ANSWERS TO REVIEWERS AND INTERACTIVE DISCUSSIONS

Bromine partitioning in the tropical tropopause layer: implications for stratospheric injection

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General Answer

We are grateful to anonymous reviewers #1 and #3, Dr. Sinnhuber and Dr. Saunders for their constructive comments and suggestions, which helped us to improve the manuscript. In the present revised version we have fully addressed all the reviews and interactive comments, including updates on references, clarifying descriptions of model configurations, rephrasing of misleading implications and corrections/improvements on tables and figures.

To facilitate the reading, the original comments made by the reviewers have been copy-pasted here using **bold font**, while our answers are given in regular font. Additionally, we have copied into this response letter the current changes made to the original manuscript, using a *blue* and/or *italic* font type.

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1 Reviewer_#1

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1.1 General Remarks

Fernandez et al. present a modelling study about the partitioning of inorganic bromine in the tropical tropopause layer. Using global and box simulations, they investigate the source and product gas injection of bromine, in particular from VSLS. Special emphasis is exerted on the role of heterogeneous reactions, which are crucial for understanding bromine chemistry in the TTL. The study is well written and yields interesting results, for example the existence of a "tropical ring of inorganic bromine" in the TTL region. I recommend the manuscript for publication in ACP after addressing the following (mostly minor) comments.

We thank the reviewer_#1 for his/her very useful comments.

1.2 Specific Comments

• Section 2: The authors state that the global simulations where conducted for repeated 2000 conditions, whereas the the input data was from a previous CAMChem run. I was just wondering if this previous run reproduced the exceptional La Niña event during 2000. If that is the case, this would possibly affect your results from your "CTM-like" run as the atmospheric conditions were not quite exemplarily during this year.

Our "CTM-like" setup includes high frequency meteorological input from a previous CAM-

Chem climatic simulation that was configured in FR (free running) mode. In this way, the meteorological fields that we use for all sensitivity simulations are identical, but at the same time, are not representative of the meteorological conditions of any specific year. Indeed, the Sea-Surface Temperature (SST) and Sea-Ice coverage (SEAICE) fields included as boundary conditions are currently monthly averages from a 10 years-long period within the 2000 decade. So our model does not reproduce the typical behaviour of any of the El Niño/La Niña events observed during the modelled period. The text was modified as follows in order to make this point clear:

…A model spin-up of 15 years considering constant boundary conditions representative of the 2000 decade have been performed to ensure stratospheric stabilization of halogen sources, and the last of a 3 years-long simulation was used to compute the bromine atmospheric burden for all sensitivity runs.…

…To avoid dynamical perturbations, all sensitivities were performed in SD mode considering a high frequency meteorological input from a previous CAM-Chem FR climatic simulation.…

…The model was configured with prescribed sea surface temperatures (SST) and ice-coverage for the 2000 decade (Rayner, 2003), so results are not representative of the meteorology of any specific year (i.e., the SD mode used here does not reproduce the specific characteristics of any of the El-Niño/La-Niña type events within the modeled period).…

- **Section 2.1.4: I share the previous referee's concern of omitting ice uptake of HBr and HOBr, which are major nighttime reservoirs. The study by Aschmann et al. (2011) found no significant impact of HBr uptake, as stated in this section, however, this omission casts some doubt on the extraordinary high values of convectively transported Bry (see point below).**

We understand the concerns of reviewers #1 and #2 about not considering removal by ice-uptake for HBr and HOBr. But we would like to highlight that, for both species, an efficient washout on liquid droplets is considered throughout the troposphere. As shown in Fig. 10a, the SA (surface area) for liquid droplets (SA_{LIQ}) largely surpasses the surface area for ice crystals (SA_{ICE}) up to ~10 km, so the abundance of bromine species in the MBL and FT is controlled by washout due to liquid droplets, and not due to ice-uptake. Indeed, within CAM-Chem, the bromine removal in the lower troposphere is controlled by wet- scavenging of HBr (it is the dominant species and has a large acid dissociation constant), for which we have used an effective Henry's law constant of $K_H^{eff}(HBr)=7.2\times10^{13}$ M atm^{-1} in agreement with other studies (Yang et al., 2005; Parrella et al., 2012). Then, the large amounts of Br_y transported by rapid convection from the MBL and FT to the TTL cannot be attributed to the "omitted" ice-uptake of HBr and HOBr, as that process does not impact on the removal of Br_y below the lower limit of the TTL (i.e. ~12 km). It is also worth noting that for the other abundant species within the TTL ($BrONO_2$ and BrCl) CAM-Chem includes scavenging by ice-uptake.

Several previous publications have focused on the impact of considering different efficiencies for ice-uptake and washout of inorganic bromine species within the TTL (Sinnhuber and Folkins, 2006; Aschmann et al., 2011). As pointed out in the manuscript, the aim of this work was not to focus on the impact of considering different washout efficiencies, but to present a global picture of the implications of considering a full chemistry scheme of tropospheric bromine chemistry. Indeed, Aschmann and Sinnhuber (2013) found for their reference simulation (i.e. considering heterogeneous recycling and ice-uptake for HBr) that "the VSLS contribute completely to stratospheric bromine thus ruling out dehydration as an efficient loss process for bromine”.

Following both reviewers concerns, we have included the following lines in the manuscript. Please, see also the answer to reviewer_#2.

…An effective Henry’s Law washout efficiency considering the acid dissociation constant has been used for HBr, the most abundant bromine reservoir in the lower troposphere ($K_H^{eff}(HBr)=7.2\times10^{13}$ *M atm*$^{-1}$*, see Table S2). Uptake of HBr on liquid surfaces regulates the bromine scavenging within the MBL and FT in agreement with previous studies (Yang et al., 2005; Parrella et al., 2012).…*

…Our approach is consistent with the modelling framework of Aschmann and Sinnhuber (2013), who report that in their reference setup the organic VSL sources “contribute completely to stratospheric bromine thus ruling out dehydration (within the TTL) as an efficient loss process for bromine”…

• Heterogeneous reactions on ice, Table S1: I was surprised that the reaction of BrONO2 + HBr has not been included. It links two major nighttime reservoirs with =0.3 (Sander et al., 2011). Is there a specific reason to leave it out?

As we are implementing a full bromine chemistry scheme into a global model ranging from the ocean surface to the middle stratosphere, we have decided to keep the total number of chemical equations to a minimum. The reaction $BrONO_2 + HBr \rightarrow Br_2 + HNO_3$ was not considered because previous sensitivity studies showed that its impact on the bromine partitioning is negligible compared to the direct hydrolysis of bromine nitrate $BrONO_2 + H_2O \rightarrow HOBr + HNO_3$. Indeed, in our scheme the heterogeneous release of Br_2 back to the gas phase can proceed in a two-step process: 1st the $BrONO_2$ hydrolysis followed by reaction R1 in the main text ($HOBr + HBr \rightarrow Br_2 + H_2O$). The local Br_2 night-time maximum at 17 km in the vertical profiles (see modified Fig. 11) is a consequence of the Br_2 production due to this 2 step recycling, and is insensitive to whether or not $BrONO_2$ + HBr is included. We will however include it for completeness in the next version of the model.

• Br2: With a single exception on p. 17873, l. 26 the nighttime abundance of Br2 is mentioned nowhere. As many heterogeneous reactions lead to the production of Br2 I assume that this species has to be a major “reservoir” during nighttime. I think it would be illustrative to include it in the discussion of (nighttime) Bry partitioning and add it to Figs. 1 and 11, as the abundance of Br2 is a direct indicator of the effectiveness of heterogeneous reactions.

