	
(R22) CHBr ₂ O ₂ +HO ₂	$k(T)=3.30E-13 \exp(820/T)$	As Table 1 (Reaction R9)	
(R23) CH ₂ BrO ₂ +NO	$k(T)=4.00E-13 \exp(300/T)$	d	MCM
(R24) CH ₂ BrO ₂ +HO ₂	$k(T)=3.30E-13 \exp(820/T)$	d	MCM
(R25) CH ₂ BrO ₂ +HO ₂	$k(T)=3.30E-13 \exp(820/T)$	As (Reaction R24) and equal partitioning of products	MCM
(R26) CHBr ₂ OOH+OH	$k(T)=1.90E-12 \exp(190/T)$	As Table 1 (Reaction R12)	
(R27) CHBr ₂ OOH+hv	a	As Table 1 (Reaction R13)	
(R28) CH ₂ BrOOH+OH	$k(T)=1.90E-12 \exp(190/T)$	d	MCM
(R29) CH ₂ BrOOH+hv	a	Assume cross sections of CH ₃ OOH	JPL
(R30) CHBrO+hv	a	As Table 1 (Reaction R15)	
(R31) Br _y washout	c	As Table 1 (Reaction R16)	

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Table 3. CTM experiments performed.

Run	Convection	Br_y lifetime	Vertical levels	[OH]
B	yes	Infinite	38	1×
S_{NOCONV}	no	Infinite	38	1×
S_{10}	yes	10 days below cold-point	38	1×
S_{20}	yes	20 days below cold-point	38	1×
S_{40}	yes	40 days below cold-point	38	1×
$S_{20\text{H}}$	yes	Infinite	38	2×
S_{L31}	yes	Infinite	31	1×
S_{SLIMCAT}	no	Infinite	38 ($\sigma-\theta$)	1×

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Table 4. Mean modelled lifetimes (days) of CHBr_3 and CH_2Br_2 in the tropics in different regions from the surface to cold-point (~17 km, ~95 hPa). Lifetime with respect to photolysis (τ_{hv}), OH (τ_{OH}) and overall local lifetime (τ_{local}).

Source Gas	Pressure/hPa	τ_{hv} /days	τ_{OH} /days	τ_{local} /days
CHBr_3	1000	28	35	16
CHBr_3	1000–500	28	42	17
CHBr_3	500–200	25	132	21
CHBr_3	200–95	33	292	29
CH_2Br_2	1000	21004	53	52
CH_2Br_2	1000–500	20495	66	65
CH_2Br_2	500–200	13231	243	237
CH_2Br_2	200–95	2535	655	453

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Table 5. Summary of modelled total Br, SGI and PGI for CHBr_3 and CH_2Br_2 with Br_y lifetimes of 10, 20, 40 and ∞ days below the cold-point tropopause.

Source Gas	Br_y Lifetime	SGI/ppt	PGI/ppt	Total Br/ppt	%SGI
CHBr_3	10 days	0.377	0.345	0.722	53
CH_2Br_2	10 days	1.594	0.099	1.693	94
Total	10 days	1.971	0.434	2.415	81
CHBr_3	20 days	0.377	0.732	1.109	34
CH_2Br_2	20 days	1.594	0.194	1.788	89
Total	20 days	1.971	0.92	2.891	68
CHBr_3	40 days	0.377	1.323	1.700	22
CH_2Br_2	40 days	1.594	0.334	1.928	82
Total	40 days	1.971	1.657	3.628	54
CHBr_3	∞	0.377	3.168	~ 3.6	11
CH_2Br_2	∞	1.594	0.763	~ 2.4	66
Total	∞	1.971	3.931	~ 6.0	33

