Review for manuscript acp-2016-031

The manuscript of Navarro et al., reports on Cam-Chem (Community Atmosphere Model with Chemistry) modelling of the partitioning of inorganic bromine in the tropical tropopause layer (TTL) for NASA ATTREX deployments of the Global Hawk over the eastern and western Pacific Ocean in 2013 and 2014. From the previous version the manuscript is now somewhat complemented including information on the heterogeneous processing of bromine and chlorine on ice particles. Due to the more vigorous deep convection and hence colder temperatures in the TTL and sustaining a larger occurrence of cirrus ice in the TTL of western as compared to the eastern Pacific, heterogeneous processes could indeed reveal some differences in the photochemistry in both areas. Including details of the heterogeneous processing and the irreversible removal of chlorine and bromine from the TTL by sedimentating particles may cover a novel aspect in the study, and as such could render the present study even more valuable to the readers of ACP.

Unfortunately, reactions to my previous comments (mostly, but not all related to how measurements and model predictions need to be compared in state-of-the-art studies) are mostly missing in the present manuscript due to any reason. In order to make it again clear, a state-of-the-art intercomparison of measurements and model predictions would either involve (a) a comparison of the forward-simulated measurements including their specific features (here briefly called one-to-one inter-comparison), or (b) by using a Bayesian approach a comparison of measured and modelled probability density distributions (and their moments) of the targeted quantities. Both approaches have been widely used in past studies, and it is known by not so doing the information contained in measurements cannot be properly exploited, or is even misinterpreted (see minor comment 2). So it is up to the authors to provide a tighter inter-comparison of the various measurements with the model predictions than in the past and present a version of the manuscript which goes beyond what is already known about bromine in the TTL. Alternatively, the authors may mainly focus on modelling, but then a larger number of sensitivity runs on the relevant processes (c.f. heterogeneous activation and irreversible removal of the halogen and their relevant parameters) need to be presented.

While I tried to review the present manuscript as independently as possible from the previous version, I'm recalling here my major comments however in a less abstract but in a more illustrative way than previously put forward (see below). So once the authors will have decided on the focus of study/manuscript, they may either fully include my comments when it addresses measurement/model inter-comparison, or in case they focus their study on mostly modelling then they may circumvent them, while providing instead a series of sensitivity runs on the relevant parameters for their study.

Beside these more general comments, rather than only providing some major comments as done in my previous review, I did a more comprehensive review by adding a section called 'minor comments' which lists typos, and minor issues to be clarified as well as a section 'list of references' of which the references are worthwhile to be included in any revised version.

Response: We would like to thank Prof. Pfeilsticker for the time spent on reevaluating this manuscript, and for the supportive comments that help to improve the text. Here, we address their concerns:

Major comments:

1. Comparison with measured data and 'averaging' (c.f. on page 5, line 3 and 4; These continuous measurements of ozone were averaged to match the location where GWAS samples were collected, and then compared to CAM-Chem outputs.):

By referring to my comments 1 and 2 of the previous review, how was the averaging performed and inferred from what pdfs?

In order to make my comment 2 (and in part 1) more clear my question points to the following:

Since the sampling time of the NOAA-2 polarized O3 photometer is 1 Hz (corresponding to a column of air of about 180 m in length) but the CAM-Chem has a spatial resolution of 1° (longitude) x 1° (latitude) (page 5, line 19) or about 110 km x 110 km, how was the measured O3 averaged, and how were the higher moments of the pdf calculated and how do these quantities compare with corresponding quantities calculated from the CAM-Chem simulation c.f. how were the errors bars in your Figure 2 calculated?

A similar question related to the averaging may arise when comparing the trace gases measured in AWAS air samples (where the sampling time was about 25 s at 14 km and 90 s at 18 km, corresponding to columns of air of being 4.5 km and 16.1 km long, respectively), and the model.

Further since one can reasonably assume (e.g., when assuming a constant pumping rate), that the concentrations measured by the individual in-situ instruments are spatial averages of the probed air columns, it is not so clear how these statistical measures calculated from observed quantities compare to those (c.f. the average and the variance) calculated from modelled data? Noteworthy is here that the inferred mean/variances are obviously different in the measured and modelled ozone (see your Figure 2), while any respective information on the variances of modelled and measured brominated source gases is still missing in Figure 3.

Remark: The question related to the appropriate 'averaging' of geophysical parameters is largely justified since the concentrations of stratospheric trace gases and tracers may show long-range correlations which are likely different in the measurements than portrayed in the model (for details see Van Leuwen, 2009, and the references provided in my previous review). Moreover, quantities having long-range correlations (as they occur in geophysical fluids), the central limit theorem teaches (and mandates) that the inferred statistical quantities are scale-dependent and that accordingly the quantities (here concentrations) are in general not Gaussian distributed (for the refs see my previous review). Accordingly, the calculation of the relevant statistical quantities requires the knowledge of the underlying (non-Gaussian) pdf, which when known could alternatively to a one-to-one inter-comparison (as c.f., done in Werner et al., 2017) be used in a Bayesian approach in the inter-comparison (e.g., Van Leuwen, 2009, and the references provided earlier).

