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Contribution of very short-lived substances to stratospheric bromine loading: uncertainties and constraints

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Abstract

Very short-lived substances (VSLS) still represent a major factor of uncertainty in the quantification of stratospheric bromine loading. One of the major obstacles for short-lived source gases in contributing to the stratosphere is generally thought to be loss of inorganic bromine (Br_y) in the tropical tropopause layer (TTL) due to dehydration. We use sensitivity calculations with a three-dimensional chemistry transport model comprising a consistent parametrization of convective transport and a comprehensive chemistry scheme to investigate the associated processes. The model considers the two most important bromine VSLS, bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2). The organic bromine source gases as well as the resulting profile of inorganic bromine in the model are consistent with available observations. In contrast to its organic precursors, Br_y is assumed to have a significant sorption capacity regarding sedimenting liquid or frozen particles thus the fraction of intact source gases during their ascent through the TTL is a critical factor. We find that source gas injection is the dominant pathway into the stratosphere, about 50 % of $CHBr_3$ and 93 % of CH_2Br_2 is able to overcome the cold point tropopause at approximately 17 km altitude, modulated by the interannual variability of the vertical transport efficiency. In fact, our sensitivity calculations indicate that the extent of source gas injection of $CHBr_3$ is highly sensitive to the strength of convection and large-scale ascent; in contrast, modifying the photolysis or the destruction via OH yields a significantly smaller response. In principal, the same applies as well to CH_2Br_2, though it is considerably less responsive due to its longer lifetime. The next important aspect we identified is that the partitioning of available Br_y from short-lived sources is clearly shifted away from HBr, according to our current state of knowledge the only member of the Br_y family which is efficiently adsorbed on ice particles. This effect is caused by very efficient heterogeneous reactions on ice surfaces which reduce the HBr/Br_y fraction below 15 % at the tropical tropopause. Under these circumstances there is no significant loss of Br_y due to dehydration in the model, VSLS contribute fully to stratospheric bromine. In addition, we conduct several

ACPD
12, 30283–30326, 2012

sensitivity calculations to test the robustness of this result. If heterogeneous chemistry is ignored, the HBr/Br_y fraction exceeds 50 % and about 10 % of bromine from VSLS is scavenged. Dehydration plays a minor role for Br_y removal under the assumption that HOBr is efficiently adsorbed on ice as well since the heterogeneous reactions alter the partitioning equilibrium of Br_y in favor of HOBr. In this case, up to 12 % of bromine from VSLS is removed. Even in the extreme and unrealistic case that adsorbed species on ice particles are instantaneously removed the maximum loss of bromine does not exceed 25 %. In conclusion, considering the average abundance of bromine short-lived source gases in convective updrafts of 6 parts per trillion by volume (pptv) we find a most likely contribution of VSLS to stratospheric bromine in the range of 4.5–6 pptv.

1 Introduction

In recent years, more and more attention has been paid to very short-lived substances (VSLS) as important contributors to stratospheric bromine loading. A little more than a decade ago it was thought that these species, whose average tropospheric lifetime is less than six months, are unable to reach the stratosphere and are therefore not relevant as sources for ozone-depleting substances. However, we now have plenty of observational evidence and simulation results suggesting that the stratospheric mixing ratio of inorganic bromine (Br_y) in the range of 19.5–24.5 pptv (Montzka and Reimann, 2011) cannot be solely explained with the well known and considerably longer-lived source gases such as methyl bromide (CH_3Br), Halon-1211 ($CClBrF_2$) or Halon-1301 ($CBrF_3$); a significant part must be originated from other sources, most likely VSLS.

Satellite observations of bromine monoxide (BrO) indicate a contribution of VSLS to stratospheric inorganic bromine (Br_y^{VSLS}) in the range of 3–10 pptv (Sinnhuber et al., 2005; Sioris et al., 2006; McLinden et al., 2010; Salawitch et al., 2010); a similar study with BrO data from a balloon-borne instrument suggests 5.2 pptv (Dorf et al., 2008). Several modeling studies found a wide range for Br_y^{VSLS}, though the inherent differences between the approaches make a direct comparison difficult: 0.8–3 pptv

(Dvortsov et al., 1999; Nielsen and Douglass, 2001; Sinnhuber and Folkins, 2006; Kerkweg et al., 2008; Gettelman et al., 2009; Aschmann et al., 2009; Hossaini et al., 2010); 4.8–5.2 pptv (Schofield et al., 2011; Liang et al., 2010; Aschmann et al., 2011; Hossaini et al., 2012) and 6–7 pptv (Warwick et al., 2006). The most important bromine VSLS are bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) with an average tropospheric lifetime of 24 and 123 days and an average mixing ratio in the marine boundary layer (MBL) of 1.6 and 1.1 pptv, respectively (Montzka and Reimann, 2011). However, some studies suggest that also the combination of several other minor VSLS may contribute a significant amount of bromine (e.g. Warwick et al., 2006; Hossaini et al., 2012; Brinckmann et al., 2012).

Despite the increased scientific effort in the last years, two major uncertainties still challenge the quantification of Br_y^{VSLS}. The first point is the emission strength of VSLS. Predominantly of natural origin, produced by marine lifeforms such as macroalgae and certain phytoplankton groups, local mixing ratios of the short-lived source gases in the MBL can be much higher than the above mentioned average values, especially in coastal or upwelling areas (e.g. Carpenter and Liss, 2000; Quack and Wallace, 2003; Yokouchi et al., 2005; Butler et al., 2007; Brinckmann et al., 2012). Due to the scarcity of constraining observational data the spread of emission estimates is therefore no surprise (e.g. 400–1400 $Gg\,Br\,yr^{-1}$ for $CHBr_3$; Yokouchi et al., 2005; Warwick et al., 2006; Butler et al., 2007; Carpenter et al., 2009; O'Brien et al., 2009; Liang et al., 2010; Ordóñez et al., 2012) and reflects our lack of knowledge in this area.

The second point is the vertical transport. One generally agrees that tropical deep convection is the most important pathway for air parcels into stratosphere, lofting them above the level of zero radiative heating (LZRH) where they can ascend further (e.g. Corti et al., 2005; Sinnhuber and Folkins, 2006; Fueglistaler et al., 2009). The critical question is, what fraction of short-lived source gases reaches the stratosphere intact, commonly referred to as source gas injection (SGI). The corresponding contrary mechanism is called product gas injection (PGI), i.e. the amount of product gases produced by the decay of short-lived source gases that enter the stratosphere. The

ACPD
12, 30283–30326, 2012

relative fraction of SGI/PGI is a critical factor, as several species among the inorganic bromine product gases are soluble and can be scavenged by falling rain or ice particles, in contrast to their insoluble organic precursors (e.g. Law and Sturges, 2007). In this context, the efficient dehydration of tropospheric air in the exceptional cold tropical tropopause layer (TTL) plays an important role, as the drastic "freeze-drying" of ascending air parcels is suspected to remove a significant share of soluble tracers as well. However, the dehydration mechanism itself is a complex phenomena and still subject to current discussions (e.g. Sherwood and Dessler, 2001; Holton and Gettelman, 2001; Fueglistaler et al., 2005, 2009). Most modeling studies that investigate the contribution of Br_y^{VSLS} assume a fixed washout lifetime for Br_y, typically in the range of 10–30 days in the troposphere and above (Dvortsov et al., 1999; Nielsen and Douglass, 2001; Sinnhuber and Folkins, 2006; Warwick et al., 2006; Hossaini et al., 2010) suggesting that 60–80 % of Br_y^{VSLS} is lost due to dehydration. Models that use a more complex representation of the dehydration process show a significantly lower impact on Br_y^{VSLS}, in the order of 5–8 % in the TTL (Liang et al., 2010; Aschmann et al., 2011). In fact, when taking into account heterogeneous reactions on particles or aerosols as suggested by, e.g. von Glasow et al. (2004); Salawitch (2006) our previous study (Aschmann et al., 2011) indicates that loss of Br_y due to scavenging in the TTL vanishes almost completely.

In this study, we mainly concentrate on the latter aspect, the loss of inorganic bromine due to scavenging, as this process is thought to be one of the major obstacles for short-lived source gases in contributing to stratospheric bromine loading and is of critical importance for assessing the ozone depletion potential for VSLS. In extension of our previous modeling work in Aschmann et al. (2011), we present an ensemble of sensitivity calculations with a three-dimensional (3-D) chemistry transport model (CTM) to investigate the intricate relationship among the involved processes controlling direct source gas injection of VSLS and the impact of dehydration in the TTL on inorganic bromine in more detail.

2 Model description

The model used in this study is the isentropic Bremen 3-D CTM (B3DCTM) with 29 levels from 330 to 2700 K (about 10–55 km) and a spatial resolution of 2.5° lat. × 3.75° lon. which has been used and evaluated in previous studies (e.g. Sinnhuber et al., 2003, 2011; Aschmann et al., 2009, 2011). Meteorological input is derived from the ERA-Interim (EI) reanalysis of the European Centre for Medium-Range Weather Forecasts (ECMWF; Dee et al., 2011). Large-scale vertical transport is calculated from diabatic heating rates, complemented by a fast and localized convective transport component based on convective detrainment rates. Both heating and detrainment rates are obtained from the EI data set.