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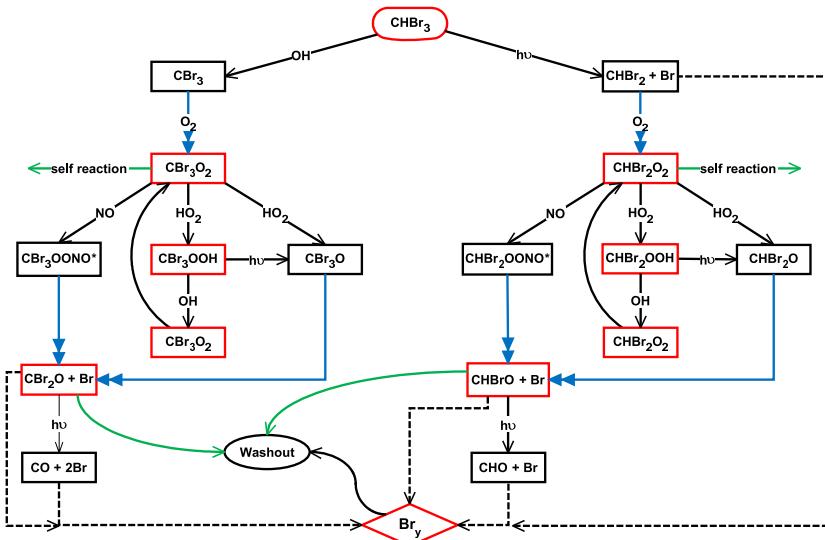


Fig. 1. Scheme for the tropospheric degradation of CHBr_3 . The red boxes denote the 9 organic species (1 SG+6 PGs) considered directly in the scheme, i.e. species whose production and loss are both calculated explicitly (see text). Black boxes denote species which are sufficiently short-lived for exclusion from the scheme. Blue lines therefore denote rapid reactions, dashed lines indicate the production of Br_y and green denotes reactions not considered in the present scheme.

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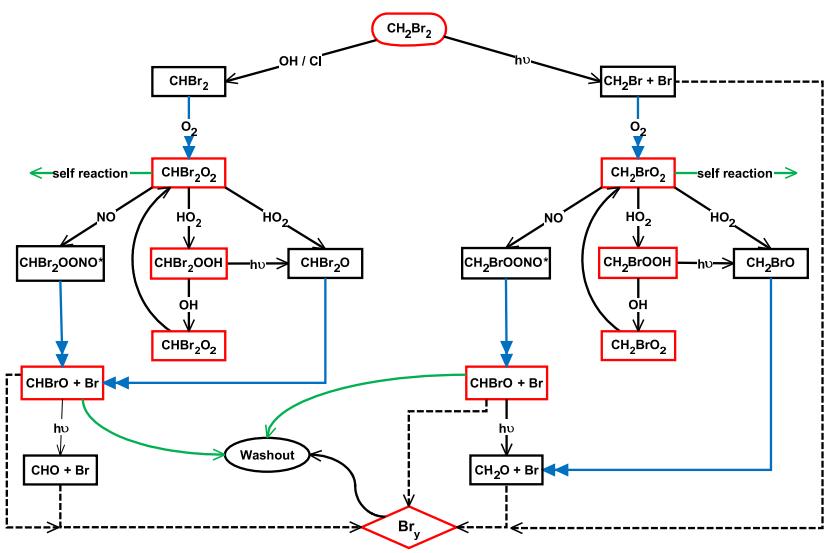


Fig. 2. As Fig. 1 but for CH_2Br_2 .