So some explanation (beyond the word 'average') is needed how the discussed quantities (ozone and the tracers) are inter-compared e.g., and how the mean and uncertainty/error bars in Figures 2 and 3 were calculated. (Comment: Here you may also anticipate the problem of inter-comparing remotely sensed quantities with modelled quantities since the former are usually not uniformly sampled over an air column like samples provided by in-situ measurements but via an observation dependent averaging kernel, see my remark/comment I. 3 in the previous review and in consequence the minor comment 2 below).

Finally, because the underlying statistic of the involved concentrations is non-Gaussian, care has to be taken that derivatives of inferred quantities, c.f. ratios as used to calculate the [Br]/[BrO] ratio, are not biased (see my comment 1, and comment II. 5, second paragraph in my previous review).

Response:

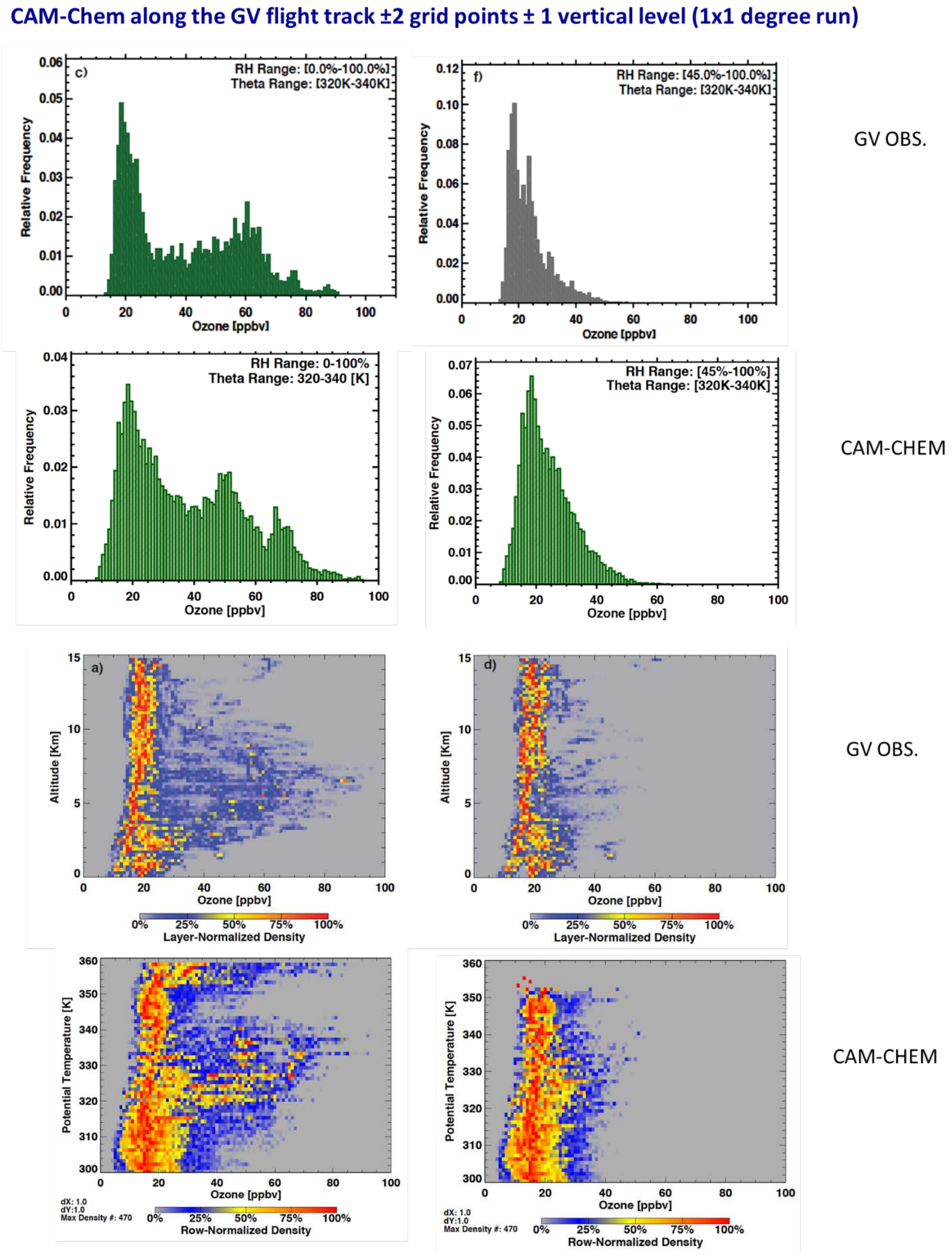
As we emphasized before, this model study was performed simultaneously to the study published by Navarro et al., 2015. Thus, average of measurements and model is the appropriate procedure in order to be consistent with the previous methodology. The methodology is supported by

1- The average of continues measurements of ozone over the whole air sampling times based on previous studies that employed a Whole Air Sampler (e.g. Blake et al., 1997;Blake et al., 2001;Blake et al., 2003;Blake et al., 1999;Blake et al., 2004;Schroeder et al., 2014)

2- The study of Olson et al., 2012, which showed measurement-model inter-comparisons of binned data in altitude profiles used to characterize continues measurements of acetaldehyde (taken with TOGA and PTR-MS instruments) that were interpolated to match the whole air sampling times regardless the differences of the WAS filling time (8 s at 150 m and 90 s at 12 km). Similarly, the study of Kormann et al., 2003 that showed the observation-modeled inter-comparison of averages in the altitude profile of formaldehyde in the marine boundary layer of the Mediterranean Sea.