The reviewer has correctly pointed out the importance of Br_2 abundance as an indicator of the occurrence of heterogeneous reactions for certain regions of the atmosphere. In the manuscript, our selected indicators were BrCl and HOBr, because the nighttime formation of these species is much more rapid than the nighttime formation of Br_2 in the TTL, the main region of interest. We had originally decided not to include the Br_2 profile in Figs. 1 and 11 because the reaction rate for R2 is almost an order of magnitude faster than the rate for R1 (see Fig. 10c) in the TTL, consistent with BrCl being the dominant nighttime bromine reservoir in that region. However, the nighttime abundance of Br_2 surpass that of BrCl in the MBL and lower troposphere. We have therefore followed the reviewer’s suggestion and, upon revision, we will add profiles of Br_2 to the night-time partitioning panels. Accordingly, a discussion on its importance has been added to the text as follows:

…During nighttime, BrCl, HOBr and $BrONO_2$ dominate the inorganic bromine budget in the TTL and stratosphere, while HBr dominates in the FT and MBL (Fig 1B). Large volume mixing ratios of the diatomic Br_2 and BrCl species are maintained in the first few kilometres above the oceans due to the occurrence of heterogeneous recycling reactions over sea-salt aerosols (see Table S1). As the average depletion for bromide is larger than for chloride, the calculated abundance of Br_2 surpasses that of BrCl in the MBL. Their abundance decrease rapidly with increasing altitude following the vertical profiles of SA_{SSLT} (see Fig. 10a). The abundance of BrCl in the upper TTL increases due to the efficient heterogeneous recycling of inorganic chlorine reservoirs (i.e., HCl), which turns out to be more efficient than the Br_2 production via HOBr + HBr (see Sect. 3.3)….

…Second, the greater SA_{SSLT} existent in the WP region compared to the average Tropics (Fig. 10A) enhances the sea-salt aerosol recycling flux of Br_2 and BrCl. The resulting Br_y abundances within the MBL of the western pacific show a ~3-fold increase for the cam_Full_Br scheme ($Br_y^{Tropics} \approx 3.3$ pptv and $Br_y^{WP} \approx 10.6$ pptv), mostly due to the recycling of bromine released from the shortest lived of all the VSL species considered (CH_2IBr)….

- **Convective transport of Bry: The amount of PGVSL given in this study is largely dependent on convectively transported Bry released from sea salt aerosols from the MBL to the free troposphere or even higher (Sect. 3.2 and 3.5). Given that sea salt aerosols are apparently a major source of Bry even in the TTL (which is in contradiction with the results of Yang et al., 2005), there is little information given about the treatment of sea salt aerosols in the model.**

We have added the following sentence in the model description in order to clarify the treatment of sea salt aerosols in CAM-Chem.

…The sea-salt aerosol scheme considers four size bins for SSLT based on Mahowald et al. (2006). The formation of sea-salt aerosol in each size bin is a function of wind speed and humidity. The surface area density (SA_{SSLT}) used in this work is derived from the NaCl mass in each size bin and the effective radius of that bin. Sea-salt is lost through dry deposition (including gravitational settling) and wet removal. Overall the lifetime of sea-salt is less than 1 day (see Mahowald et al. (2006) for details)…

Having said that, we believe that the reviewers statement that in our model simulations “sea salt aerosols are apparently a major source of Bry even in the TTL” is not strictly correct. All the sensitivities presented in section 3.4 clearly indicates that the additional source of Br_y from sea-salt only impact on the PG_{VSL} levels reaching the upper TTL within strong convective regions, while they represent only a minor contribution (< 3%) to the PG_{VSL} injection for the tropical annual average. We have added the next sentence in the manuscript to make this point clear. Additional discussion on the importance of sea-salt aerosols is given in the reply to reviewer _#2, regarding the difference between our study and that of Liang et al. (2014).

… Finally, note that in the case of the tropical annual average the Br_y loading in the TTL is controlled by SG_{VSL} decomposition (mostly $CHBr_3$, Fig. 2A) and the sea-salt contribution represents < 3% of the PG_{VSL} reaching the upper TTL. Then, the additional inorganic source released from sea-salt only impact on the stratospheric bromine injection within strong convective regions, while due to the longer timescales of the dominant large scale ascent, sea-salt recycling reactions do not affect the average tropical PG_{VSL} injection on the global scale…

Furthermore, I'm puzzled by the effectiveness of convective transport of Bry in the model. In Sect. 3.2 it is stated that the Bry mixing ratio in the TTL may reach up to 3 pptv during vigorous convection events, roughly half of the Bry mixing ratios at the surface.

Firstly, according to Romps and Kuang (2010) only about 30% of air detraining in the TTL is actually from the boundary layer, the rest is entrained further upwards. Secondly, I'm surprised that such a large fraction of potentially soluble Bry "survives" the convective uplift, even when considering heterogeneous recycling. As stated by the previous referee this in contradiction with the recent study by Liang et al. (2014).

(Romps and Kuang, 2010) focus on the rapid convective transport of "undiluted" plumes, i.e. those air masses transported without being mixed with environmental air from their surroundings on their way up. In our CAM-Chem simulations, sea-salt heterogeneous recycling are responsible of maintaining large amounts of Br_y up to 3-5 km. Then, even when the convective transport is actually diluted by intrusion of surrounding air masses at higher altitudes than the MBL, those air masses would still be rich in inorganic bromine, thus favouring the rapid transportation of Br_y from the lower troposphere until the lower limit of the TTL. We have modified the manuscript in order to make this point clear. Please see Table 4, where *cam_NoSSLT* sensitivity indicates that when SSLT recycling reactions are turned off, the total Br_y reaching the lower TTL in the WP is reduced by a factor of 2.5 - 7 during periods of vigorous convection.

For further comments related to the differences between our results and those of Liang et al., (2014), please refer to the answer to Reviewer_#2 (BMS).

…Due to the fast vertical transport during convective events (hours to days), SG_{VSL} have not completely decomposed, and an additional source of Br_y in the lower TTL of the WP region arise from the detrainment of bromine-rich air masses entrained in the MBL and lower troposphere. Model sensitivities (see Table 4) indicate that during strong convection within the WP region the efficient sea-salt recycling occurring up to a height of ~3 km increase significantly the Br_y loading in the lower troposphere (see Fig. 11), and approximately half of the Br_y released in the MBL can reach the lower TTL ($Br_y^{MBL} \approx 7.9$ pptv and $Br_y^{12\ km} \approx 3.6$ pptv)…

1.3 Technical Remarks

– p. 17858, l. 2: switch "degradation" and "inorganic".

– p. 17873, l. 26: "..., being HOBr the dominant...". Some words are missing here.

Changes in response to both of these comments are made in the corrected manuscript.

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2 Reviewer_#2_BMS

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Fernandez et al. use a global model, together with sensitivity calculations from a box model, to investigate the processes that control the transport of bromine from very short-lived substances through the tropical tropopause layer and into the stratosphere. Two key findings of this study are that a "tropical ring of atomic bromine" is predicted for the TTL and that heterogeneous reactions in the TTL and in the troposphere are important for the VSLS product gas injection. The manuscript is generally well written and significantly adds important aspects to previous studies by investigating the role of heterogenous reactions and the role of atomic bromine in the TTL. I recommend publication in Atmos. Chem. Phys. after consideration of the following comments.