The model incorporates a comprehensive chemistry scheme originally based on the chemistry part of the SLIMCAT model (Chipperfield, 1999). It was updated and extended for this work and includes 59 species and about 180 photochemical reactions. With respect to bromine species, it contains the major long-lived gases CH_3Br, $CBrClF_2$ and $CBrF_3$ together with the two most important VSLS, $CHBr_3$ and CH_2Br_2. As the model does not explicitly contain the boundary layer and the free troposphere, assumptions about the mixing ratio of source gases in this altitude region must be made in order to model convective exchange with the upper troposphere. This mixing ratio is essentially a free parameter in the model and is in the following referred to as detrainment mixing ratio (for details, see Aschmann et al., 2009). For the detrainment mixing ratio of long-lived source gases, we rely on climatological data such as WMO scenario A1 (Daniel and Velders, 2011). For the short-lived $CHBr_3$ and CH_2Br_2, we simply assume a fixed and uniform detrainment mixing ratio of 1 pptv, which is consistent with the estimated tropical average of these species in the marine boundary layer (e.g. Montzka and Reimann, 2011). On the product gas side, the partitioning among the inorganic bromine family is explicitly calculated, comprising the species Br, BrO, HBr, HOBr, $BrONO_2$ and BrCl. Table 3 lists all included gasphase, heterogeneous and

ACPD
12, 30283–30326, 2012

photolytic reactions for bromine tracers along with the utilized kinetic data from the JPL recommendations 2011 (Sander et al., 2011).

The chemistry scheme contains an equilibrium treatment of liquid aerosols, nitric acid trihydrate and ice particles and is taken unchanged from Aschmann et al. (2011). For our study, we concentrate mainly on the heterogeneous chemistry on ice surfaces which is clearly dominating at the tropical tropopause as illustrated by Fig. 1. Over most of the TTL region the average reaction rates on ice exceed those on other particles surfaces by several orders of magnitude, only at the upmost levels of the upper troposphere/lower stratosphere (around 17 km altitude) the relative importance of liquid aerosol reactions increases. A related and equally important aspect for this study is the uptake of inorganic bromine product gases on ice surfaces. According to the recent IUPAC recommendation only HBr is efficiently adsorbed on ice under atmospheric conditions (Crowley et al., 2010). The partitioning between gasphase and surface adsorption can be described by a quasi-Langmuir model:

$$[\mathrm{HBr}]_\mathrm{s} = [\mathrm{HBr}]_\mathrm{g}^{0.88} \cdot K_\mathrm{linC} \cdot A \quad (1)$$

Here, K_linC denotes the partition coefficient for HBr on ice (4.14×10^5 cm) and A the available surface area density of the ice particles. In the model, A is calculated from the effective particle radius which is approximated from the total ice volume in a particular grid box and an assumed number density of ice particles of $10\,\mathrm{cm}^{-3}$. Particles and adsorbed species sediment with a prescribed fall velocity (Sect. 3.2.2).

We conduct a number of sensitivity calculations where we changed certain aspects of model. The sensitivity runs are described in detail in the corresponding sections (Sects. 3.1, 3.2), for an overview refer to Tables 1 and 2. All runs have been started 2004 from a 25-yr reference simulation with the same model and are integrated until end of 2006. Only the last year is used for analysis, the rest discarded as spin-up. We picked the year 2006 for our analysis because it is relatively unaffected by the El Niño Southern Oscillation (ENSO) that would otherwise strongly influence the transport of short-lived substances (e.g. Aschmann et al., 2011; Ashfold et al., 2012).

ACPD
12, 30283–30326, 2012

3 Results

3.1 Source and product gas injection of VSLS

In a first step, we analyze the relative fraction of source and product gas injection for bromine VSLS in the TTL. The basis for this study is formed by a set of reference simulations with our unperturbated standard model (Sect. 3.1.2). The variability of the results is then investigated by a series of sensitivity calculations described in Sect. 3.1.3.

3.1.1 Definitions

In this paper, the fraction of SGI and PGI of VSLS is estimated from the amount of source and product gases at the top of the tropical tropopause ("cold point tropopause"), which is assumed here to be located at 380 K or about 17 km altitude. Since neither dehydration of tropospheric air nor deep convection plays a significant role above this altitude (e.g. Dessler, 2002; Fueglistaler et al., 2009), it is justified to perform the distinction between SGI and PGI here. Source gas injection of both VSLS can be directly obtained from the mixing ratios of the corresponding species at 380 K from a simulation which includes these species. For convenience, the SGI mixing ratios are multiplied with a factor corresponding to the number of bromine atoms in the source gas molecule (×3 for $CHBr_3$, ×2 for CH_2Br_2) to ensure direct comparability with the PGI mixing ratios. To determine the product gas injection of $CHBr_3$ against the background of the ubiquitous long-lived bromine source gases we use the difference of Br_y mixing ratios at 380 K between a run with additional $CHBr_3$ included and a run with only long-lived source gases. Likewise, PGI of CH_2Br_2 is calculated using the difference in Br_y mixing ratios between the former run with additional $CHBr_3$ and a simulation where both $CHBr_3$ and CH_2Br_2 are included. Therefore, we generally have three variants of a single model experiment, each denoted by a suffix: for example, the reference simulation contains three runs, $SC0_a$, $SC0_b$ and $SC0_c$; where (a) denotes a run with only long-lived bromine source gases, (b) a run with additional $CHBr_3$ and

ACPD
12, 30283–30326, 2012

(c) a run with both $CHBr_3$ and CH_2Br_2 included (e.g. Fig. 2). In practice, only the (c) variant exists for several model experiments, as the limited changes in the particular run allows the reuse of the reference simulations $SC0_a/SC0_b$ to calculate the corresponding PGI (Table 1). Unless noted otherwise, the given mixing ratios in this paper are tropical means, i.e. zonal and meridional averages in the range of 20° N–20° S.

3.1.2 Reference simulation

The unperturbated state of the model is described by the reference simulation runs $SC0_{a-c}$. Figure 2 shows the averaged tropical profiles (20° N–20° S) for the corresponding Br_y profiles obtained from calculations without any VSLS, only $CHBr_3$ and with $CHBr_3$ and CH_2Br_2 included ($SC0_a$, $SC0_b$ and $SC0_c$, respectively) in 2006. The resulting fraction of source and product gas injection of bromine source gases, calculated as described in Sect. 3.1.1, is illustrated in Fig. 3. Obviously, Br_y below 17 km is dominated by short-lived source gases since only a minor fraction of the combined long-lived source gases (CH_3Br, $CClBrF_2$, $CBrF_3$) decays below the cold point (≈ 2 %). This is not surprising considering the typical photochemical lifetime of these species in the troposphere, which is in the case of the anthropogenic halons Halon-1211 and Halon-1301 in the range of decades (16 and 65 yr, respectively; Montzka and Reimann, 2011). In fact, the small amount of Br_y in run $SC0_a$ at the tropopause is likely originated from the considerably shorter-lived CH_3Br, having a typical lifetime of about nine months. More interesting is the prominent role of SGI also for the short-lived source gases: the troposphere-stratosphere exchange of CH_2Br_2 is clearly dominated by SGI (94 %), and even for the shorter-lived $CHBr_3$ more than the half of this species reaches the stratosphere intact (52 %). Note that the sum of SGI and PGI for $CHBr_3$ with 2.998 pptv (not rounded) is slightly lower than the expected 3 pptv, considering the assumed detrainment mixing ratio of 1 pptv for $CHBr_3$. This discrepancy represents the negligible effect of dehydration at the tropopause on inorganic bromine as discussed in Aschmann et al. (2011). This phenomena will be investigated in more detail in Sect. 3.2.

ACPD
12, 30283–30326, 2012

Source and product gas injection is obviously directly coupled to vertical transport and thus variable over time. Figure 4 illustrates this variability for the reference simulation and shows the tropical mean SGI mixing ratios for $CHBr_3$ and CH_2Br_2 along with the primary drivers of vertical transport in the model, the diabatic radiative heating rate and the convective detrainment rate, averaged in the vertical range above the LZRH up to the cold point. The importance of SGI for VSLS is significantly correlated to these proxies (correlation VSLS vs. heating/detrainment rate: $r = 0.67$, 0.59 for $CHBr_3$; $r = 0.42$, 0.44 for CH_2Br_2), although the correlation coefficients and the amplitude is larger for the shorter-lived $CHBr_3$. The relative fraction of SGI for the latter species varies in the range of 40–60 %. In case of CH_2Br_2 the relative fraction shows little variation (92–95 %), as this tracer is less dependent on rapid vertical transport in order to reach the stratosphere due to its longer lifetime.