3- An analysis of annual ozone climatology and ozone probability distribution functions (PDFs) on 12 different regions around the world using NCAR CAM-Chemo model. The climatology evaluate the model performance regarding ozone averages, seasonality, inter-annual variability and the shape of ozone distribution. For the region of Japan for example, model and observations showed good agreement in PDFs for two stations at 500 hPa, and a good reproduction of a bimodal distribution of one of the stations at 800 hPa (Tilmes et al., 2012).

4- A study (unpublished yet) of CAM-Chem ozone PDFs along all the flight track of CONTRAST campaign (carried out at the same time of ATTREX over WP). The following figures illustrate the reasonable agreement between model and observations, particularly at relative humidity (RH) conditions of 45%-100%.



CAM-Chem along the GV flight track ±2 grid points ± 1 vertical level (1x1 degree run)

GV OBS.

CAM-CHEM

GV OBS.

CAM-CHEM

Figure 1: four figures on top: observations–modelled inter-comparison of ozone concentrations during CONTRAST 2014. Four figures on the bottom: densities inter-comparison.

As the reviewer mentioned the average of geophysical parameters is largely justified for stratospheric trace gases and tracers that show long-range correlations. However, careful considerations have to been taken on the way of treating discrete and continues variables. We agree with the reviewer that the central limit theorem and the Bayesian approach is appropriated for the model-measurements inter-comparison, but these conditions only apply for continues variables, not for the discrete measurements we obtained once ozone concentrations were average over the whole air sampling times. Wilks, 2011 pointed out the different parametric probabilities distribution, where there is a clear definition of the discrete a continuous distribution of atmospheric variables. Based on this information, the statistical approach used for our discrete distributions are reduced to find the expected values E(x):

$$\mu = E(x) = \sum xp(x)$$

Where μ= mean, x= discrete variable, and p(x)= corresponding probability of the discrete variable.

Which by definition, it is equivalent to:

$$\mu = \frac{1}{n}\sum_{i=1}^{n} xi$$

Similarly, for discrete random variables the standard deviation was calculated by summing the product of the square of the difference between the value of the random variable and the expected value, and the associated probability of the value of the random variable, taken over all of the values of the random variable, and finally taking the square root.

$$\sigma = \sqrt{(x-\mu)^2 p(x)}$$

Which equivalent formula is,

$$\sigma = \sqrt{E(x^2) - [E(x)]^2}$$

Since modelled and measurements were later on binned into 1km of altitude (as we follow the methodology of Navarro et al., 2015) the standard deviations showed in figure 2 represent the ±1σ variation from the binned values.

Regarding to the errors in figure 3, we omitted the illustration of the ±1σ variation from the binned values to avoid cumbersome plots. Instead, errors of slope and interception of the lineal regression are presented in each plot as the goal of the figure is to show the correlation derived from these regressions.

We took into consideration this comment from the reviewer. However, statistical approaches are out of the scope of this manuscript. We modified the statement on page 6 line 7 to clarify the methodological approach of our discrete measurements. The text now reads:

"The current modelling study was conducted as part of the work described by Navarro et al., (2015), and it follows the same methodology and statistical analysis for discrete variables."

Also appropriate references were added to the methodology of O_3 observations in page 5, line 4-8. Now the text reads:

“To merge the measurements taken over different time scales, these high-rate measurements of ozone were averaged to match the sample collection times of each GWAS sample (~30 – 90 sec) (Blake et al., 1997;Blake et al., 2001;Blake et al., 2003;Blake et al., 1999;Blake et al., 2004;Schroeder et al., 2014), and then the merged data were compared to CAM-Chem outputs (Kormann et al., 2003;Olson et al., 2012).”

Similarly, we emphasized the meaning of the error bars of figure 2, by adding a sentences to page 5 line 32 to page 6 line 2. Now the text reads:

“Once each independent flight track was extracted from the model output, all atmospheric quantities were averaged into 1 km altitude bins, standard deviations were calculated, and the model was compared with measured data.”

And we added another sentences to page 6, line 24-26 to point out the errors of the lineal regression of figure 3. Now the text reads:

“Figure 3 shows the correlation between average measurements and model outputs of the 1 km of altitude bins for O_3, $CHBr_3$ and CH_2Br_2 over the WP and EP, as well as the linear regression equations with and associated uncertainties in slopes and intercepts.”