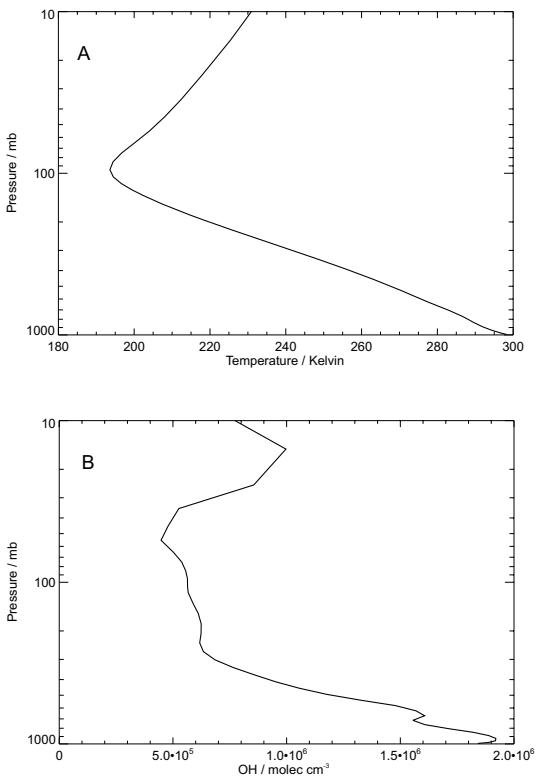


Fig. 3. Tropical ($\pm 20^\circ$ latitude) annual mean zonal mean profiles of (a) temperature (K) from model run B (i.e. ECMWF analyses) and (b) specified (24-h mean) OH concentration profile used in CTM experiments.

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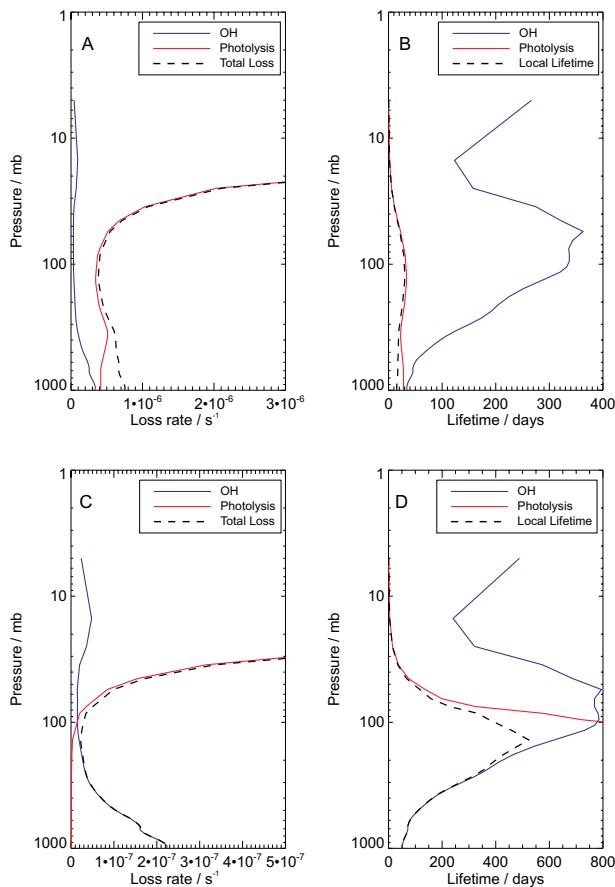


Fig. 4. Tropical ($\pm 20^\circ$ latitude) annual mean zonal mean profiles of (a) CHBr_3 loss rate (s^{-1}) due to photolysis (red line), reaction with OH (blue line), and the overall total (black dashed line), and (b) CHBr_3 lifetime (days) due to the same processes from the TOMCAT model runs. Panels (c) and (d) are the equivalent panels for CH_2Br_2 .