3.1.3 Sensitivity calculations

To identify the determining factors that control source and product gas injection of bromine VSLS we have conducted a set of sensitivity calculations for comparison with the reference simulation SC0. As shown in Table 1, a single parameter has been altered in each run: the first four sensitivity calculations concentrate on the photochemical degradation of the short-lived source gases. In run $SC1_c$ and $SC3_c$, the loss rate due to photolysis and hydroxyl radical reaction is modified by 50 % (i.e. factor 1.5) for $CHBr_3$, respectively. The same applies for CH_2Br_2 in the runs $SC2_c$ and $SC4_c$. The second part of the sensitivity calculations deals with the vertical transport. Run $SC5_c$ changes the detrainment rate d_c below 353 K ($\approx$ 14 km) by 50 %, i.e. below the mean level of zero radiative heating whereas run $SC6_c$ does the same above this layer (> 353 K). Finally, run $SC12_c$ globally alters the diabatic radiative heating rate ω_r by 50 % over the entire altitude range. Note that for every described sensitivity calculation we also conducted a second run with the opposite change of parameter (i.e. factor 0.5; denoted as $\overline{SCn}$ in contrast to SCn, with run number n), as one cannot rely that the model necessarily responds linearly to the modifications.

ACPD
12, 30283–30326, 2012

The resulting absolute values for SGI and PGI of bromine VSLS can be found in Table 1. More illustrative are the relative differences introduced by the parameter changes in relation to the reference simulation, i.e. $(\mathrm{SGI}_{\mathrm{SC}n} - \mathrm{SGI}_{\mathrm{SC0}})/\mathrm{SGI}_{\mathrm{SC0}}$ with sensitivity run number n, as presented in Fig. 5 for source gas injection. The first interesting point is the small impact of photochemistry on the amount of short-lived source gases at the tropopause. SGI mixing ratios of both $CHBr_3$ and CH_2Br_2 hardly change (2 % at most) despite the relatively large modification of the photolysis/OH-reaction rate (± 50 %) in the runs SC1-4. In contrast, the perturbation is considerably larger in the simulations with altered vertical transport, at least for $CHBr_3$. A 50 % increase in detrainment below 353 K does not change the amount of $CHBr_3$ reaching the stratosphere significantly (≈ 1 %), as the majority of air detraining below the LZRH tends to subside again. The residual effect is most likely caused by the vertical variations of the LZRH which, for example, shows an annual cycle (e.g. Bergman et al., 2012). However, SGI of $CHBr_3$ shows a stronger response to increased detrainment above the LZRH (8 %) and the overall vertical ascent diagnosed by diabatic heating rates (6 %). There is clear evidence that the interplay between localized deep convection and large-scale vertical transport is the primary controlling factor for the injection of short-lived source gases into the stratosphere. An interesting fact to note is the more pronounced response to a decrease of the aforementioned parameters in the contrary runs ($\overline{\mathrm{SC5}}_\mathrm{c}$, $\overline{\mathrm{SC6}}_\mathrm{c}$, $\overline{\mathrm{SC12}}_\mathrm{c}$). Here, the relative differences are larger (−3 %, −13 %, −12 %, respectively) compared to their positive counterparts which is most likely caused by a "saturation" effect of VSLS abundance in the TTL region. Apparently this model region is well-mixed even for VSLS up to an extent that any further increase in convective activity or diabatic transport will not increase their mixing ratios much further. In principle, the same applies also for CH_2Br_2, however the absolute and relative effect is much smaller. Actually this is not surprising, given the comparatively long photochemical lifetime of this species which makes it more independent from rapid vertical transport. In fact, SGI of CH_2Br_2 shows the strongest response to the modification of radiative heating (+1 %, −2 %), i.e. the slow large-scale transport.

ACPD
12, 30283–30326, 2012

3.2 Impact of dehydration on inorganic bromine

Most previous studies assumed that the dehydration of the TTL represents an effective process to remove Br_y^{VSLS} by scavenging (e.g. Dvortsov et al., 1999; Nielsen and Douglass, 2001; Warwick et al., 2006; Hossaini et al., 2010; Schofield et al., 2011). However, there is some observational evidence that VSLS are fully contributing to stratospheric bromine loading. Salawitch et al. (2010) deduced a significant contribution of VSLS to stratospheric bromine in the range of 5–10 pptv by comparing BrO observations from multiple platforms in the Arctic. Considering the current estimates of VSLS mixing ratios in the boundary layer (1.6 and 1.1 pptv for the most abundant species, $CHBr_3$ and CH_2Br_2, respectively; Montzka and Reimann, 2011), this means a dominant part of the available bromine from VSLS is able to reach the stratosphere. This is consistent with our findings: Fig. 6 presents observations of organic bromine source gases (CBr) including $CClBrF_2$, $CBrF_3$, CH_3Br, $CHBr_3$ and CH_2Br_2 from aircraft observations Cr-AVE (Kroon et al., 2008) and TC4 (Toon et al., 2010) together with the corresponding values for the reference simulations $SC0_{a-c}$, similar to Salawitch et al. (2010). We generally achieve good agreement with the observational data for the run $SC0_c$ with additional 5 pptv from VSLS ($CHBr_3$ and CH_2Br_2), summing up to a total of about 20 pptv of CBr in the troposphere. The interesting point here is that the associated Br_y profile of run $SC0_c$ also reaches 20 pptv at an altitude where all organic source gases are degraded (around 30 km), i.e. the VSLS contribute completely to stratospheric bromine thus ruling out dehydration as an efficient loss process for bromine. This is fully consistent with the recent estimations of stratospheric inorganic bromine of 19.5–24.5 pptv (Montzka and Reimann, 2011). In fact our Br_y mixing ratio is rather at the lower end as we do not include some minor bromine source gases in the model, for example Halon-2402 (average boundary layer mixing ratio of ≈ 0.5 pptv) and the VSLS CH_2BrCl, $CHBr_2Cl$, $CHBrCl_2$ (totaling ≈ 1.1 pptv; Montzka and Reimann, 2011). However, as these species are sufficiently long-lived in the troposphere with average lifetimes of 20 yr for Halon-2402 and 150, 69 and 78 days for the VSLS, respectively,

ACPD
12, 30283–30326, 2012

one can safely assume that they would fully contribute to stratospheric bromine loading in the model. The resulting mixing ratio of stratospheric Br_y would be then around 22 pptv and therefore perfectly match the WMO estimate.

We came to a similar conclusion regarding the ineffectiveness of dehydration as a loss process for Br_y^{VSLS} in our previous study with a similar model setup (Aschmann et al., 2011). The main reasons we found were on the one hand the effectiveness of heterogeneous reactions in converting potentially soluble bromine reservoir species to insoluble reactive species, on the other hand the adsorption of Br_y on falling ice particles was found to be not very efficient as well, even if one ignores heterogeneous chemistry. In this study, we investigate the associated processes in more detail and test the robustness of our previous findings. Section 3.2.1 examines the partitioning of inorganic bromine in the TTL whereas Sect. 3.2.2 analyzes the efficiency of the adsorption process itself.

3.2.1 Partitioning of inorganic bromine

The partitioning among the inorganic bromine species in the TTL region between the LZRH and the cold point is a crucial factor determining the loss of Br_y due to dehydration given the fact that only certain species among the Br_y family can be scavenged by falling droplets or particles. HBr, HOBr and $BrONO_2$ are generally thought to be highly soluble in liquid water (e.g. Law and Sturges, 2007), however, the situation for ice, the most likely phase of water in the extraordinary cold TTL, is much more uncertain. According to Crowley et al. (2010), currently only HBr is considered to be efficiently adsorbed on ice particles, thus the fraction of HBr to Br_y is an important factor for the loss of bromine due to dehydration.

The partitioning of Br_y at the TTL is the result of a complex interplay of gasphase, photolytic and heterogeneous reactions. Table 3 lists the associated reactions in the model whereas Fig. 7 provides an overview along with typical mixing ratios/number densities of the involved species together with typical reaction rates during day and night in the TTL at 362 K (15.5 km), i.e. within the altitude range where dehydration is most relevant. At this height and under sunlit conditions (panel a), there is approximately 1.1 pptv of Br_y available, provided mainly by the decay of $CHBr_3$ (80 %). 0.8 pptv can be allotted to the reactive species BrO (0.29 pptv) and Br (0.5 pptv), the rest to the reservoir species HBr and HOBr (0.16 and 0.15 pptv, respectively). BrCl and $BrONO_2$ are only available in insignificant amounts due to rapid photolysis. The most prominent feature of the Br_y photochemistry at this particular altitude is the rapid interconversion between Br and BrO, driven mainly by the photolysis of BrO (P1) and the reaction of Br with O_3 (R1). BrO also reacts rapidly with HO_2 forming HOBr, balanced by the efficient photolytic destruction of the latter species (P2) which in turn leads again to Br. HBr is efficiently formed by the reactions with HCHO and HO_2, clearly outweighing the loss via photolysis and OH reaction. Actually, the fraction of HBr to Br_y would exceed 50 % if only the photochemistry would be taken into account (Fig. 8). However, heterogeneous reactions on ice particle surfaces represent a very efficient conversion mechanism for bromine reservoir species. Although the conditions that allow the formation of ice particles are rarely matched, relative to the scale of the whole TTL, the conversion rates of the heterogeneous reactions are so large that they are able to significantly alter the tropical Br_y partitioning (Figs. 1, 7). The most important reactions (H2, H3) link HBr and HOBr to their chlorine counterparts (HOCl and HCl, respectively), leading both to the formation of BrCl which is quickly photolyzed to Br (P5). Also efficient are the reactions of HBr with HOBr (H1) and with $ClONO_2$ (H7).