2. Model constraints and boundary conditions: Further if the manuscript attempts to provide novel insights into model’s predictive skills on the budget and photochemistry of the considered species within the TTL, more information is needed than provided on how the model is constrained and on how the boundary conditions (for the relevant gases) are chosen.
Being more specific, it is unclear how Cly is constrained (or calculated) in the model due to the provided contradictory information. For example, on page 7, line 16 to 18, it is said that ‘Considering all flights, the maximum Cly abundances are < 85 pptv in the WP and < 182 (????) for the EP, with a global mean tropical annual Cly mixing ratio of 50 pptv in agreement with previous reports (Marcy et al., 2004; Mébarki et al., 2010).’ while in Table 1 a range of Cly (day) 1 - 515 pptv (WP) and 1 - 969 pptv (EP) is mentioned. Further, in order for reader to judge the predictive skills of the model, the results need to be compared with previous Cly observations (and eventually modelling) in the TTL beyond the Marcy et al., 2004 study actually mentioned in the manuscript, e.g., Marcy et al., 2007; Mébarki et al., 2010; von Hobe et al., 2011; Jurkat et al., 2014, and many others.
Here, similar than previously asked for (and again asked for here) the budget and partitioning of bromine (comment II., #5, first paragraph in the previous review), it would be worthwhile to provide information on the altitude dependent partitioning of Cly (including chlorine the condensed phase) and how the budget is closed with respect to the total organic chlorine.
Next, since you state (c.f., page 7, line 34; ‘The scenario over the EP is slightly different (from the WP) as levels of NO2 and O3 define a high NOx regime’), information on the implemented sources for NOx in the model is completely missing. Providing such information was already asked for in my previous review (comment II. 4.), primarily since measured and as well as the modelled NO2 in Werner et al. (2017) does not support the predicted ‘high NOx regimes for the EP. In this context, your statement on Page 8, line 7 is not appropriate in this context (see my

minor comment 2, and my remark 3 in the previous review). In consequence you have to face the findings of Werner et al., (2017) regarding NO2, i.e. measured and SLIMCAT modelled NO2 does not support the Cam-Chem prediction of a ‘high NOx regime’ in the TTL of the EP.

Response: We appreciate the reviewer for highlighting some inconsistencies in the manuscript and for pointing out model descriptions or configurations that were unintentionally omitted and may shed light respect to how relevant processes were implemented in our study.

a) Cl_y is calculated explicitly in the model and solved at each timestep ($Cl_y = Cl + 2\times Cl_2 + ClO + OClO + 2\times Cl_2O_2 + HCl + HOCl + ClONO_2 + ClNO_2 + BrCl$). Source constraints are based on the CFCs and HCFCs surface mixing ratios following (Meinshausen et al., 2011) as well as on emission of VSL chlorinated species included in the model (CH_2BrCl, $CHBr_2Cl$, $CHBrCl_2$). Accordingly we added the following lines to Section 2.2 (page 5, line 23-24):

“It is worth noting that all inorganic halogen species (i.e., Cl_y and Br_y) are not constrained but explicitly solved at each timestep.”

Following the Editor suggestion, we have now moved the additional Figures (required by Prof. Pfeilsticker during previous round of review) from the supplement into the main text (new Figures 5 and 6), and relate them to the original Figure 5 (now Figure 7) (page 7, line 33 to page 8 line 6). Thus, now it is possible to observe the inferred Br_y and Cl_y mixing ratios for each independent flight, as well as the campaign average for both WP and EP. To avoid the contradictory information presented in previous draft, and to relate our findings to previously published results regarding inorganic chlorine in the UTLS, we have modified the text as follows (page 7, lines 21-26):

“It is worth noting that even when the maximum inorganic chlorine levels for individual flights are larger in the EP, BrCl is not the dominant night-time reservoir, while in the WP, where BrCl dominates, maximum Cl_y mixing ratio is almost half the concentration predicted for the EP (see Table 1 and Figures 5 and 6). Maximum Cl_y abundances averaged for all flights within each region show < 85 pptv in the WP and < 182 pptv for the EP (see Fig. 7), with a global mean tropical annual Cl_y mixing ratio of 50 pptv in agreement with previous reports (Marcy et al., 2004; Fernandez et al., 2014;Hobe et al., 2011;Jurkat et al., 2014;Mébarki et al., 2010).”

b) Regarding the altitude dependent partitioning for Br_y and Cl_y, Figure 4 in the main text show the vertical extent of the inorganic bromine partitioning within the WP and EP. The respective organic (i.e. VSL_{org}) profiles have already been described in Navarro et al., (2015), so it is not necessary to repeat them here. Finally, as current work focus strictly on bromine and not on chlorine, we are confident that knowledge of the total Cl_y atmospheric levels is enough for the purposes of current work. Indeed, HCl dominates inorganic chlorine partitioning in the region of study (Marcy et al. (2004); Hobe et al., 2011) and is the main species affecting heterogeneous recycling of Br_y reservoirs (Fernandez et al., 2014). Thus, we added the following sentence (page 7, line 28-30):

“Note that within the TTL, HCl dominates the Cl_y partitioning, with modelled mixing ratios up to 1 order of magnitude larger than those found for HOCl and $ClONO_2$ (see Fig. 10 in Fernandez

et al., 2014). Further knowledge of the complete partitioning between inorganic chlorine species is beyond the scope of this work."

Please see also the answer to minor comment 5 regarding the role of heterogeneous reactions in controlling the Br_y and Cl_y removal in the TTL.

c) We added information on the NOx sources in the Methodology section (page 5, lines 21-23):

"Global emissions of important ozone precursors (NOx, CO, VOCs) were obtained through a harmonization exercise of reactive emissions between years 2000 and 2005 for different RCP (Representative Concentration Pathways) scenarios (Meinshausen et al., 2011, Lamarque et al., 2011)."