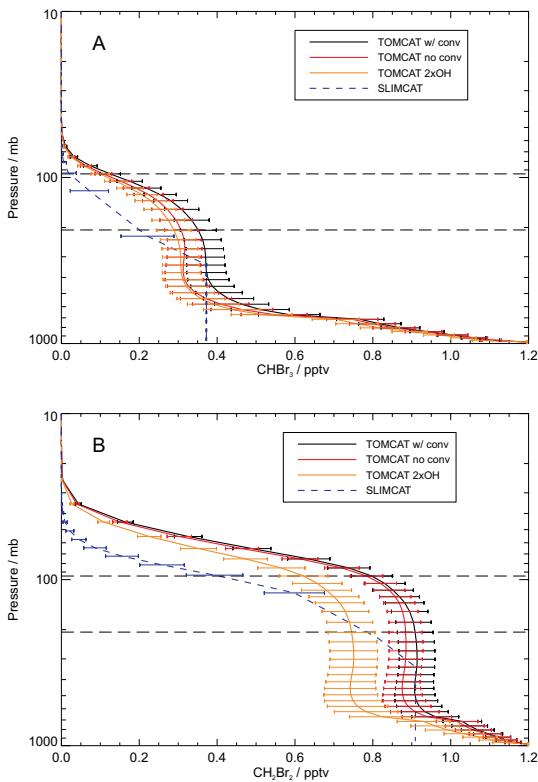


Fig. 5. Tropical ($\pm 20^\circ$ latitude) annual mean zonal mean modelled profiles of **(a)** CHBr_3 and **(b)** CH_2Br_2 . Black line denotes output from the run *B* (i.e. with convection), red line denotes output from sensitivity run S_{NOCONV} (no convection), orange line from run $S_{2\text{OH}}$ and dashed blue line from run S_{SLIMCAT} . Variability in time and space shown with ± 1 standard deviation. The location of the cold-point tropopause (CPT) and the base of the TTL (black dashed lines) are shown for reference.

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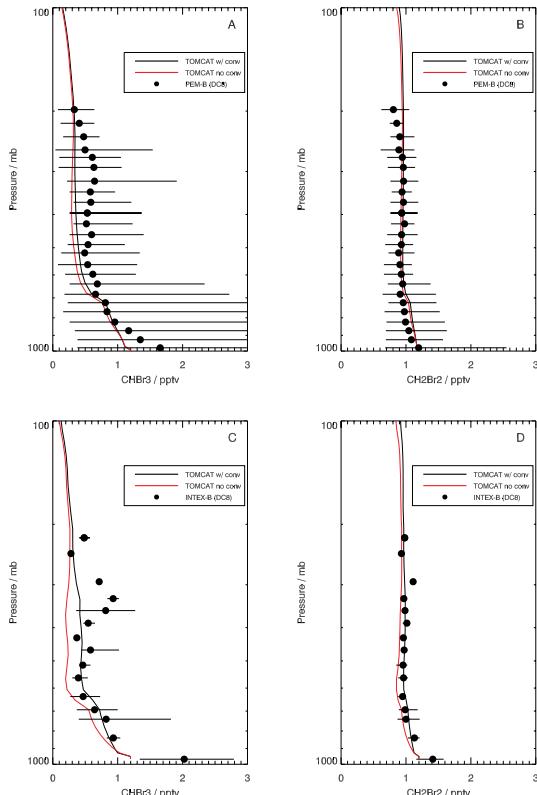


Fig. 6. Comparison of observed DC-8 profiles and model results for (a) CHBr₃ and (b) CH₂Br₂ from the PEM TROPICS-B mission (March-April 1999). The observations have been averaged vertically in ~0.5 km bins for tropical latitudes and between 84° and 211° W longitude. The model (runs *B* and *S_{NOCONV}*) is sampled over the same spatial domain and over the same months (for 2007). (c) and (d) are similar plots for the NASA INTEX-B campaign (March 2006). The observations have been averaged at tropical latitudes and between 95° and 99° W longitude. Horizontal lines on all observations denote min-max variability.

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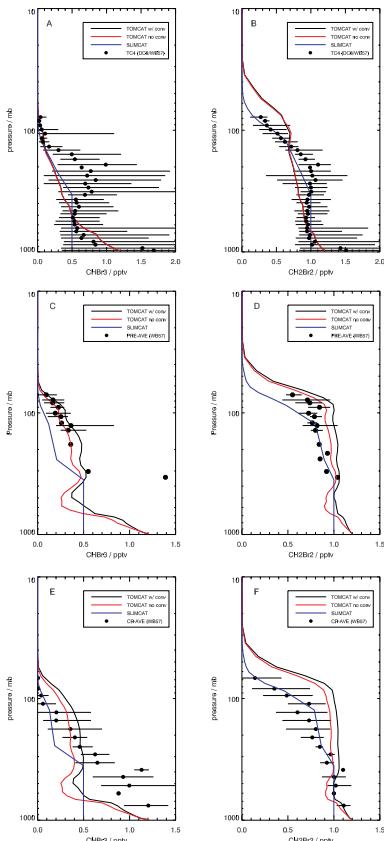


Fig. 7. Comparison of observed DC-8 and WB57 profiles and model results for (a) CHBr_3 and (b) from the NASA TC4 campaign (July–August 2007). (c) and (d) are similar comparisons for the PRE-AVE campaign (January–February 2004). (e) and (f) are similar comparisons for the CR-AVE campaign. (January–February 2006). The TC-4 observations have been averaged in tropical latitudes and between 70° and 106° W longitude. The PRE-AVE observations are averaged in tropical latitudes and between 81° and 85° W longitude. Similarly, the CR-AVE observations have been averaged at tropical latitudes and between 79° and 86° W longitude.