During nighttime, the mixing ratio of Br_y is lower, about 0.8 pptv, as there is no substantial destruction of organic source gases that balances the continued inflow of Br_y-free air provided by convection. The concentration of Br drops drastically due to the absence of photolytic production and also the amount of BrO is roughly halved, leaving most inorganic bromine in the form of reservoir species. Heterogeneous reactions play again an important role in controlling the partitioning among the reservoir species: due to the lack of dissociating radiation and the abundance of chlorine compounds BrCl becomes the largest reservoir with 0.26 pptv, closely followed by HOBr (0.25 pptv). The concentrations of $BrONO_2$ and especially HBr are lower (0.1 and 0.01 pptv, re-

ACPD
12, 30283–30326, 2012

spectively), as there are efficient heterogeneous reactions present that rapidly convert these species.

To isolate the effect of heterogeneous chemistry, we first conducted a sensitivity calculation without any heterogeneous chemistry included ($SC7_c$, Table 2), similar as in Aschmann et al. (2011). The omission of these efficient conversion reactions thoroughly changes the Br_y partitioning: given the same conditions as presented in Fig. 7 for reference run $SC0_c$, the mixing ratio of HBr reaches 0.35 pptv whereas the fraction of both reactive species (Br, BrO) drops to about 0.1 pptv, each. As the overall abundance of Br_y at this level is reduced to 0.63 pptv this means that more than 50 % of inorganic bromine is in the form of HBr. In the reference simulation, the fraction is below 15 %. The corresponding profiles for HBr and Br_y from run $SC0_c$ and $SC7_c$ are presented in Fig. 8. The difference in inorganic bromine between the two simulations represents the loss due to dehydration, which ranges from 0.4 to 0.6 pptv depending on the season, being slightly higher compared to our previous study with an earlier model version (0.3–0.4 pptv; mainly attributable to subtle changes in the vertical transport calculation and the update of kinetic data; Aschmann et al., 2011). Considering the assumed detrainment mixing ratio of 1 pptv each for $CHBr_3$ and CH_2Br_2, which corresponds to a maximum possible contribution of 5 pptv of Br_y from short-lived sources, this means that about 10 % of Br_y^{VSLS} is lost due to dehydration.

Obviously the partitioning of Br_y strictly constrains the loss of bromine due to dehydration. As the heterogeneous reactions significantly alter the partitioning we performed the sensitivity calculation $SC19_c$ (Table 2) where we changed the uptake coefficient γ for the most important reactions that convert adsorbed HBr (reactions H1, H3, H7; Table 3, Fig. 7) by ± 50 %. However, the observed effect on Br_y is negligible (≈ 0.02 %). Apparently the heterogeneous reactions are efficient to such an extent that the partitioning of Br_y is robust even against relatively strong changes of the uptake coefficients (the relative uncertainty of the corresponding coefficients is generally lower than 50 %; Sander et al., 2011).

ACPD
12, 30283–30326, 2012

Another aspect that could potentially influence the partitioning is a secondary channel of the reaction of BrO with HO_2 (R12). This reaction has a comparatively large turnover rate (Fig. 7) and generally leads to the production of HOBr, though it is possible that there is also a small yield of HBr (e.g. Mellouki et al., 1994; Bedjanian et al., 2001). Lary (1996) conducted a modeling study which investigates the effect of this additional channel and found that it can significantly increase the abundance of HBr above 20 km in mid latitudes. We reproduced this experiment with an assumed yield of HBr-production from reaction R12 of 0.1 % in run SC17c and can basically confirm the findings of Lary (1996) for mid latitudes. In the tropics, however, we find that the differences in HBr abundance within the crucial altitude range between LZRH and cold point are negligible (< 0.004 pptv).

3.2.2 Adsorption of HBr

Section 3.2.1 discusses the importance of Br_y partitioning for the susceptibility of inorganic bromine to dehydration, however, the actual loss process is the adsorption of these tracers on sedimenting particle surfaces, especially HBr on ice particles. As described in the model description in Sect. 2, we use a simple parametrization based on Eq. (1) to calculate the reversible uptake of HBr on ice surfaces, avoiding microphysical details. Since important details of the microphysical uptake of bromine species are still unknown or poorly quantified, a significant advantage of this simplified approach is the reduced effort in exploring the parameter space, as there are relatively few variables to consider. In our previous study where we used the same approach (Aschmann et al., 2011), we found that on average only 20–40 % of available HBr in each model grid box is actually on the ice surface.

Table 2 presents the conducted sensitivity runs together with the main indicator for dehydration efficiency, the mixing ratio of Br_y upon entering the tropical stratosphere at 380 K (≈ 17 km). The primary parameters that have been altered are: (1) temperature (± 2 K, run $SC10_c$) which constrains the amount of ice in the TTL and consequently the available surface area density A; (2) partition coefficient K_{linC} of Eq. (1) (± 50 %, run $SC13_c$) which regulates the fraction of gasphase and adsorbed HBr and (3) sedimentation velocity (± 50 %, run $SC11_c$) that controls the displacement and eventual removal of adsorbed species. To single out the impact of the adsorption process and avoid the problem of HBr-depletion by heterogeneous reactions (see Sect. 3.2.1), the mentioned sensitivity runs are calculated without heterogeneous chemistry and thus cannot be compared directly to the reference simulation $SC0_c$ but to run $SC7_c$ which bears the same modification. The relative difference in Br_y at 380 K between the sensitivity calculations and run $SC7_c$, i.e. $(Br_{y\,SCn} - Br_{y\,SC7})/Br_{y\,SC7}$, is illustrated in Fig. 10.

The impact of the 2 K-temperature modification on inorganic bromine at the top of the TTL is small, about ± 0.5 % compared to $SC7_c$. This is an interesting result as even this relatively small temperature change significantly alters the amount of H_2O (± 30 % at 380 K, Fig. 9) and in turn the available ice particle surface, though apparently without notable consequences for the efficiency of the heterogeneous chemistry.

More important is the partition coefficient K_{linC} for HBr which directly controls the fraction of this species on the ice surface. Varying this parameter by ± 50 % changes the amount of Br_y by −5 % and 10 % (for an increase/decrease, respectively), indicating a moderate sensitivity of inorganic bromine to this variable.

The sedimentation velocity of the ice particles constrains the actual loss of adsorbed species. In the model, this velocity is fixed to about 1.5 km day^{-1} which corresponds according to the utilized parametrization by Böhm (1989) to an average effective particle radius of 10 µm. Note that we showed in Aschmann et al. (2011) that the actual particle radii occurring in the model are generally smaller (about 0.5–2 µm) and we do not explicitly calculate microphysical ice particle growth which may lead to larger sizes. In situ aircraft observations of subvisual cirrus clouds in the TTL show that the distribution of ice particle radii peaks at about 5–9 µm (e.g. McFarquhar et al., 2000; Peter et al., 2003; Lawson et al., 2008; Weigel et al., 2011), i.e. our simplified assumption represents a reasonable value. Increasing the fall velocity by 50 % leads to a change of Br_y at 380 K of −3 % and 6 % for the opposite effect.

ACPD
12, 30283–30326, 2012

In a recent modeling study that explicitly calculates the microphysical uptake of bromine species (Marécal et al., 2012), the authors assume that tracers on ice particles are instantly washed out, arguing that the particles quickly grow by riming into fast-falling graupel and hail particles in the free troposphere. Actually, there is observational evidence that even at the tropopause large hydro meteors can be formed with effective radii above 100 µm in temporary layers of significant water vapor supersaturation introduced by displacement of air parcels due to gravity waves (e.g. Jensen et al., 1996, 2008). We tested this hypothesis in our sensitivity calculations $SC14_c$ and $SC15_c$. In both runs ice and adsorbed HBr is instantaneously removed whereas $SC14_c$ contains heterogeneous chemistry and $SC15_c$ not. Figure 10 shows the drastic removal of Br_y under this conditions, almost reaching −70 % for the latter run. This does not change much if heterogeneous reactions are taken into account ($SC14_c$), 67 % of inorganic bromine at 380 K or 1.23 pptv are lost. Considering that at 380 K 1.57 pptv of Br_y is originated from short-lived source gases (Fig. 3), this means that a large fraction of bromine from VSLS which is in product gas form is removed (≈ 80 %). However, when compared to the total amount of bromine from VSLS (5 pptv), the loss does not exceed 25 % even under these extreme circumstances since a majority of VSLS in this altitude region is still intact and is therefore not affected by scavenging. Interestingly, a change of the sedimentation velocity ($SC11_c$) or even the instantaneous removal of ice particles ($SC14_c$) does not significantly affect the resulting water vapor profile in the TTL region, as illustrated in Fig. 9. In fact, the resulting profile from run $SC14_c$ is even closer to the satellite observations below 15 km than the reference simulation $SC0_c$.