Even though is not necessary to include the following information in the manuscript, it is worth noting here that these studies showed consistent impacts on tropospheric ozone and determined that the different scenarios for methane mixing ratios will strongly impact tropospheric ozone, much more so than the difference in NOx emissions between RCPs.

Regarding the distinction between a High-NO_x and a Low-NO_x regime, we agree with the reviewer that our previous comparison between EP and WP NO_x conditions was erroneous and misleading. NO_x levels in the EP are somewhat higher than in the WP, but they increase at most by a factor of 2, and always remain below 50 ppt, well into a Lox-NO_x regime. Thus, even the different NO_x abundances produce a different proportion of $BrONO_2$ partitioning between EP and WP, there is not a mechanistic change from a Low-NO_x regime to a High-NO_x regime: in both regions the Low-NO_x regime prevails. In addition to the small NO_x differences, there are large SAD-ICE changes between the EP and WP which affect the overall reaction rate of heterogeneous reactions (1) to (6) within each region. The largest the SAD-ICE, the faster the conversion from $BrONO_2$ to BrCl, Thus, in the WP where SAD-ICE levels are ~1 order of magnitude larger than in the EP, $BrONO_2$ mixing ratios are smaller and BrCl mixing ratios are larger. We have corrected this misinterpreted feature at several sentences in the manuscript, which now reads:

"The western-to-eastern differences in the partitioning of inorganic bromine are explained by different abundances of ozone (O_3), nitrogen dioxide (NO_2), total inorganic chlorine (Cl_y) and the efficiency of heterogeneous reactions of bromine reservoirs (mostly $BrONO_2$ and HBr) occurring on ice-crystals." (page 1, lines 26-28)

"The scenario over the EP is slightly different as levels of NO_2 and O_3 are larger, while the Surface Area Density of ice-crystals (SAD-ICE) is reduced (see Section 3.3)." (page 8, line 12-13)

"Hence, the EP daytime average concentrations of ozone (up to ~ 300 ppb), Cl_y (max Cl_y ~ 181 ppt) and NO_2 (max NO_2 ~ 48 ppt) are almost twice as high as those over the WP (Fig 7d), while SAD-ICE levels are up to 1 order of magnitude smaller (see Fernandez et al., 2014). Higher concentrations of ozone were associated with enhanced production of BrO (Fig 7c). Meanwhile, during dark hours, the higher NO_2 concentrations and the slower rate of heterogeneous

reactions of bromine reservoirs (see Section 3.3), lead to the predominant formation of $BrONO_2$ and the reduction of BrCl levels over the EP (Fig 7c).” (page 8, line 22-26)

“Also, Br shows a smooth variation during the day, slightly decreasing its abundance as the SZA increases, while the temporal evolution of BrO is more variable, mostly under the higher NO_x levels prevailing in the EP (Fig. 7).” (page 9, line 12-14)

“Thus, neglecting ice-recycling reactions (1) to (6) prevents the heterogeneous conversion of $BrONO_2$ to BrCl, and gas-phase bromine nitrate (which is formed mainly by the termolecular reaction of BrO + NO_2 + M during twilight) remain as the dominant Br_y species during the night for both EP and WP regions.” (page 11, line 22-26)

“The smaller impact of turning off heterogeneous reactions in the EP can be explained considering the less efficient inorganic bromine recycling occurring on the smaller SAD-ICE prevailing in this region.” (page 11, line 29-31)

“Indeed, Hobe et al., (2011) suggested that the coupling of chlorine and nitrogen compounds in the tropical UTLS may not be completely understood, which would also impact on the bromine burden.” (page 11, line 32-34).

Minor comments:
1. Page 1, line 30 cont.: Your statement on the stratospheric sources of bromine does not include inorganic bromine being transported from the troposphere into the TTL and LS, for which previous experimental studies provided quite some evidences, c.f., Dorf et al., 2008, Laube et al. 2008; Brinckmann et al., 2012; Schmidt et al., 2016; Werner et al., 2017, and others. So please clarify.

Response: The original initial sentence of the introduction points out to the general role played by bromine (without separating the organic and inorganic fraction) in the stratosphere, and requires no further clarification. The next paragraphs extend specifically on (first) organic source gases and (later) on product gas sources produced in the troposphere. Thus, is only when reaching page 3, line 1, that we added the following sentence to make explicit mention to the Product Gas contribution:

“These previous studies, as well as many others (Dorf et al., 2008, Brinckmann et al., 2012, Liang et al., 2010, etc.), highlighted the importance of Br_y product gas transportation from the lower troposphere into the TTL and lower stratosphere as well as its impact on ozone.”

Having said this, we would like to highlight a couple of sentences from the original manuscript (one of them also in the introduction) which clearly shows that the direct Br_y transport from the troposphere into the TTL has been considered and analyzed in this study.

“For example, the location and timing of emissions, the transport dynamics and dehydration processes in the tropical tropopause layer (TTL) (Liang et al., 2010), and the occurrence of heterogeneous recycling reactions on sea-salt aerosol and ice-crystals (Fernandez et al., 2014)

affect the total amount of inorganic bromine that can be injected to the stratosphere.” (page 2, line 16-19).