Thanks to Bjorn-Martin for his very constructive comments.

2.1 General Comments

One of the key messages of this study is the important role of heterogenous recycling for inorganic bromine. However, I am slightly confused on which types of surfaces heterogenous reactions are considered in the troposphere. In particular, is recycling on tropospheric non-sea-salt aerosol included? Fig. 7a shows SA_LIG throughout the troposphere from the surface to the upper troposphere. Is this all sea-salt aerosol?? Section 2.1.3 list only reactions on stratospheric sulfate aerosol, NAT, ice particles and sea-salt aerosol. Table S1 list reactions on stratospheric sulfate aerosol, NAT, "waterice aerosol" and sea-salt aerosol.

Within the troposphere, there are only two different types of surface areas (SA) where heterogeneous reactions occur: i) sea-salt aerosols (SA_{SSLT}) and ii) ice-surfaces (SA_{ICE}). Reviewers concerns on SA_{SSLT} reactions are addressed below after the next reply. The rest of the reactions shown in Table S1 occur on ice-crystals formed by condensation of water vapor in the cold TTL (SA_{ICE}). Tropospheric heterogeneous reactions for halogen species occurring over other types of surfaces (such as tropospheric sulfate, carbonate or other forms of liquid/solid aerosols) are not considered in our CAM-Chem setup. The SA_{LIQ} vertical profile shown in Fig. 10a was included only as an indicator of the vertical extent where wet-scavenging of bromine species occur.

Within the stratosphere, additional heterogeneous reactions that occur over other types of surfaces (such as stratospheric sulfate aerosol, NAT, and ice-crystals) are also considered. In order to make these points clear, we have corrected Table S1 and modified Section 2.1.3 in the following way (and replace the term ice-particle for ice-crystals in the whole text):

...Mechanistic improvements with respect to previous works (Ordóñez et al., 2012; Saiz-Lopez et al., 2012) are mainly based on the implementation of heterogeneous reactions for HBr, HOBr and $BrONO_2$ on tropospheric ice-crystals and stratospheric aerosol surfaces...

In addition to a recycling of HBr and HOBr to active bromine, sea-salt aerosols provide non-stoichiometric reactions that act as an additional source of bromine. It would be interesting if numbers could be given of how large this additional flux of bromine is in this model simulation. How are sea-salt aerosols treated in the model? By providing a flux of sea-salt aerosols and subsequent loss due to deposition? Or by prescribing a sea-

salt aerosol surface area? How detailed is the treatment of bromine depletion or enrichment in sea-salt aerosols (e.g., Sander et al., Inorganic bromine in the marine boundary layer: a critical review, Atmos. Chem. Phys., 3, 1301-1336, 2003) in the cam_Full_Br-simulation? Given that the role of sea-salt aerosols is one of the key points of the present study, I feel that more details should be provided here.

Even when we are using a simplified approach, the CAM-Chem implementation of bromine recycling within SSLT aerosol is one of the more complex parameterizations included in a global model. Sea-salt production and loss processes are computed for each gridbox above the ocean, and the transport, growth and deposition of SSLT aerosols is computed on-line (we do not used a prescribed SSLT Surface Area) following Mahowald et al. (2006) (please, see also the answers to Reviewer_#1). The bromide depletion of the SSLT aerosol is treated in a simple way, and an average DF (depletion factor) considering the chloride and bromide composition of a typical marine aerosol has been used.

…Heterogeneous recycling reactions of HOBr, $BrNO_2$ and $BrONO_2$ (and their equivalent chlorine compounds) are also considered to proceed on sea-salt aerosol surfaces (SA_{SSLT}), considering that the rate limiting step is the uptake of halogen species on the aerosol surface (McFiggans et al., 2000). Within this approach we assume that the initial chloride and bromide existent in the bulk of the aerosol is large enough for the heterogeneous reaction to occur until the sea-salt aerosol is removed by washout…

…Note that this process represents an additional source of inorganic bromine and chlorine in the troposphere, independent from the oceanic flux of VSL halocarbons described above (i.e. these are non-stoichiometric reactions releasing Cl and Br atoms from sea-salt aerosols to the gas phase). An average depletion efficiency of 0.65 and 0.35 for bromide and chloride, respectively, has been considered following Ordóñez et al. (2012) (see Table S1). The annual SSLT bromine source yields 2.9 Tg yr^{-1} (53% in the Southern Hemisphere) of which only 1.3 Tg yr^{-1} are released within the tropics. The contribution of SSLT heterogeneous reactions to the Br_y loading for different geographical and vertical regions is analyzed in Sect. 3.4…

…Finally, note that in the case of the tropical annual average the Br_y loading in the TTL is controlled by SG_{VSL} decomposition (mostly $CHBr_3$, Fig. 2A) and the sea-salt contribution represents $< 3\%$ of the PG_{VSL} reaching the upper TTL. Then, the additional inorganic source released from sea-salt only impact on the stratospheric bromine injection within strong convective regions, while due to the longer timescales of the dominant large scale ascent, sea-salt recycling reactions do not affect the average tropical PG_{VSL} injection on the global scale...

I'm a bit worried about exclusion of ice uptake for HOBr and HBr (p.17865). Why does the implemented scheme give unrealistic results? Are there any mistakes or unrealistic assumptions that have been identified? How do you judge that the results are unrealistic, given that basically no measurements exist of these species in the TTL?

The implementation of the NEU scheme (Neu and Prather, 2012) is based on the uptake and hydrolysis of nitric acid (HNO_3). Several sensitivity simulations have shown that when the NEU scheme is applied to halogen hydro- and oxo- acids, a very efficient washout of inorganic bromine (and iodine) species exists. Then, total Br_y values between 10 and 15 km are below 0.05 pptv (as low as 0.01 pptv), indicating that the contribution of inorganic bromine should be neglected over all the troposphere, and the total VSL contribution to stratospheric loading should be half of that presented in the manuscript. Indeed, when ice-uptake is included for HBr, more than 90% of the Br_y released from the photodecomposition of VSL-species above the lower TTL limit (12 km) is removed as soon as the carbon bond is broken. This is in large contrast to the balloon-based measurements of Dorf et al. (2008), which showed a rapid increase of the BrO mixing ratio within the TTL, in a region where large amounts of ice-particles are continuously formed. These so-called "unrealistic results" are not apparent by comparing model and measured HBr or HOBr because, as the reviewer correctly states, such measurements do not exist in the TTL. Rather, results using the NEU scheme are deemed to be inconsistent with the abundance of Br_y inferred from the Dorf et al. (2008) measurements of BrO, and the abundances and lifetimes of the long-lived bromocarbons given in the 2010 WMO/UNEP report. Nonetheless, in response to the reviewer's comment, we have removed the word "unrealistic" from the revised paper.

We have updated the manuscript in the following way to highlight these results. Please, see also the answer to reviewer_#1 on this point.