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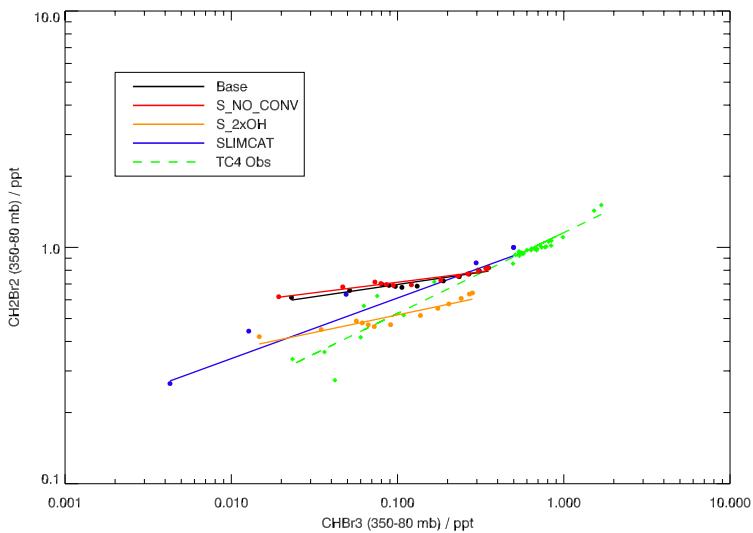


Fig. 8. Correlation plot of observed CH_2Br_2 versus observed CHBr_3 between 350 and 80 hPa from the TC-4 campaign (Fig. 7a). Also shown are model results from runs *B*, $S_{2\text{OH}}$, and S_{SLIMCAT} , in the same region. Power lines of best fit are included on all data sets of the form, $Y=(aX)^b$.

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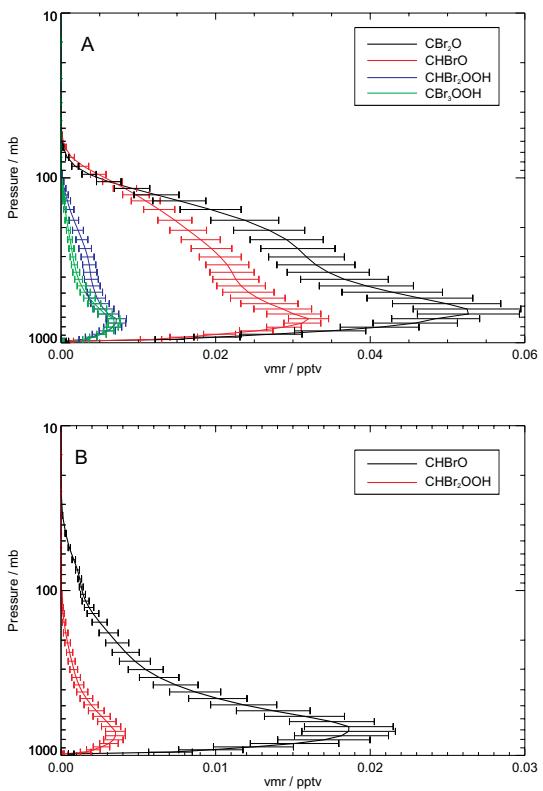


Fig. 9. Modelled tropical ($\pm 20^\circ$ latitude) annual mean zonal mean profiles of the principal organic PGs arising from (a) CHBr₃ and (b) CH₂Br₂ degradation in the tropics. The assumed surface mixing ratio of both SGs is 1 pptv. The output is from run B with variability in time and space shown with ± 1 standard deviation.