“Additional Br_y and Cl_y sources from sea-salt heterogeneous dehalogenation in the lower troposphere are parameterized (Ordóñez et al., 2012; Fernandez et al., 2014).” (page 5, line 18-19)

2. Page 8, line 7: However, previous studies have shown large associated uncertainties in TTL NO2 measurements based on remote sensing instruments (Weidner et al., 2005; Butz et al., 2006; Bauer et al., 2012).
This sentence demonstrates that the authors did not appreciate (or even understand) my comment 3 outlined in length in the previous review (see also comment 1 above).
So recall my argument now expressed in more simple terms. First all three cited studies refer to measurements where the sensor was not deployed within the air mass of interest, but NO2 (and some other species) were measured somehow remotely (from a balloon or even satellite). Now in order to see the difference of the previous studies with the study of Werner et al., (2017) just make a drawing to compare the different observation geometries i.e. compare the line of sights for sensors looking (from a great distance) slant through the layer of interest (the former three studies) and those inspecting NO2 (horizontally) along the layer of interest (Werner et al., 2017, and inspect Figure 5 in Stutz et al., (2017). Then compare the different path lengths over which the skylight is absorbed and how they differ in length, since the path length is one decisive parameter in optical absorption measurements which determines the detection sensitivity. For the exercise you can fairly assume that all sensors have the same detection limit (in terms of optical density for NO2) since they all operate at the photon electron shot noise and receive about the same skylight radiance.
Second, since the bulk of stratospheric NOx is located somewhere at around 30 km, sensors (satellites and balloons) which attempt to measure the comparable lower amounts of NO2 located below (or behind) this NO2 layer, i.e. NO2 in the UT/LS and TTL, are more affected by any NO2 changes within this high-located NO2 layer than a comparable sensors measuring below and horizontally along the layer of interest (c.f. on the Global Hawk). So as argued in my previous review, in remote sensing you cannot compare a detection limit inferred for a specific measurement with another measurement without considering the individual observation geometries (to which the remote sensors refer to averaging kernels), even when assuming the same instrument is used.
By summarizing there are two observation-geometry related advantages of remote-sensing instruments being deployed within the layer of interest over those inspecting the studied air masses from ‘far away’. In consequence, you have to appropriately considered the NO2 (and BrO) measurements, their detection limits and errors explained in length in Stutz et al., (2017), rather by assigning to them uncertainties which suite best to your study.

Response: Details of remote sense deployments and functionalities are beyond the scope of this manuscript. However, the text has been modified to point out the reviewer’s comments. The text now reads (page 8, line 18-21):

“However, previous studies have shown large associated uncertainties in NO_2 measurements based on remote sensing instruments, which also depends on the individual observation

geometries and instrument operation times (e.g. 30% of total relative error of NO_2 measurements below 25Km (Weidner et al., 2005), and 50 % for satellite measurements from SAGE II bellow 25 km (Bauer et al., 2012)).”

3. Page 8, line 10: These results are in good agreement with the partitioning of Bry found by (Werner et al., 2017) where BrO is the daylight dominant species over EP. In fact, your results and conclusion (page 11, line 14 – 20) are suggesting something else. Accordingly, you need to reconsider this statement.

Response: Starting with minor comment 3, and extending through minor comments 4 and 6, we understand the reviewer is worried about our results are suggesting that the tropical rings of atomic bromine is a constant feature of the tropical atmosphere. However, we clearly show in Figures 4 and 5 that within our CAM-Chem modelling studies BrO is usually the dominant species during daytime (not atomic Br), and made it clear in the text since the first draft version (Page 7, lines 16-20).

“At the tropopause level (~17 km) and integrated over all flights and SZAs, the inorganic partitioning showed ~ 43 % (0.79 ppt) of abundance of BrO during daylight and ~61 % of BrCl (0.94 ppt) during night-time over WP. On the other hand, 48 % (1.43 ppt) of Bry is presented as BrO during daylight and 56 % (1.41 ppt) as BrONO2 at night-time over EP (Fig 4). Atomic bromine is the second most abundant species during the day, with mean daytime values of 0.64 ppt and 0.57 ppt for the WP and EP, respectively.

The specific statement highlighted by the reviewer (Page 8, line 26-29 of current version) states:

“These results are in good agreement with the partitioning of Br_y found by Werner et al. (2017) where BrO is the daylight dominant species over EP, and the estimates of Fernandez et al. (2014), which suggested BrO and $BrONO_2$ as the dominant species in the TTL over the entire tropics during daytime and midnight, respectively.”

and we do not find any contradictory message respect to what has been said before and/or the referenced papers.

Regarding the only sentence in our conclusions that the reviewer mention to be “suggesting something else” (page 11, line 14-20 (old) and page 12, line 10-14 (new)), we have slightly modified it as follows, so there is no space left for the reader to infer in between line the message we are trying to give.

“Reactive species like atomic Br become the dominant Br_y species in patchy regions of the Eastern and Western Pacific TTL during daylight, following the large inhomogeneity of ozone abundances within these regions strongly influenced by deep convection. The low ozone and cold conditions, in combination with the rapid photochemical equilibrium between BrO and Br, favour Br/BrO > 1 for patchy regions of the TTL and are consistent to previous results about the proposed tropical ring of atomic bromine.”