…Then, the halogen removal scheme in CAM-Chem was implemented with ice-uptake turned on for all chlorine species and for $BrONO_2$, $BrNO_2$, BrCl and Br_2, considering that the removal of this reservoir halogen species occurs at liquid, ice, and mixed-phase clouds in the troposphere (Neu and Prather, 2012). For the rest of Br_y species (BrO, HOBr, HBr) the removal scheme considered only washout due to liquid clouds. An effective Henry's Law washout efficiency considering the acid dissociation constant has been used for HBr, the most abundant bromine reservoir in the lower troposphere ($K_H^{eff}(HBr)=7.2\times10^{13}$ M atm^{-1}, see Table S2). Uptake of HBr on liquid surfaces regulates the bromine scavenging within the MBL and FT in agreement with previous studies (Yang et al., 2005; Parrella et al., 2012).…

…Then, even when inorganic bromine removal in the lower troposphere is highly dependent on $k_H(HBr)$, its impact decreases within the TTL. Our approach is consistent with the modelling framework of Aschmann and Sinnhuber (2013), who report that in their reference setup the organic VSL sources "contribute completely to stratospheric bromine thus ruling out dehydration (within the TTL) as an efficient loss process for bromine"…

In this study, "rapid transport of Bry-rich air masses from the MBL to the lower TTL reduces the wet-deposition of PG_VSLS species" (p.17880). This appears to be in contrast to the recent paper of Liang et al. (Atmos. Chem. Phys., 14, 5781-5792, 2014), who found that stronger convection leads to more wet-deposition of Bry in their model. So details of the scavenging and wet-deposition in the models seem to be crucial? In this light, giving more details on the treatment of wet-deposition in the current model simulations and a discussion of its effects could be helpful.

A complete description of the wet-scavenging routines implemented in CAM-Chem, including the Neu and Prather scheme, is given in the specific journal Geoscientific Model Development (Lamarque et al., 2012). We have therefore decided to not provide further details in this paper, besides a description of the processes that are included within each scheme:

…The removal of halogen species in CAM-Chem occurs via washout and scavenging in water and ice clouds (Lamarque et al., 2012; Ordóñez et al., 2012), treating each of the Br_y species independently. Both nucleation scavenging (rain-out) and impaction scavenging (below-cloud washout) are implemented in the wet-removal schemes (see Lamarque et al. (2012) for details)…

…CAM-Chem has been updated to include ice-uptake removal of halogen species following an equivalent procedure to that used by Neu and Prather (2012) for HNO_3. The distinguishing features of the Neu and Prather scheme are related to the partitioning between in-cloud and below-cloud scavenging, the treatment of soluble gas uptake by ice and the overlap of condensate and precipitation within a column (Lamarque et al., 2012)...

With respect to the discrepancies between our results and those reported by Liang et al., (2014), we have added the following paragraph in section 3.4.2:

…Our results show that in the MBL and lower troposphere of the WP region, the total Br_y abundance is up to a factor of 3 larger relative to the abundance modeled for the entire tropics (Figs. 1c and 11c). This substantial change can be attributed to the larger occurrence of sea-salt recycling reactions in coastal regions with strong convection, and their rapid vertical transport to the TTL: cam_NoSSLT sensitivity indicate that total PG_{VSL} in the MBL is reduced ~7.5 pptv when sea-salt reactions are turned off, decreasing the inorganic bromine reaching the coldest point tropopause by ~ 2.2 pptv. This uncertainty to Br_y loading in the TTL due to SSLT recycling is of similar magnitude to the uncertainties recently found by Liang et al. (2014) due to changes in convection strength (~2.6 pptv), although they modeled a reduction in stratospheric bromine injection for their maximum convection conditions. It is worth noting that Liang et al. (2014) did not considered heterogeneous reactions for HBr nor HOBr, and compared different sensitivities where not only the initiation and relaxation of convection was altered, but also the evaporation of rain and cloud formation was modified, i.e. the washout efficiency between sensitivities was changed. In contrast, all of the CAM-Chem sensitivities considered identical removal schemes and parameterizations, and we have focused on addressing the changes in Br_y loading when we shift from the dominant large-scale ascent (tropical annual average) to the periods and regions where strong convective events are frequent (tropical Western Pacific)….

Table 4 gives for the cam_Full_Br-simulation more total bromine from VSLS in the Western Pacific upper TTL (7.8ppt) than in the lower TTL (7.6ppt). What does that mean? Is this transported into the Western Pacific from other regions? Does this apparent increase in VSLS-bromine with altitude provide an estimate for the uncertainties associated with these numbers?

We thank BMS for his careful read. Table 4 had some unintentional rounding errors which have now been corrected. The 0.2 pptv (model difference is actually 0.173 pptv) still exist between the upper TTL (17 km) and lower TTL (12 km) levels. This increase in total bromine for the monthly average can be attributed to different local transport pathways within our definition of the WP region (0° < Lat < 20ºN and 120ºE < Lon < 165ºE): *i)* transport from other latitudes and longitudes outside the defined WP; and *ii)* intrusion events and/or subsidence from the Br_y rich stratosphere. In any case, these small differences between lower and upper TTL levels show random variations when averages for different months are computed and are not observed when larger areas are considered. The following lines have been added in section 3.4.2.

…It is worth noting that for the cam_Full_Br scheme, the total bromine (i.e., SG_{VSL} + PG_{VSL}) loading in the upper TTL is slightly larger than in the lower TTL (see Table 4). This increase for the monthly average can be attributed to different local transport pathways within our definition of the WP region (0° < Lat < 20ºN and 120ºE < Lon < 165ºE): i) transport from other latitudes and longitudes outside the defined WP; and ii) intrusion events or subsidence from the Br_y rich stratosphere…

2.2 Specific Comments

p.17859, l.28: "increases lifetime of the more hydrophilic inorganic portion": not fully clear what that means. I guess you mean the lifetime of inorganic bromine against washout is increased by shifting the balance more to the hydrophilic portion? The lifetime of the hydrophilic portion itself should not change, right?

We appreciate the reviewer for highlighting this redaction error. The referred sentence has been modified as follows:

… increases the lifetime of tropospheric bromine against washout by shifting the balance to the more hydrophilic inorganic portion…

p.17861, l.23: Would be good to specify for how long the 5 sensitivity calculations have been run: 15 years as well, or only for the last 3 years?

All sensitivity simulations were performed only for the last 3 years. In order to make it clear, the text has been modified as follows:

… A model spin-up of 15 years considering constant boundary conditions representative of the 2000 decade have been performed to ensure stratospheric stabilization of halogen sources, and the last of a 3 years-long simulation was used to compute the bromine atmospheric burden for all sensitivity runs…

p.17861, l.26: What is "dynamical transport" in contrast to just "transport"?

Transport and dynamical transport point out to exactly the same phenomenon. We have removed the word “dynamical” in this line to avoid confusion.

p.17863, l.26: I suppose you specify surface mixing ratios not surface concentrations?

Yes, that is correct. The manuscript has been modified accordingly.

p.17864, ll.15: Again, it is not clear if recycling on tropospheric non-sea-salt aerosols is included, or not.

No, it is not included. Please refer to previous answer. The text has been modified in the following way:

… Mechanistic improvements with respect to previous works (Ordóñez et al., 2012; Saiz-Lopez et al., 2012) are mainly based on the implementation of heterogeneous reactions for HBr, HOBr and $BrONO_2$ on tropospheric ice-crystals and stratospheric aerosol surfaces…

p.17865, l.27: Define "NEU". Does this refer to Neu and Prather (2012)?

Yes it does. The text has been modified accordingly. Please see also previous answer.

…Then, the halogen removal scheme in CAM-Chem was implemented with ice-uptake turned on for all chlorine species and for $BrONO_2$, $BrNO_2$, BrCl and Br_2, considering that the removal of this reservoir halogen species occurs at liquid, ice, and mixed-phase clouds in the troposphere (Neu and Prather, 2012). For the rest of Br_y species (BrO, HOBr, HBr) the removal scheme considered only washout due to liquid clouds…

p.17867, l.2: the word "recent measurements" and the reference to the now more than 10-year old study by Marcy et al. (2004) sound contradicting.