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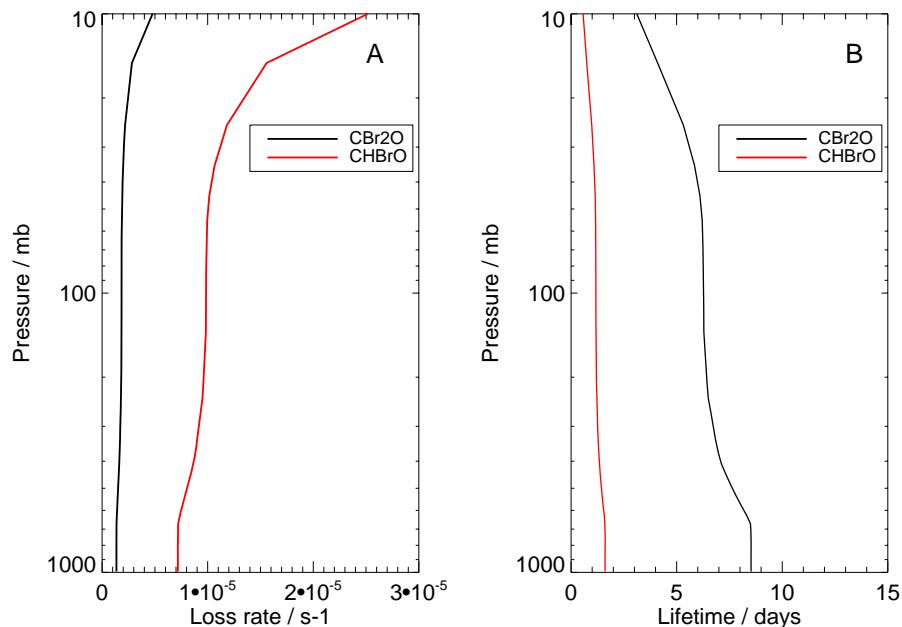


Fig. 10. Modelled tropical ($\pm 20^\circ$ latitude) annual mean zonal mean profiles of (a) the loss rate (solely due to photolysis) and (b) the lifetime of CBr₂O (black line) and CHBrO (red line).

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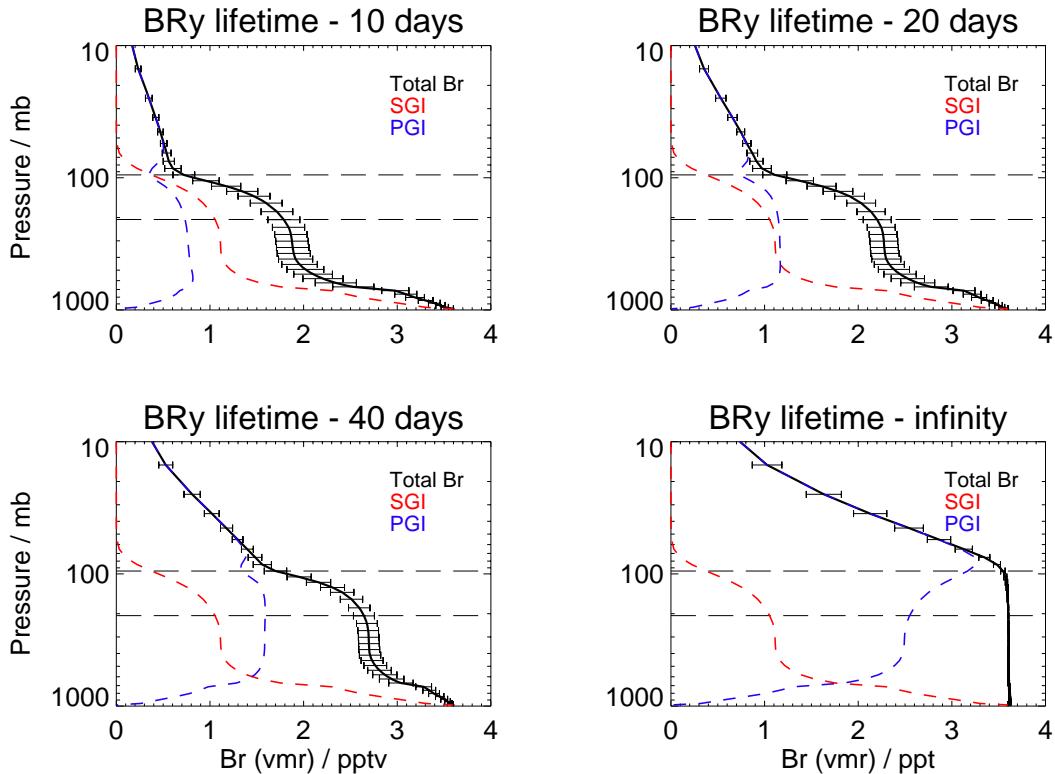