Additionally, the first line in the Conclusions now states (page 12, line 4-6):

"Our estimates of the Br_y partitioning in the TTL over the Pacific Ocean showed that mostly BrO and in a lesser extent atomic Br are the dominant species during daytime hours, while BrCl and $BrONO_2$ are predicted to dominate the TTL Br_y at night-time over the WP and EP."

4. Page 9, line 29: These results are in good agreement with the statements of Fernandez et al. (2014), which suggested Br/BrO > 1 during strong convective periods over the WP warm pool region. This finding is not surprising given that the same model (with similar/same model parameters and inputs) were used. So the statement does not add new evidences on Br/BrO > 1 in the TTL etcetera.

Response: Even when the halogen chemical mechanisms used in Fernandez et al. (2014) and in current work are similar (for both gas phase and heterogeneous processes), we disagree that current study and Fernandez et al., used equivalent model configurations or inputs. Fernandez et al. was configured with 1.9º×2.5º lat-lon spatial resolution and 26 vertical levels, considered only monthly and annual output and used meteorological fields from a free running (FR) simulation representative of the 2000th decade. In the present study, CAM-Chem was executed on the specified dynamics (SD) mode using the meteorological fields prevailing at the time of the campaigns (years 2013 and 2014) with a spatial resolution of 1° (longitude) × 1° (latitude) and 56 vertical levels (from the surface to ~ 3.5 hPa). In addition, the model provided hourly output that was sampled at exactly the same times and locations as the ATTREX measurements. These features, explained in the methodology of the model, add the originality to this work, thus we consider this a major outcome as we were able to confirm the previous results of Fernandez's study. See also answer to minor comments 3 and 6.

5. Page 10, lines 20 to 22: … the absence of ice-crystal reactions increases the total inorganic fraction by 7% and 12% over the EP during the day and night, respectively. …. I see no specific reason why ice-crystals should change the amount of Bry (or Cly), except that Bry (or Cly) is heterogeneously removed from the gas phase, which (if the case) you should then mention and quantify in the manuscript. Again I emphasize (see comment 5, first paragraph) to show in a separate figure how (a) Bry (and Cly) is partitioned among all (organic and inorganic) gaseous bromine (and chlorinated) species (b) the fractions being up-taken by particle, and (c) the fraction being permanently removed by sedimentation (comment II.) #5, first paragraph in the previous review).

Response: There is not any non-stoichiometric heterogeneous reaction removing directly HBr from the gas phase in our model setup. To make it clear how heterogeneous reactions can affect the washout of bromine in the TTL, we added the following sentence in Section 3.3 (page 11, line 1-5):

"Including heterogeneous reactions in the chemical mechanism changes the relative partitioning between Br_y species, and consequently, the abundance of the dominants species that controls effective removal are altered. Thus, turning on and off heterogeneous reactions will change the bromine sinks within the UT and TTL, as the relative efficiency of effective washout for each independent Br_y species are different (i.e., individual Henry's Laws constant are considered for each species)."

We also added the following sentence in the methodology section to describe the washout parameterization implemented in CAM-Chem (page 5 line 24-28).

"Losses in CAM-Chem are parameterized following a large-scale precipitation scavenging algorithm that includes a physical treatment of scavenging through improvements in the formulation of the removal in sub-grid-scale cloudy environments, and includes washout as well as ice phase uptake of soluble inorganic bromine species (each of them with an independent Henry's Law constant) within the water column (see Neu and Prather, 2012 and Fernandez et a., (2014) for details)."

From the three independent points emphasized by the reviewer, item a) requested Bry (and Cly) inorganic (and organic) vertical profile information. The answer has been already given in the response to mayor comment 2 above. Regarding items b) and c), including additional figures showing the bromine fraction being uptake by water and/or ice particles, as well as the fraction being removed by sedimentation, is not the focus of current work. Expanding on these issues here will enlarge enormously the manuscript and change the main focus of this paper, which is to escort the Navarro et al., (2015) study by addressing the inorganic bromine abundance consistent with the previous reported measurements. We agree with the reviewer that heterogeneous uptake and washout is a very important issue, and as such it will be address in another forthcoming paper specifically focused on comparing the different type of halogen removal parameterizations. Here, we have just expanded the description of washout processes of the dominant species, and computed the change in the total inorganic bromine burden for the full scheme compared to the sensitivity case that neglected heterogeneous reactions. The original text (page 10, lines 20-22) now reads: (page 11, lines 6-19).