We have removed the word “recent”.

p.17867, l.5: I don’t think there is anything wrong with the assumptions for SA_ICE here, but I don’t understand the rationale of assuming H2O=12.5ppm (saturation

mixing ratio for the assumed conditions) and then calculating SA_ICE by condensing 12.5ppm of water.

We used 12.5 ppm for the H_2O mixing ratio because this is the saturation mixing ratio for T=200 K, p=130 hPa, typical conditions in the TTL. Of course within the real world, and within CAM-Chem, H_2O will be highly variable. Our intent for Figure 8, which is the reference for this text, was to show the extreme sensitivity of bromine partitioning to ambient O_3, all else held constant at some reasonable level.

With regards to SA_{ICE}: both in the actual TTL and within CAM-Chem representation of this region, values of SA_{ICE} will be highly variable. The text on line 6, page 17867 makes this point. The important of Figure 7 is to show that if ice is present, nighttime reservoirs form rapidly without any adjustment period, due to the large surface area. In the absence of ice, there is an adjustment period. This distinction persists regardless of the actual value of SA_{ICE}, provided some reasonable value is used. Of course, in the real world, the full amount of water vapor will not condense: i.e., gas phase water will not be zero. The uncertainty in SA_{ICE} is driven however by the number of nucleating particles and the initial abundance of water vapor prior to condensation, both of which are quite variable.

We have modified the text as follows:

… Box model results are insensitive to assumptions regarding values of H_2O, SA_{ICE}, and CO in the TTL, provided some reasonable value is used…

p.17870, l.13: why limited to O3 between 50 and 500ppb?? Fig. 8 shows that the Br/Bry ratio even increases further for O3 lower than 50ppb (as expected).

p.17871, l.8: now a range of 50ppb to 25ppb is given. Why the lower bound of 25ppb?

Changes in response to both of these comments are given altogether here. We had mistaken the value in the first sentence. The lower limit value has been unified to 25 ppbv, which should be taken as an approximate value. Please see also a related answer to reviewer_#3.

With regards to the upper O_3 limit, it is worth recalling that the 1st sentence makes reference to the "tropical ring of atomic bromine", while the 2nd points out to the condition that the ratio Br/BrO >1. Then, as both O_3 and Br_y mixing rations increase with altitude within the TTL, large atomic Br levels are modelled to co-exist with large values of BrO (being the ratio smaller than unity for large O3 mixing ratios, and greater than unity for low ozone). Then, the temperature and ozone conditions prevailing within the atomic tropical ring and producing a ratio Br/BrO > 1 are different. We have include the following sentence in the text to reflect this fact:

…The altitude where the Br/BrO ratio peaks is usually located just below the maximum level of atomic Br, as a consequence of a compromise between the decrease of temperature and the increase of O_3 towards the lower stratosphere…

p.17874, ll24: why are the sensitivity calculations shown in Figs. 8 and 9 done for Run_0, when you say a few lines above that "conditions of Run_0 are unrealistic"?

This was a typo in the submitted paper; much thanks for catching!. Figure 8, as had been stated in the caption, is for Run 1a conditions.

p.18879, l.1: this will lead to an increase in the Br/BrO ratio in the WP, but the

statement that this "corresponds to a stronger formation of the tropical ring of atomic bromine" is a bit misleading, as this does not enhance the ring of atomic bromine around the tropics outside of the WP. Or do you suggest that this also leads to higher Br/BrO outside of the WP?

Thanks a lot to the reviewer for highlighting this misleading implication. The sentence has been modified as follows:

...First, there is a clear predominance of atomic Br as the most abundant Br_y *species during daytime, which corresponds to a localized enhancement of the bromine atoms forming the inhomogeneous tropical ring, as well as a marked increase in the Br/BrO ratio in the WP (see Fig. 4)...*

Fig. 7: Something is wrong here with the notation of the runs. E.g., panel (c) states that Run_1b is SA_ice & Cly=0, while the caption states that Run_1b is SA_sulf & Cly=50ppt. According to Table 2, the caption to Fig. 7 is wrong.

We are grateful to the reviewer for addressing this error. The caption of the figure has been modified to be consistent to the table and text.

Fig. 10b: I guess the scale for Cly has to be "pptv", not "ppmv"

Yes, correct units for the central panel are pptv. We have corrected them in the figure.

In panel (a) you give also the SA for liquid droplets. Would it make sense to show also HOBr + HBr for liquid in panel (c)?

As described above, heterogeneous recycling reactions R1 (HOBr + HBr) and R2 (HOBr + HCl) were modeled to take place only on ice-crystals. This has been clarified in the reviewed manuscript, and was described at length above in the response to reviewer #1.

Figure 10 was intended to show how other atmospheric variables besides bromine species affect the tropospheric bromine partitioning. Special care was taken to describe the vertical variation of the surface area (SA) of different types of aerosols and particles within the tropical region, as those surfaces largely determine the rate of reaction when the free-regime approximation is considered. Indeed, and following the reviewer comments on the importance of describing the sea-salt implementation in CAM-Chem, we have added to panel (a) of Figure 10 two additional lines representing the SA for sea-salt aerosols (SA_{SSLT}) for the Tropics and the WP region.

...The vertical variation of the surface area density of ice particles (SA_{ICE})*, liquid droplets* (SA_{LIQ})*, stratospheric sulfate aerosols* (SA_{SULF}) *and sea-salt aerosols* (SA_{SSLT}) *between 20ºN−20ºS is presented in Fig. 10A...*

2.3 Technical corrections

p.17859, l.10: double bracket

Supplement, Table S1: What is the meaning of the "§"-sign after water-ice aerosol reactions?

The double bracket and the unused symbol have been removed from the main text and supplement.

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3 Reviewer_#3

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The present paper reports on a modelling study of inorganic bromine and its partitioning in the tropical tropopause layer. Consequences for the injection of bromine into the stratosphere are discussed. In the manuscript, the relevance of bromine atoms for the photochemistry and budget of bromine in the tropical tropopause layer (TTL) are correctly emphasized. The manuscript thus constitutes a valuable and original contribution to improve our understanding of the TTL photochemistry and physics.

We are very grateful to the reviewer for his/her positive comments.

My minor concerns with the present study addresses the robustness and permanence of the postulated ring of Br atoms located within the TTL around globe (e.g. in the abstract it is written: We propose the existence of a "tropical ring of atomic bromine" located approximately between 15 and 19 km and 30o N to 30o S). In fact, as correctly indicated in the discussion at various places in the manuscript, due to its strong T and ozone dependence of the Br/BrO ratio, the ring of Br atoms might be much more variable in space and time (ergo patchy) than the sentence in the abstract is indicating. Therefore, I recommend to change this notion ' of ring of Br atmos' in a manner which more correctly expresses its patchiness.

The reviewer concern about the patchiness of the tropical ring is well founded as this natural photochemical phenomenon never completely surrounds the whole planet as a homogeneous "layer" or "cloud". As indicated, the ring shows considerable variation in intensity (concentration, widths and thickness) and location (it follows the sun).

As the acception of the word used for the phenomenom strictly points out to the Br atom concentration increase with altitude and the increased Br/BrO ratio, we believe that either cloud or ring could be used as both have advantages and disadvantages among the other. Anyhow, we believe that the word "ring" is still the more appropriate/descriptive term describing this feature. Due to the fact that ring doesn't imply that it is patchy or not, and following the reviewer suggestions, we have included the adjective "inhomogeneous" in the abstract to represent its patchiness, and include a couple of sentences in the text pointing out to this feature.