Finally, we tested the hypothesis that HOBr is adsorbed on ice surfaces as well. A kinetic study of Chu and Chu (1999) found that continued exposure of ice films to HOBr eventually leads to saturation. However, the process cannot be described as a Langmuir process and is difficult to quantify. Nonetheless, for our sensitivity study we simply assume that the adsorption of HOBr on ice proceeds identically to the one of HBr, i.e. we apply Eq. (1) with the same value for K_{linC} also to HOBr. Run $SC16_c$ contains the standard heterogeneous chemistry whereas $SC23_c$ was calculated without. In the

ACPD
12, 30283–30326, 2012

latter case, the response to this effect in the Br_y mixing ratio is about −4 % compared to the unperturbed run without heterogeneous reactions ($SC7_c$; Fig. 10). However, when comparing the runs with these reactions included, $SC16_c$ and $SC0_c$, the impact is significantly larger, exceeding −30 %. As a matter of fact even the absolute mixing ratio of Br_y is lower, 1.25/1.32 pptv for $SC16_c$/$SC23_c$ in contrast to 1.83/1.37 pptv for $SC0_c$/$SC7_c$. This means that in this case the heterogeneous chemistry actually promotes the loss of inorganic bromine due to dehydration in contrast to our previous findings, as long as HOBr is adsorbed as well. This is because the partitioning among the bromine reservoir species is shifted from HBr towards HOBr by heterogeneous conversion, especially during nighttime (Fig. 7). In fact, a partitioning analysis as presented in Fig. 7 but for run $SC7_c$ reveals (not shown here) that the HOBr mixing ratios are smaller by a factor of 3–5 when heterogeneous chemistry is switched off. Related to the available amount of bromine from short-lived sources (5 pptv), the loss due to dehydration under this circumstances adds up to about 12 %.

4 Discussion and conclusions

This study investigates the processes that control source and product gas injection of bromine from short-lived source gases and the associated loss of inorganic bromine in the TTL. The sensitivity calculations are conducted utilizing the 3-D isentropic CTM framework that has been already evaluated against observations and was used for related topics in earlier studies (Aschmann et al., 2009, 2011). In the model, we consider the two most abundant bromine VSLS, bromoform and dibromomethane, each with an assumed uniform boundary layer mixing ratio of 1 pptv, thus the maximum possible contribution of VSLS to inorganic bromine would be 5 pptv. This is in good agreement with available observations (Fig. 6), though we do not include some minor bromine short-lived source gases which may even increase the contribution of VSLS by 1 pptv to aproximately 6 pptv (e.g. Hossaini et al., 2012).

ACPD
12, 30283–30326, 2012

Our results suggest that even for the short-lived tracers source gas injection is the dominant pathway into the stratosphere. The relative fraction of SGI averaged in the tropics varies with convective and large-scale vertical transport in the range of 40–60 % and 92–95 % for $CHBr_3$ and CH_2Br_2, respectively. This is in good agreement with the modeling studies of Hossaini et al. (2010, 2012) who find SGI fractions of about 50 % for $CHBr_3$ and 90 % for CH_2Br_2. Brinckmann et al. (2012) give a lower estimate, 21/74 % for $CHBr_3$/CH_2Br_2, based on a single balloon observation above Teresina, Brazil. In another modeling study, Liang et al. (2010) find a fraction of 50 % for both VSLS combined, which is also lower than in our model (68 % for both species). The absolute values of SGI/PGI mixing ratios, however, are difficult to compare as they are strongly dependent on the assumed emissions or boundary layer concentrations, which may vary significantly between the different studies and are still poorly constrained by observations due to the scarcity of data. Our average tropical SGI/PGI mixing ratios are 1.54/1.45 pptv for $CHBr_3$ and 1.88/0.12 pptv for CH_2Br_2. Especially in the case of $CHBr_3$ the tropical mixing ratio at 380 K or 17 km in our model with about 0.5 pptv is likely highbiased, as the available aircraft and balloon measurements of this species generally show lower values at this altitude, in the range of 0–0.3 pptv (e.g. Kroon et al., 2008; Laube et al., 2008; Aschmann et al., 2009; Hossaini et al., 2010; Liang et al., 2010; Toon et al., 2010; Aschmann, 2011; Hossaini et al., 2012; Ordóñez et al., 2012; Brinckmann et al., 2012, see also Fig. 6). The most probable explanation for this discrepancy is the simplified treatment of convective uplifting of short-lived source gases in the B3DCTM. As our model does not explicitly contain the boundary layer and the free troposphere, we have to assume a fixed uniform detrainment mixing ratio for VSLS which is certainly not the optimal representation for such a short-lived species. We demonstrated the impact of regional emissions in Aschmann et al. (2009) which are completely ignored in this study for the sake of simplicity. On the other hand, the discrepancies between our model and observations are generally smaller for the more long-lived CH_2Br_2, that means the assumption of a fixed detrainment mixing ratio seems more justified in this case.

ACPD
12, 30283–30326, 2012

Contribution of very short-lived substances

J. Aschmann et al.

The extent of source gas injection of the investigated VSLS is not very sensitive to changes in the photochemical decay in general. More important, particularly for shorter-lived species like $CHBr_3$, are variations in convective and large-scale vertical transport, in particular in the crucial range between the LZRH and the cold point. This confirms the findings of a recent study by Bergman et al. (2012), who did a detailed analysis of vertical transport in the TTL and came to a similar conclusion. For the considerable longer-lived CH_2Br_2, the overall sensitivity is smaller and the photochemical degradation is of equal importance compared to the vertical transport.

The second part of this study investigates the impact of dehydration on inorganic bromine in the TTL. In our previous study (Aschmann et al., 2011) we found that loss of Br_y due to dehydration is negligible, in contrast to most earlier modeling studies which used a fixed washout lifetime for Br_y (e.g. Dvortsov et al., 1999; Nielsen and Douglass, 2001; Warwick et al., 2006; Hossaini et al., 2010). In the present study, we look into the involved processes in more detail to further refine our results. Adsorption of soluble species on ice particles may play an important role in the exceptional cold TTL and as only HBr is currently known to be efficiently adsorbed on ice (Crowley et al., 2010), the partitioning of Br_y is a critical factor. Our partitioning analysis shows that heterogeneous reactions on ice surfaces efficiently shift the equilibrium in the Br_y family from HBr towards the insoluble Br and BrO. The average tropical HBr/Br_y fraction drops from about 50 % to 15 % in the range between LZRH and cold point, if heterogeneous reactions are taken into account, strictly constraining the possible loss of Br_y due to dehydration in the first place. Apparently these reactions are efficient to such an extent that even relatively strong changes to the associated uptake coefficients (± 50 %) do not alter the Br_y partitioning significantly, as shown by our sensitivity calculations. Due to the efficiency of the heterogeneous chemistry in converting HBr we find no considerable loss of Br_y. In contrast, if these reactions are switched off, 0.4 to 0.6 pptv of Br_y are scavenged (i.e. about 10 % of Br_y^{VSLS}), which is slightly higher compared to our previous estimate (0.3–0.4 pptv; Aschmann et al., 2011). The relative loss is conspicuously smaller compared to previous modeling studies which used a simple washout lifetime

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |

ACPD
12, 30283–30326, 2012

Contribution of very short-lived substances

J. Aschmann et al.

for Br_y (60 %; Hossaini et al., 2010) or remove a fixed percentage of Br_y upon entering the stratosphere (38 %; Schofield et al., 2011) but is consistent with the results of Liang et al. (2010) who modeled the dehydration process in more complexity and found a relative loss of 5 % in the upper troposphere.

The adsorption process itself that leads to the actual loss of bromine in TTL is not sensitive to moderate changes in temperature. Although the amount of ice and therefore the available particle surface is drastically changed by even a relatively small change of ambient temperature (in our case, ± 2 K), the loss of Br_y is not significantly affected. More important are the sedimentation velocity of ice particles and the partition coefficient K_{linC} for HBr. A ± 50 % perturbation of these variables yields a change of Br_y loss in the range of ± 3–10 %. The removal of Br_y becomes more effective if adsorbed species on ice particles are instantaneously removed. Marécal et al. (2012) argued in their modeling study about the transport and uptake of bromine species in the TTL that the majority of ice particles quickly grow by riming and therefore acquire high fall velocities, so that the assumption of instantaneous removal is justified. If this is indeed the case also for the TTL, our sensitivity calculation suggests that about 1.2 pptv of Br_y^{VSLS} is lost which corresponds to 80 % of the available product gas from VSLS in the upper TTL region (25 % of the total contribution of VSLS to stratospheric bromine). Finally, we tested the hypothesis that HOBr is adsorbed on ice the same way as HBr. Under this circumstances, about 0.6 pptv or 12 % of Br_y^{VSLS} is removed. This is caused by the fact that the heterogeneous chemistry shifts the balance in the Br_y family away from HBr not only towards Br and BrO, but also towards HOBr which in turn is deposited on the ice.

In a condensed form, the main points of our study can be summarized as follows:

1. Most crucial for the contribution of VSLS to stratospheric bromine is the extent of source gas injection for these species, as they are not affected by scavenging. The fraction of source gas injection is about 50 % for $CHBr_3$ and 93 % for CH_2Br_2. In the case of $CHBr_3$, our results suggest that this fraction is critically dependent on vertical transport, especially convection above the level of zero radiative heating,

ACPD
12, 30283–30326, 2012

in contrast to uncertainties in photochemical degradation which are remarkably less important. For CH_2Br_2, the overall sensitivity is smaller as it is less reliant on rapid vertical transport in order to reach the stratosphere due to its considerable longer lifetime.