Fig. 11. Modelled tropical ($\pm 20^\circ$ latitude) annual mean zonal mean profiles of SGI, PGI and total Br arising from CHBr_3 degradation in the tropics from runs (a) B , (b) S_{10} , (c) S_{20} and (d) S_{40} . These runs assume a CHBr_3 surface mixing ratio of 1.2 pptv. The location of the cold-point tropopause (CPT) and base of the TTL (black dash lines) are shown for reference.

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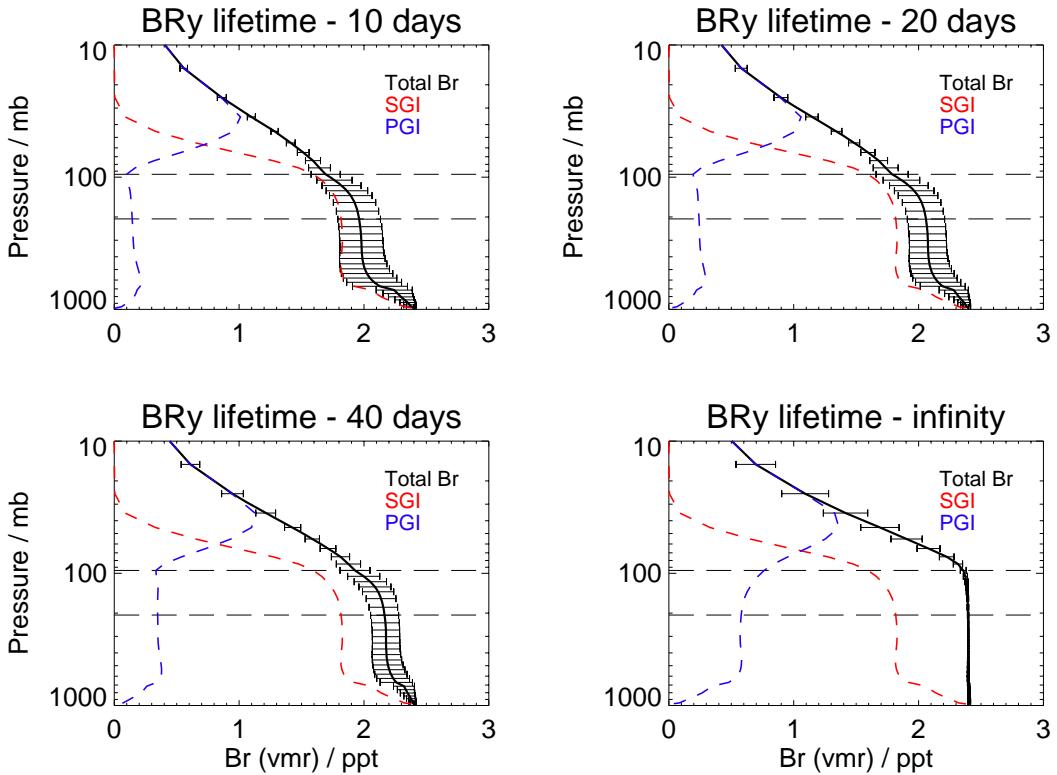


Fig. 12. As Fig. 11 but for CH_2Br_2 . The assumed surface mixing ratio of CH_2Br_2 is 1.2 pptv.

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