Having said that, we recall that the widely used term ozone "hole" doesn't imply that that the ozone depletion is always homogeneously low in ozone, nor that the hole implies the complete absence of ozone molecules within the south pole.

... We propose the existence of a "tropical ring of atomic bromine" located approximately between 15 and 19 km and 30ºN to 30ºS. Daytime Br/BrO ratios of up to ~4 are predicted within this inhomogeneous ring in regions of highly convective transport, such as the tropical Western Pacific….

…It is worth recalling that due to its strong ozone and temperature dependence, the proposed tropical ring of atomic bromine should occur as an inhomogeneous ring of Br that follows the illuminated portion of the earth with variable mixing ratios at various longitudes, latitudes and altitudes…

… Even when the geographic distributions of Br and BrO differ (Figs. 5A and 5B), the Br/BrO ratio follows the spatial patterns of O_3 and temperature (Figs. 5D and 5E) and defines the inhomogeneous extension of the tropical ring…

… First, there is a clear predominance of atomic Br as the most abundant Br_y species during daytime, which corresponds to a localized enhancement of the bromine atoms forming the inhomogeneous tropical ring, as well as a marked increase in the Br/BrO ratio in the WP (see Fig. 4)…

3.1 Further recommendations

1. The definition of the vertical extent of the TTL (as given on page 17860 line 21 to 25 in the paper) is not compatible with more recent definitions of the TTL, as for example given in the studies of Fueglistaler et al., (2009), or even more recently in the paper of Randel and Jensen (2013). Both studies are not mentioned in the manuscript. In these studies and mich more other studies addressing TTL dynamics and/or radiation, the TTL is defined by the layer between the level of zero radiative heating (LZRH at 150 hPa/355 K/14 km) and the cold point (CP) tropopause (at 70 hPa/425 K/18.5 km) (see the abstract of the Fueglistaler et al., 2009 paper), somehow in contradiction with the definition (12 to 17 km) preferred in the present study.

For the present study we decided to use the TTL definition given in the 2010 WMO/UNEP Ozone Assessment Report (see Table 1.7 and Fig. 1.9 in Montzka et al., (2011)). Box 1.4 of that report gives the following definition of the TTL:

"tropical tropopause layer: a layer exhibiting properties of both the stratosphere and troposphere. In this Assessment we follow the definition of the TTL as used in Law and Sturges et al. (2007). The bottom of TTL is taken as the region of maximum convective outflow (about 12 km altitude, or 345K potential temperature) and the upper end is identical to the tropical cold point tropopause (about 17 km or 380 K potential temperature)".

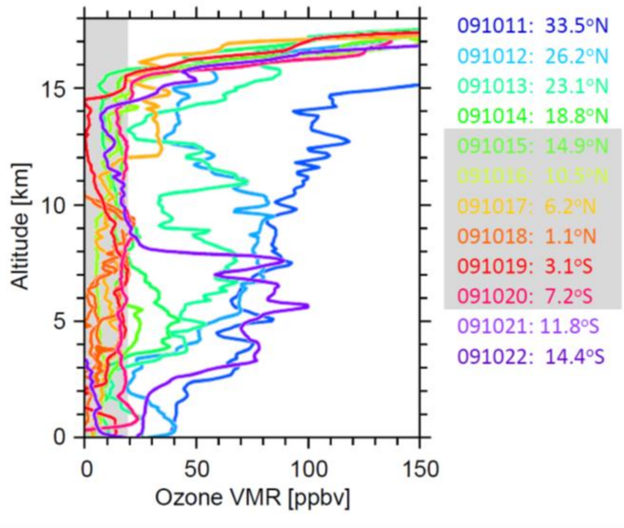
We have however modified the main text to address other definitions, as those suggested by the reviewer:

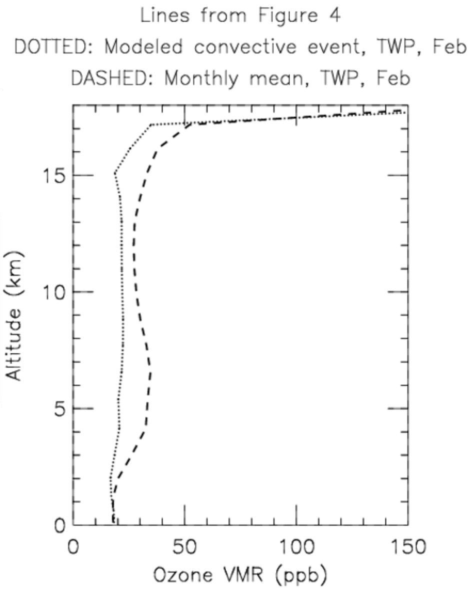
…The TTL definition used here has been taken from the 2010 WMO/UNEP report (Montzka et al., 2011). Differences on the upper and lower TTL limits with respect to other studies (Fueglistaler et al., 2009; Randel and Jensen, 2013) has no bearing on the scientific results of this study…

2. Previous ozone measurements within the TTL (e.g., SHADOZ, Thompson et al., 2003, cited in the paper), as well as more recent measurements within the TTL of the West Pacific indicate that in most cases (> 90 %) the ozone concentrations were larger than for example indicated by Figure 4 and 5. Accordingly since the modelled Br/BrO ratio largely depends on TTL ozone, digging-into the statistics of measured within the TTL would certainly reveal the patchiness of this postulated ring of Br atmos.

We disagree with the statement that in most cases (90%), measured ozone abundances in the TTL of the tropical Western Pacific (TWP) exceed those shown in Figures 4 and 5.

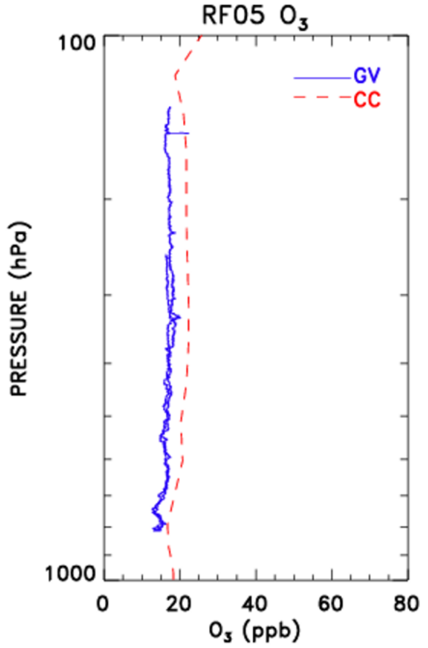
The figures below compare ozonesonde measurements obtained in the TWP by Rex et al. ACP 2014 (left; their figure 1) to the two ozone profiles in the TWP shown in Figure 4 of our paper (right):

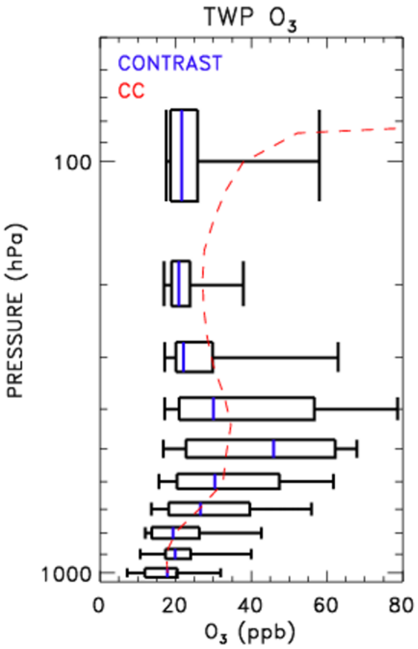




For the Rex et al. figure, the six profiles obtained between 15 Oct 2009 and 20 Oct 2009 were in the TWP, which they emphasize via use of grey shading. Within the TWP, a broad region of ozone about 20 ppb is seen throughout the troposphere, with a rapid rise of O_3 not seen until about 16 km altitude. For the CAM-Chem calcluations, which are for the month of Feburary, ozone is about 20 ppb within the convective event, slightly higher throughout the TWP when averaged over the entire month, and displays a rapid rise just above the top of the TTL (i.e., above 17 km) similar to that seen by the sondes.