2. Since only certain species (more precisely: only HBr) among the family of inorganic bromine are susceptible to adsorption on ice particles, the partitioning within the family is an important factor. We find that the partitioning is clearly dominated by heterogeneous chemistry which shifts the equilibrium away from HBr towards Br, BrO, and, to a lesser extent, HOBr.

3. Heterogeneous activation effectively prevents loss of inorganic bromine, if only HBr is assumed to be adsorbed on ice particles. If these reactions are ignored, about 10 % of Br_y^{VSLS} can be removed by scavenging. A loss of similar magnitude is examined if HOBr is assumed to adsorb on ice as efficiently as HBr. To improve our understanding of the role of dehydration for the removal of inorganic bromine it is therefore crucial to further extend our knowledge about surface and uptake processes on particles also for other species than HBr.

4. Ice particle growth represents an uncertainty factor in most simulations, as this process is generally not microphysically resolved in global models though it is directly related to the sedimentation velocity of ice in the TTL. We found no large sensitivity to moderate changes of this quantity in our model, only if the majority of ice particles grows fast enough to justify an instantaneous removal of ice from the TTL up to 25 % of bromine from VSLS may be lost.

5. If one assumes that there is on average about 6 pptv of bromine from short-lived sources in convective updrafts, we find a most likely contribution of VSLS to stratospheric bromine in the range of 4.5–6 pptv. This is fully consistent on the one hand with observations of source gases in the troposphere and on the other hand with Br_y estimates derived from BrO observations in the stratosphere.

ACPD
12, 30283–30326, 2012

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ACPD
12, 30283–30326, 2012

Contribution of very short-lived substances

J. Aschmann et al.

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ACPD
12, 30283–30326, 2012

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Table 1. Overview of conducted transport-related sensitivity calculations and the corresponding source and product gas injection mixing ratios (in pptv) for 2006 (for the nomenclature of the runs, see Sect. 3.1.1). The parameters j photolysis rate, k rate constant, d_c convective detrainment rate, ϖ_r radiative heating rate have been modified each by ± 50 % (factors 1.5, 0.5) in the respective model run. The runs where a parameter is decreased are not listed here explicitly but their results are given in parentheses. For example, the SGI mixing ratio of $CHBr_3$ where the photolysis rate of this species is increased by 50 % is 1.52 pptv (run $SC1_c$). The corresponding run $\overline{SC1}_c$ with the opposite effect, 50 % reduction of $CHBr_3$ photolysis, yields a value of 1.57 pptv. Entries containing the star symbol (*) are identical to the corresponding values of the reference simulations $SC0_{a-c}$.

	$CHBr_3$		CH_2Br_2		
Run	SGI	PGI	SGI	PGI	Description
$SC0_{a-c}$	1.54	1.45	1.88	0.12	Reference simulation
$SC1_c$	1.52 (1.57)	1.48 (1.43)	*	*	Increased j for $CHBr_3$ photolysis
$SC2_c$	*	*	1.86 (1.90)	0.14 (0.10)	Increased j for CH_2Br_2 photolysis
$SC3_c$	1.52 (1.57)	1.47 (1.43)	*	*	Increased k for OH reaction with $CHBr_3$
$SC4_c$	*	*	1.85 (1.90)	0.15 (0.10)	Increased k for OH reaction with CH_2Br_2
$SC5_{a-c}$	1.57 (1.49)	1.43 (1.50)	1.88 (1.87)	0.12 (0.13)	Increased d_c below 353 K
$SC6_{a-c}$	1.67 (1.35)	1.32 (1.65)	1.89 (1.86)	0.11 (0.14)	Increased d_c above 353 K
$SC12_{a-c}$	1.64 (1.37)	1.36 (1.66)	1.90 (1.84)	0.10 (0.13)	Increased ϖ_r globally

ACPD
12, 30283–30326, 2012

Contribution of very short-lived substances

J. Aschmann et al.

Table 2. Overview of conducted dehydration-related sensitivity calculations together with the tropical averaged mixing ratio of Br_y at 380 K (in pptv) for 2006. Values in parentheses denote the sensitivity calculations where the opposite effect was applied (compare Table 1). Entries containing the star symbol (*) are identical to the corresponding values of the reference simulations $SC0_{a-c}$.

Run	Br_y @380 K	Description
$SC0_{a-c}$	1.83	Reference simulation
$SC7_c$	1.37	No heterogeneous chemistry
$SC10_c$	1.38 (1.37)	No het. chem., temperature increased by 2 K
$SC11_c$	1.32 (1.45)	No het. chem., sedimentation velocity increased by 50 %
$SC13_c$	1.30 (1.50)	No het. chem., K_{linC} for HBr increased by 50 %
$SC14_c$	0.60	Instantaneous removal of adsorbed species
$SC15_c$	0.43	No het. chem., instantaneous removal of adsorbed species
$SC16_c$	1.25	HOBr adsorbed on ice the same way as HBr
$SC17_c$	*	HBr yield of reaction R12 set to 0.1 %
$SC19_c$	*	γ increased by 50 % for reactions H1, H3, H7
$SC23_c$	1.32	No het. chem., HOBr adsorbed on ice the same way as HBr

Table 3. Gasphase, heterogeneous and photolytic reactions that control the partitioning of inorganic bromine in the model. Arrhenius A-factor, activation temperature E/R, uptake coefficient γ (for ice surfaces) and absorption cross-sections σ obtained from Sander et al. (2011).

			Gasphase reactions					A-factor	E/R
R1	Br	+	O_3	⟶	BrO	+	O_2	1.6×10^{-11}	780
R2	BrO	+	O^3P	⟶	Br	+	O_2	1.9×10^{-11}	−230
R3	BrO	+	NO	⟶	Br	+	NO_2	8.8×10^{-12}	−260
R4	BrO	+	OH	⟶	Br	+	HO_2	1.7×10^{-11}	−250
R5	BrO	+	ClO	⟶	Br	+	OClO	9.5×10^{-13}	−550
R6	BrO	+	ClO	⟶	Br	+	$Cl + O_2$	2.3×10^{-12}	−260
R7	BrO	+	BrO	⟶	2Br	+	O_2	1.5×10^{-12}	−230
R8	BrO	+	ClO	⟶	BrCl	+	O_2	4.1×10^{-13}	−290
R9	BrO	+	$NO_2 + M$	⟶	$BrONO_2$	+	M		
R10	$BrONO_2$	+	O^3P	⟶	BrO	+	NO_3	1.9×10^{-11}	−215
R11	HOBr	+	O^3P	⟶	BrO	+	OH	1.2×10^{-10}	430
R12	BrO	+	HO_2	⟶	HOBr	+	O_2	4.5×10^{-12}	−460
R13	BrO	+	OH	⟶	HBr	+	O_2	1.7×10^{-11}	−250
R14	Br	+	HCHO	⟶	HBr	+	O_2	1.7×10^{-11}	800
R15	Br	+	HO_2	⟶	HBr	+	O_2	4.8×10^{-12}	310
R16	HBr	+	OH	⟶	Br	+	H_2O	5.5×10^{-12}	−200
R17	HBr	+	O^1D	⟶	Br	+	OH	1.5×10^{-10}	0
R18	HBr	+	O^3P	⟶	Br	+	OH	5.8×10^{-12}	1500
			Heterogeneous reactions					γ	
H1	HOBr(g)	+	HBr(s)	⟶	2Br(g)	+	H_2O(s)	0.12	
H2	HOBr(g)	+	HCl(s)	⟶	BrCl(g)	+	H_2O(s)	0.3	
H3	HOCl(g)	+	HBr(s)	⟶	BrCl(g)	+	H_2O(s)	0.06	
H4	$BrONO_2$(g)	+	HBr(s)	⟶	2Br(g)	+	HNO_3(s)	0.3	
H5	$BrONO_2$(g)	+	H_2O(s)	⟶	HOBr(g)	+	HNO_3(s)	0.2	
H6	$BrONO_2$(g)	+	HCl(s)	⟶	BrCl(g)	+	HNO_3(s)	0.2	
H7	$ClONO_2$(g)	+	HBr(s)	⟶	BrCl(g)	+	HNO_3(s)	0.3	
H8	N_2O_5(g)	+	HBr(s)	⟶	Br(g)	+	NO_2(g) + HNO_3(s)	5×10^{-3}	
			Photolytic reactions					σ parametrization	
P1	BrO	+	$h\nu$	⟶	Br	+	O^3P	Gilles et al. (1997)	
P2	HOBr	+	$h\nu$	⟶	Br	+	OH	Ingham et al. (1998)	
P3	HBr	+	$h\nu$	⟶	Br	+	H	Nee et al. (1986)	
P4	$BrONO_2$	+	$h\nu$	⟶	Br	+	NO_3	Burkholder et al. (1995)	
P5	BrCl	+	$h\nu$	⟶	Br	+	Cl	Maric et al. (1994)	

ACPD
12, 30283–30326, 2012

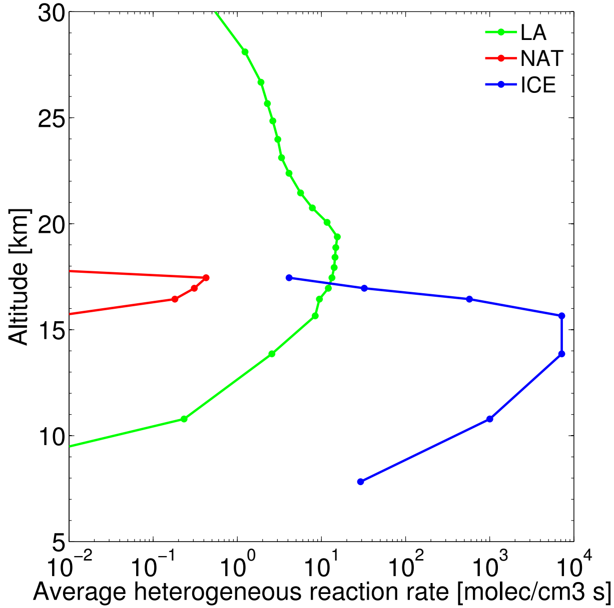

Fig. 1. Averaged tropical profiles (20° N–20° S, June, 2006) of heterogeneous reaction rates on liquid aerosols (LA), nitric acid trihydrate (NAT) and ice particles (ICE) in the CTM. The corresponding reactions are listed in Table 3.

ACPD
12, 30283–30326, 2012

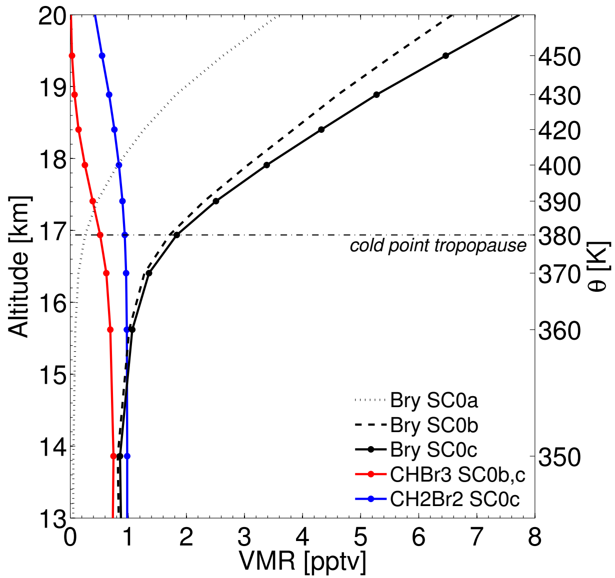

Fig. 2. Averaged tropical profiles (20° N–20° S, 2006) of inorganic bromine (Br_y), $CHBr_3$ and CH_2Br_2 from the reference simulation runs $SC0_{a-c}$.

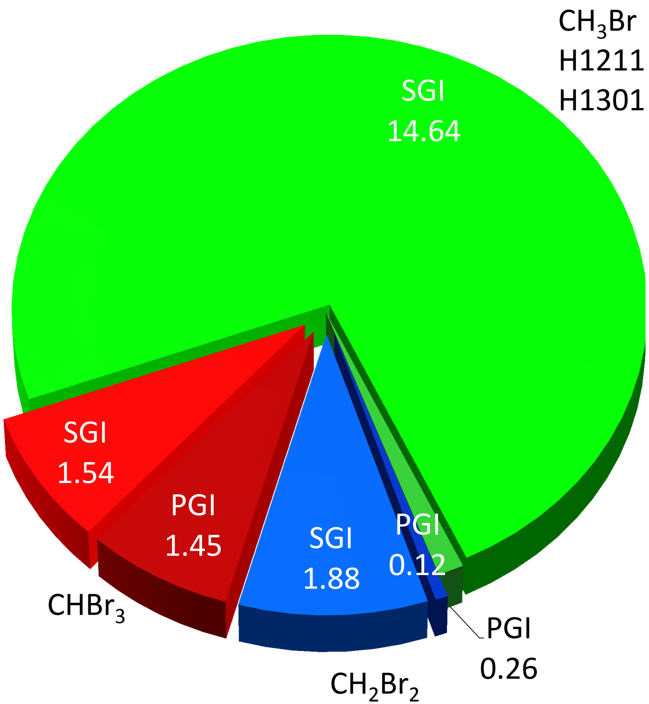

Fig. 3. Average tropical source and product gas injection (SGI/PGI) for bromine long-lived source gases (CH_3Br, H1211, H1301) and VSLS ($CHBr_3$ and CH_2Br_2) in the reference simulation run $SC0_c$ for 2006 in pptv.

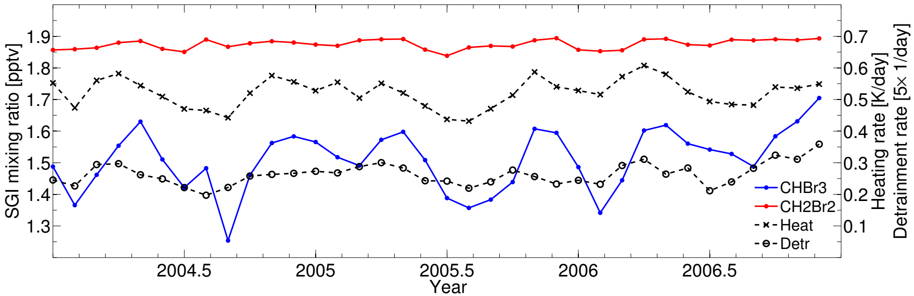

Fig. 4. Averaged tropical source gas injection of $CHBr_3$ and CH_2Br_2 (blue and red, left ordinate; given in pptv of contributed bromine) obtained from reference simulations $SC0_{a-c}$ together with ECMWF ERA-Interim radiative heating and convective detrainment rate (dashed, right ordinate). Note that the values for heating and detrainment rate are averages of the TTL region between 350 and 380 K, i.e. the upper tropopause layer above the LZRH up to the cold point. The detrainment rate is also scaled by a factor of five.

ACPD
12, 30283–30326, 2012

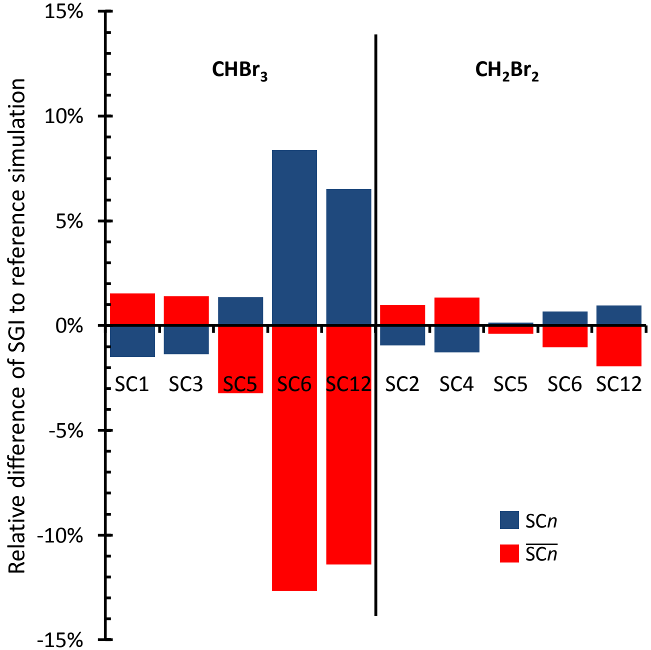

Fig. 5. Relative difference of tropical source gas injection mixing ratios of $CHBr_3$ and CH_2Br_2 between sensitivity calculations SC*n* and reference simulation SC0 for 2006. The blue and red bars denote sensitivity runs where the same parameter is modified in opposite directions (SC*n* and $\overline{\text{SC}n}$, see also Table 1).

ACPD
12, 30283–30326, 2012

Contribution of very short-lived substances

J. Aschmann et al.

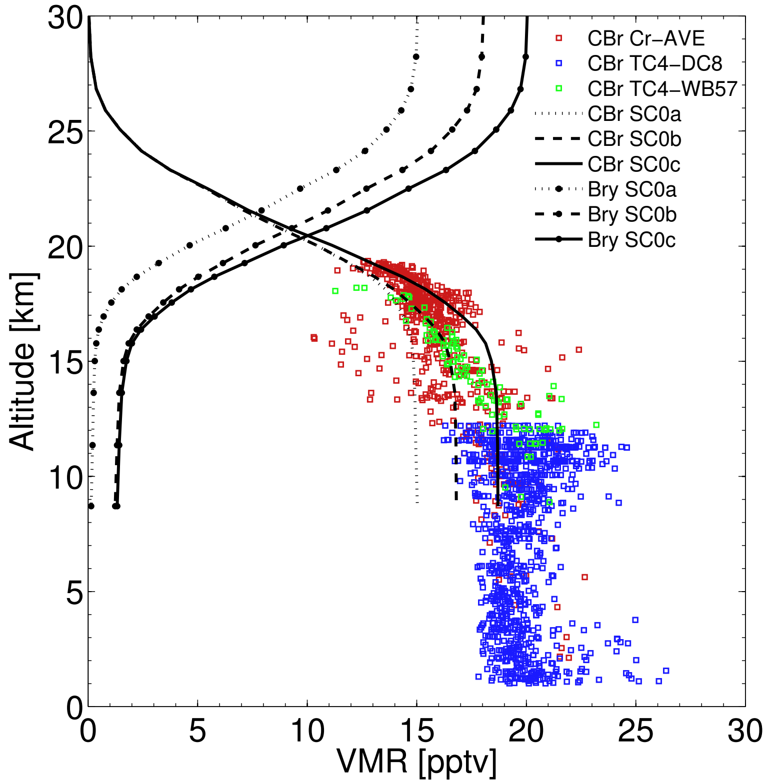

Fig. 6. Organic bromine source gases (CBr) including $CClBrF_2$, $CBrF_3$, CH_3Br, $CHBr_3$ and CH_2Br_2 from aircraft observations Cr-AVE (Kroon et al., 2008) and TC4 (Toon et al., 2010) in comparison with CBr and Br_y from the reference simulations $SC0_{a-c}$. The model data is a yearly average of 2006 for the observation area (60°–130° W; 40° N–10° S). Adapted from Salawitch et al. (2010, auxiliary material).