Further validity of the modeled profiles for O_3 is found by comparing to measurements from instrument on board the NCAR HIAPER aircraft that probed the TWP during Jan and Feb 2014, for the CONTRAST (CONvective TRansport of Active Species in the Tropics) campaign. Please, consider that CONTRAST results should be treated as preliminary data.





The figrue on the left compares the dotted line of Figure 4 (labeled CC for CAM-Chem) to a profile of O_3 measured during CONTRAST Research Flight 5 (RF05), which was a flight that sampled active convection. The figure on the right compares O_3 in the TWP during all of Jan and Feb (box and whisker plots) to the dashed line of our Figure 4 (CC). The box and whisker plots represent the 5, 25, 50, 75, and 95th percentiles of O_3 VMR in specifc pressure bins, for latatitude and longitude within 0 to 20°N and 120 to 165°E, respectively.

These figures refute the notion that the levels of ozone within the model are somehow biased low. Upon revision, we will add a citation to Rex et al. (ACP, 2014) noting the overall very good agrement of our modeled O_3 profiles in the TWP to the measurements they report in their Figure 1.

...At this altitude, monthly averaged values of Br/BrO ~2.5 are found for the WP region (see Fig. 4). The modelled ozone vertical profiles in the WP present a very good agreement with ozonesondes measurements of Rex et al. (2014), who reported that ozone loss in the boundary layer combined with convectively driven vertical mixing in the WP region is the most likely explanation for the very low O_3 mixing ratios found in the upper troposphere…

3. Since non-methane hydrocarbons (NMHC) are known to rapidly react with Br atoms, I wonder why the role NMHC may play in the TTL bromine photochemistry (i.e. by forming HB in fresh outflow or vs by efficiently destroying NMHC) is not even mentioned in a single paragraph in the manuscript.

We thank the reviewer for pointing out the importance of NMHC + Br chemistry. In our chemical mechanism, the following reactions of organic compounds and Br atoms and BrO are considered:

... For further details on bromine reactions with organic compounds, please see to Table S1 in Ordóñez et al. (2012)...

$Br + HCHO \rightarrow HBr + HO_2 + CO$
$Br + CH_3CHO \rightarrow CH_3CO_3 + HBr$
$BRO + CH_3O_2 \rightarrow Br + HCHO + HO_2$
$BRO + CH_3O_2 \rightarrow HOBr + HCHO$
$BRO + CH_3CO_3 \rightarrow Br + CH_3O_2$
$BRO + DMS \rightarrow DMSO + Br$

The oxidation of the NMHCs (C>2) will eventually produce HCHO. So, we will see an indirect impact of NHMCs on Br (and BrO). When O_3 reaches low enough levels, the reaction Br+HCHO is the primary loss process for atomic bromine.

We have added a new sentence in section 3.2 that states:

…When O_3 falls below a critical level, loss of atomic bromine occurs primarily via reaction with the formaldehyde (HCHO)…

Based on analysis of an extensive set of NMHC measurements in the TWP during CONTRAST, including of course HCHO, we are confident the reaction of atomic Br with HCHO occurs much more quickly than the reaction of Br with any other NMHC.

3.2 Corrections to the text and missing references

4.1 On page 17856, line 27: Since the idea that brominated VSLS significantly contribute to stratospheric bromine budget was mentioned earlier than the cited studies, please add the following references where appropriate:

- Pfeilsticker K., W.T. Sturges, H. Bösch, C. Camy-Peyret, M.P. Chipperfield, A. Engel, R. Fitzenberger, M. Müller, S. Payan, and B.-M.Sinnhuber, Lower stratospheric organic and inorganic bromine budget for the arctic winter 1998/99, Geophys. Res. Lett., 27, 3305-3308, 2000.

- Van Roozendael, M., Wagner, T., Richter, A., Pundt, I., Arlander, D., Burrows, J. P., Chipperfield, M., Fayt, C., Johnston, P. V., Lambert, J.-C., Kreher, K., Pfeilsticker, K., Platt, U., Pommereau, J.-P., Sinnhuber, B.-M., Tornkvist, K. K., and Wittrock, F.: Intercomparison of BrO measurements from ERS-2 GOME, ground-based and balloon platforms, Adv. Space Res., 29, 1661-1666, 2002.

We appreciate the highlighting of this omission. We have now added a citation to Pfeilsticker et al., 2000 and also to Ko et al, JGR, 1997, which to our knowledge is the very first paper to address the importance of VSLS.

4.2 On page 17859, line 8 and …. , add the following reference:

Liang, Q., Atlas, E., Blake, D., Dorf, M., Pfeilsticker, K., and Schauffler, S.: Convective transport of very short lived bromocarbons to the stratosphere, Atmos. Chem. Phys., 14, 5781-5792, doi:10.5194/acp-14-5781-2014, 2014.

Done. We has of course cited this paper several other places in the reviewed manuscript. Please see also the answers to the other reviewers where a discussion on the differences between our results and those from Liang et al. (2014) is given.

4.3 Page 17866, line 28: Reformulate the sentence (With the exception of the ozone sensitivity study (Sect. 3.3.1), all box-model simulations had been performed with an ambient O3 concentration of 25 ppbv, which is the expected ozone value existent in the TTL.), or skip the second part since this is certainly not true. In particular the insert in Figure 8 is rather honest (TTL O3 near convective outflow) and implicitly confirms the statement made in comment 2.

We do not understand this comment. An ozone mixing ratio of ~25 ppbv is representative of conditions in the TTL: there is no inconsistency between this sentence and what is shown in Figure 4. We infer the reviewer may have meant to write "dishonest" rather than "honest" with regards to Figure 8, but the model results shown in Figure 8 (conducted prior to CONTRAST) agree exceedingly well with observations of O_3 obtained during CONTRAST. We hope the following change helps to clarify this point:

…all box-model simulations had been performed with an ambient O_3 concentration of 25 ppbv, which is the expected ozone value existent in the TTL within strong convective regions…

… The vertical dashed lines denote O_3 mixing ratios of 20 and 30 ppbv, values commonly present near convective outflow in the TTL of the WP region (Rex et al., 2014)…

4.4 Page 17868, line 11: Inspect and the VSLS measurements of Laube et al., (2014) in the WP and then put study with a sentence (following line 11) into the context of our results.

Although it is no clear to us, we think the reviewer here is pointing out to Sala et al. (2014), which is now cited in this work.

... In strong convective regions the faster transport increase the total amount of SG_{VSL} reaching the lower TTL relative to the tropical annual average: our model results show an enhancement of 0.8 pptv or ~20% for the WP region in agreement with recent measurements performed in the upper troposphere (Sala et al., 2014)…

4.5 Page 17870, lines 1- 5: With respect of the patchiness of this ring of Br atoms, you may wish to reformulate this paragraph.

We have included several sentences indicating the "patchiness" of the tropical ring of atomic bromine.

…It is worth recalling that due to its strong ozone and temperature dependence, the proposed tropical ring of atomic bromine should occur as an inhomogeneous ring of Br that follows the illuminated portion of the earth with variable mixing ratios at various longitudes, latitudes and altitudes…

…Even when the geographic distributions of Br and BrO differ (Figs. 5A and 5B), the Br/BrO ratio follows the spatial patterns of O_3 and temperature (Figs. 5D and 5E) and defines the inhomogeneous extension of the tropical ring.…

4.6 Page 17874, line 15 and elsewhere: Add the reference of Mébarki et al., (2010) to Marcy et al., (2004), since they report on HCl measurements performed within the TTL over Brazil. Also discuss their findings with respect to the potential of reactivating bromine (your reaction R2).

We thank the reviewer for pointing out this reference. The following sentences had been added to the manuscript.

…Additionally, Mébarki et al. (2010) have determined a background HCl mixing ratio of ~20−30 pptv in the upper TTL not influenced by tropospheric nor stratospheric air…

…As the reaction rate for HCl recycling surpass that for HBr recycling, and the HCl abundance rapidly increase towards the upper TTL and above (Mébarki et al., 2010), BrCl shows a pronounced night-time peak at ~17 km that rapidly decrease following the SA_{ICE} profile…

4.7 Page 17877, line 27. Add a point after (Williams et al., 2009)

Thanks the reviewer for highlighting this omission.

4.8 Page 17879, line 10: Check as to whether you are fine with the statement, considering that eventually large amounts of NMHC (which efficiently react with Br atoms) are also transported by strong convection.

We are fine with the statement as written. The only important NMHC reaction, Br+HCHO, is included in the model. As noted above, an experiment designed to address this problem, CONTRAST, supports the sole importance of Br+HCHO.

4.9 Figures: Rethink if the lower horizontal dashed line is useful with respect to comment 1. In fact, the line irritated me a lot, before I realized that your TTL definition largely departs from the more recent TTL definition and that all your statements regarding Br atoms concentration et cetera refers to and eventually are only valid for the more modern definition of TTL.

As described above, we decided to use a TTL definition consistent with the last WMO report, and many other publications in the literature related to VSL brominated species. Then we have maintained the horizontal lines and altitude/pressures for the current TTL definition, although a sentence highlighting the differences respect to other refs has been explicitly included in the text.

3.3 Useful references

- Fueglistaler, S. et al. Tropical tropopause layer. Rev. Geophys. 47, 1–31 (2009).

- Randel W.J, and E. J. Jensen, Physical processes in the tropical tropopause layer and their roles in a changing climate, Nature Geoscience 6,169–176, (2013).

- Sala, S., Bönisch, H., Keber, T., Oram, D. E., Mills, G., and Engel, A.: Deriving an atmospheric budget of total organic bromine using airborne in situ measurements from the western Pacific area during SHIVA, Atmos. Chem. Phys., 14, 6903-6923, doi:10.5194/acp-14-6903-2014, 2014.

- Ashfold, M.J., N.R.P. Harris, E.L. Atlas, A.J. Manning, and J.A. Pyle, Transport of short-lived species into the Tropical Tropopause Layer, Atmos. Chem. Phys., 6309–6322/doi:10.5194/acp-12-6309-2012.

- Mébarki, Y., Catoire, V., Huret, N., Berthet, G., Robert, C., and Poulet, G.: More evidence for very short-lived substance contribution to stratospheric chlorine inferred from HCl balloon-borne in situ measurements in the tropics, Atmos. Chem. Phys., 10, 397-409, doi:10.5194/acp-10-397-2010, 2010.

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4 Interactive comments

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4.1 IC_#1_RS

The suggestion of a widespread ‘ring’ of bromine atoms in the TTL is an interesting one with a number of important ramifications, some of which are alluded to in the paper. Presumably this feature is consistent with that indicated in the Hg(0) oxidation studies of Holmes et al - 2006, 2010? They didn’t give it such a name but the profiles, for example above 200 hPa shown in Figure 1 of the 2006 paper (data from Yang et al., 2005 – already cited), seem to be indicative of the same feature. I haven’t cross-compared the model-chemistry details but it might be worth highlighting similarities/differences in approach. It may lie outside the direct scope of the authors’ paper but maybe they could comment to some degree on the specific role of such a bromine atom ring in removing elemental mercury in this part of the atmosphere as this is arguably one of the potentially most important effects? Holmes, C.D., et al. (2006) GRL, 33, L20808. Holmes, C.D., et al. (2010) ACP, 10, 12037-57.

The pioneering work of Yang et al, JGR, 2005 is cited several times in this work, but it is worth recalling that even when in their modelling study high levels of atomic Br were shown in a few of the figures, no mention was given to this model result and no comment appeared comparing modelled Br to BrO. Indeed, Aschman and Sinnhuber (2013) also reported large values of atomic Br in the TTL, but gave no mention to its spatial or temporal distribution.

The notion that the majority of Br_y could be "hiding" in the form of Br within the TTL, a region of intense recent observational scrutiny, is not mentioned (much less developed!) in any prior paper.

We thank Dr. Saunders for his very pertinent comments on the role of atomic Br on the oxidation of elementary gaseous mercury, a process that will be very interesting to analyse in relation to the appearance of the atomic tropical ring. Even though mercury oxidation is not the subject of the present paper, the following sentence has been added to the manuscript highlighting its importance, and the referred sentences have been added.

…The increase in atomic bromine levels within the middle and upper troposphere directly influences the lifetime of elemental mercury against oxidation via Hg + Br (Holmes et al., 2006, 2010)…

4.2 IC_#2_RS

Regarding the mercury pathway from my earlier comment; the identification of halogens (Br and I) invariably with Hg in aerosol sampled in the TTL (e.g. Murphy et al., 2000; 2006) provides strong evidence for a Hg + Br » HgBr2 » nucleation channel for Br from a ring/layer as proposed. Presumably the concentration of atomic Br is therefore likely to be more 'fluid' than the model predicts but with generally lower values than stated?

Murphy, D.M., Thomson, D.S. (2000) GRL, 27, 3217-20. Murphy, D.M., et al. (2006) ES&T, 40, 3163-7.

We are grateful to Dr. Saunders for pointing us to these interesting studies, which provide further indirect evidence for the presence of the Br atom ring and its potential implications of Hg oxidation in the TTL. Nevertheless, comments on the implication of the proposed ring of atomic Br for Hg is beyond the scope of our paper. Uncertainties in the level of atomic Br due to production rate of VSL bromocarbons, the role of sea salt aerosols, efficiency of aerosol washout versus heterogeneous release of labile species are likely much larger than the stated additional uncertainty. Inclusion of Hg oxidation is beyond the scope of the present study, but we note the proper modelling of this process has a whole additional set of attendant uncertainties, and there are sparse observations for testing such models. Clearly if there is a mechanism for permanently sequestering Br in aerosols, the modelled abundance of atomic Br would decline. The noted mechanism is speculative and given the environmental importance of mercury, certainly warrants additional study. Given the public record of discourse afforded by ACPD, and the fact our study does not include the modelling of mercury (which involves a myriad of complexities that may or may not ultimately support this comment), we believe it is most appropriate to reply here rather than in the revised paper.