ACPD
12, 30283–30326, 2012

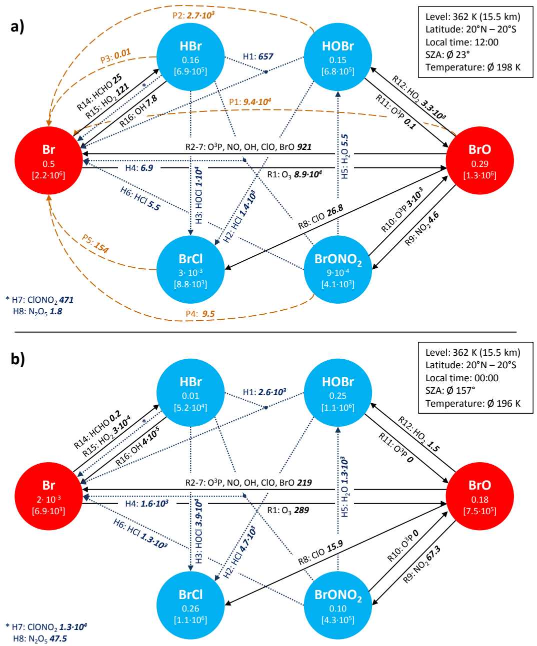

Fig. 7. Overview of Br_y chemistry in the TTL. Gasphase, photolytic and heterogeneous reactions are denoted by solid, dashed and dotted lines, respectively. The numbers represent a snapshot of reaction rates and tracer concentrations at 362 K in the tropics either under sunlit (upper panel) or nighttime conditions (lower panel) obtained from reference simulation SC0c (June, 2006). The values in the tracer circles are volume mixing ratio in pptv and number density in molec cm^{-3}. Each reaction is labeled with the reaction number (see Table 3), a possible additional reactant and the reaction rate in molec cm^{-3} s.

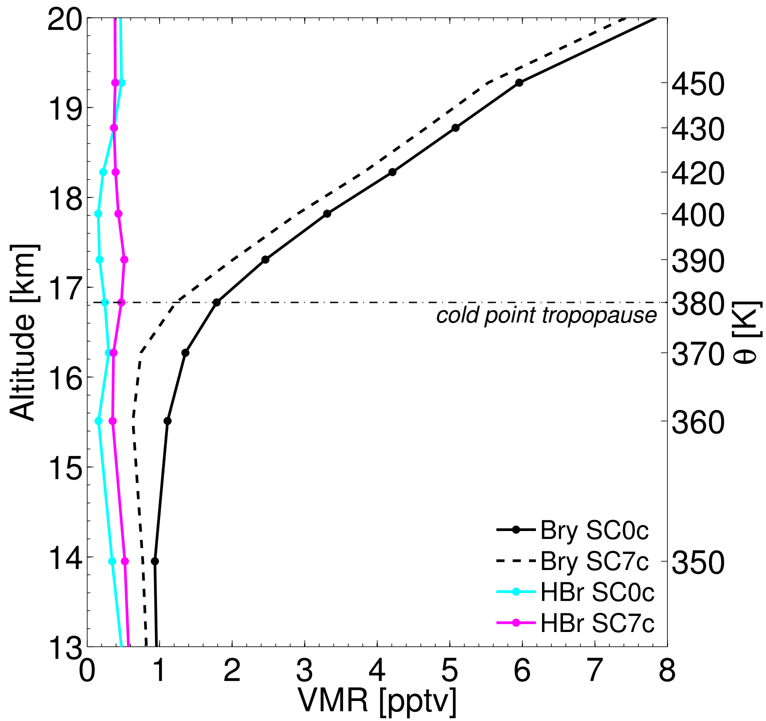

Fig. 8. Averaged tropical profiles (20° N–20° S) of Br_y and HBr from reference simulation $SC0_c$ and the sensitivity calculation without heterogeneous reactions $SC7_c$ for June 2006, 12:00 local time.

ACPD
12, 30283–30326, 2012

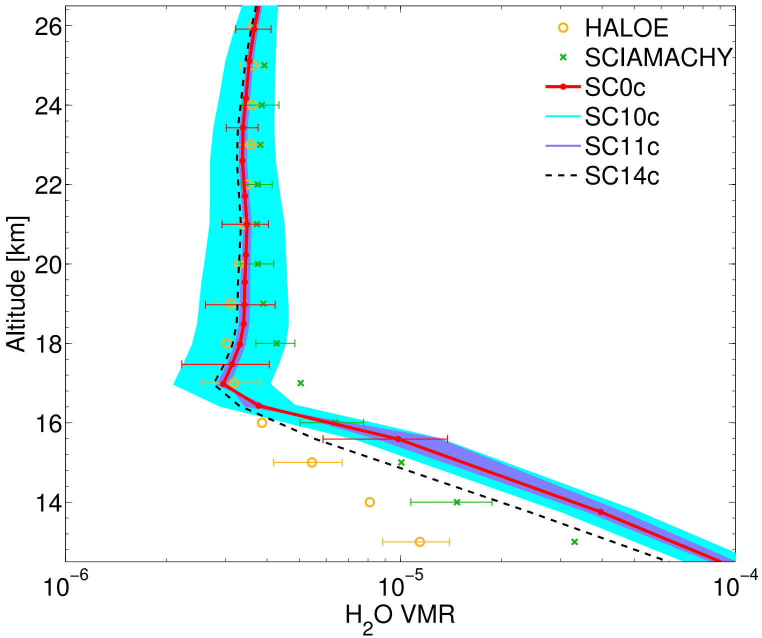

Fig. 9. Averaged tropical profiles (20° N–20° S) of H_2O from reference run $SC0_c$ and the sensitivity calculations $SC10_c$, $SC11_c$ and $SC14_c$ in comparison to satellite observations from HALOE (Grooß and Russell, 2005) and SCIAMACHY (Rozanov et al., 2010) for 2005. The shadings represent the range between the paired sensitivity runs, i.e. $SC10_c$, $\overline{SC10}_c$ and $SC11_c$, $\overline{SC11}_c$, respectively.

ACPD
12, 30283–30326, 2012

Contribution of very short-lived substances

J. Aschmann et al.

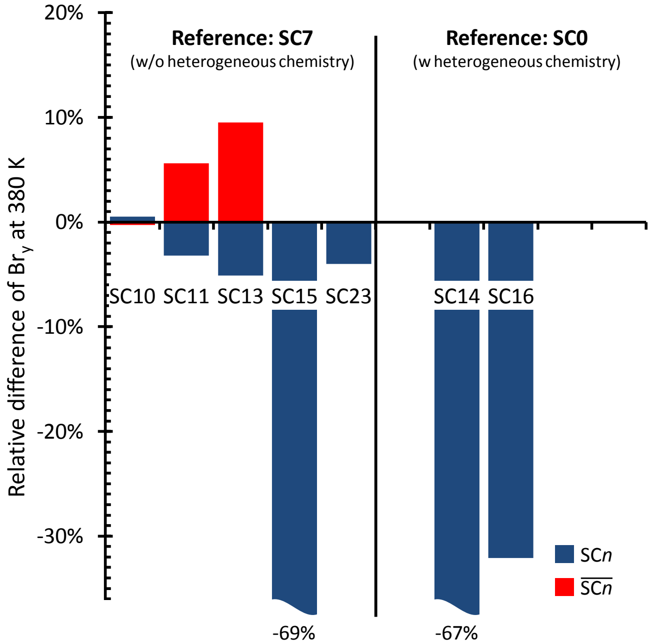

Fig. 10. Relative difference of tropical Br_y mixing ratio at 380 K between sensitivity calculation SC*n* and either SC7 (without heterogeneous chemistry, left) or SC0 (with heterogeneous chemistry, right) for 2006. The blue and red bars denote sensitivity runs where the same parameter is modified in opposite directions (SC*n* and $\overline{\text{SC}n}$, see also Table 2).

ACPD
12, 30283–30326, 2012

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J. Aschmann et al.