"*Relative to the results from the complete mechanism (Fig. 4), at 17 km, the absence of ice-crystal reactions increases the total inorganic fraction by 7% and 12% over the EP during the day and night, respectively. On the other hand, Br_y increases by 29% and 40% over the WP during day and night, respectively. This relative increase of total Br_y is mainly due to changes in the amount of HBr during the day and an enhancement of both HBr and $BrONO_2$ during the night. As BrCl is only produced by equations (4) and (5), it does not accumulate during night hours within the sensitivity study where heterogeneous reactions have been turned off (Fig.10). The mixing ratios of all other species remain very similar when comparing Figure 4 and Figure 10. Our model results show that turning off heterogeneous reactions reduces the total amount of Br_y washed out at 17 km by ~0.5 pptv and ~0.3 pptv for the WP and EP, respectively. This value is of the same magnitude but opposite direction to the results obtained by Aschmann et al., (2011). HBr is highly soluble and it would be expected that a relative increase in HBr partitioning would imply a more efficient washout. But, as explained by Aschmann et al. (2011) it is possible that a significant part of the adsorbed HBr at high altitude levels can re-evaporate within the TTL (and eventually reach the stratosphere) before being washed out. This is because the removal process does not occur right away and residence times are large in the TTL. Indeed, they found a local HBr maximum at around 17 km within an equivalent sensitivity simulation that neglected heterogeneous activation for HBr."*

6. Page 11, lines 14 to 20: Reactive species like atomic Br become the dominant Bry species in large regions of the TTL during daylight, following the large variation of ozone abundance within these regions strongly influenced by deep convection……
While I see motives for this statement when air masses are strongly influences by convection in in the TTL of the WP (and much less for the EP due to in general higher ozone there), how does the result relate to results of previous theoretical studies (beyond those of Fernandez et al., 2014)?

Response: As we mentioned in previous answers, this study is a follow up of the study carried out in 2015 (Navarro et al., 2015), which focused on the ATTREX campaign, and not the one carried out in 2014 (Fernandez et al., 2014), which first described the tropical ring of atomic bromine. Thus, we've focus on the modelled product gas distributions within the EP and WP consistent with the VSL source gas measurements reported in Navarro et al., instead of providing other model and/or measurement evidences regarding the existence of the tropical rings hypothesis on this work. Certainly, current results are expected to lie in line to our previous studies, but there are also other studies performed with other models and by other authors, that have suggested the prevalence of atomic bromine in the TTL. For Example:

"This enhancement of Br in the tropical upper troposphere was previously identified by Holmes et al. [2006] for its importance in Hg(0) oxidation and is a consistent feature of models [Fernandez et al., 2014]". (Schmidt et al., GRL, 2016. Model GEOS-Chem).

"Thus, a small amount of BrO observed in the TFT and TTL can reflect the presence of a much higher amount of Br_y*. Consequently, the full assessment of PGI requires observations of a wider suite of inorganic bromine species in the tropics"* … *"The ratio of [Br]/[BrO] increased with altitude and is significantly greater than 1 in the TTL, making Br atom the dominant daytime photoreactive* Br_y *component from ~11 km to the highest altitude we sampled (~15 km)"*. (Chen et al., JGR, 2016. See their Figure 10, panel c.)

In order to make this point clear we have modified the text as follows (Page 9, line 24-26):

"This enhancement of Br atoms in the tropical tropopause layer has also been identified in other studies and seems to be a consistent feature in global models including a complete treatment of halogen chemistry in the troposphere (Chen et al., 2016;Holmes et al., 2006; Schmidt et al., 2016;)."

See also answer to minor comments 3 and 4.

7. Page 11, lines 21 to 22: Why the contribution of inorganic bromine directly injected into the TTL is omitted here, e.g. Schmidt et al., 2016, Werner et al., 2017 and others.

Response: As we have already clarified in the answer to minor comment 1, our study considers and discusses the direct contribution of Br_y into the TTL. We find not necessary to cite other works here, as we have done it before and because in the lines highlighted by the reviewer we are summarizing only the concluding remarks of our study. Within the referred sentence, when we mention *"their transport into the TTL, as well as the efficiency of heterogeneous reactions* *involving ice-aerosols"* we are pointing out to the inorganic bromine fraction prevailing in the lower troposphere, which is transported into the TTL. But, as we see the current wording had confused the reviewer, and could also be misunderstanding to other readers, we have modified the sentence to make it clear and explicit (page 12, line 18-22):

"The variable photodecomposition of VSL$_{org}$, the transport of inorganic degradation products from the lower troposphere into the TTL, as well as the efficiency of heterogeneous reactions involving ice aerosols, play an important role in the overall upper tropospheric Br$_y$ loading and the consequent stratospheric bromine injection."

8. Page 11, line 25: …. to diminish the uncertainty of the amount of Bry that reaches the stratosphere, and properly constraint the global bromine budget.
In fact, previous studies indicated that the amount of bromine in the stratosphere is less uncertain than how and in what form (i.e. the fraction of organic and inorganic) it is transported into stratosphere. Here you need to cite at least WMO 2014, and if you like to provide an informed list of bromine-related measurements, however only those performed tropical UT/TTL/LS, you need to cite the studies of Schauffler et al., 1993, 1998, and 1999; Dorf et al., 2008; Laube et al., 2008; Brinckmann et al., 2012; Sala et al., 2014; Wang et al., 2015; Werner et al., 2017; Stutz et al., 2017 and others.

Response: The lines highlighted by the reviewer is the last sentence of the paper, and is oriented to call the scientific community to keep on going and reinforcing their efforts on measuring the speciation of inorganic bromine species in the TTL. That is why we prefer not to cite previous campaigns at this time (most of which, on the other side, have already been cited in previous sections of the manuscript).

Typos and necessary clarifications:
1. Page 2, line 30: ….. showed approximately 3 to 5 ppt for potential temperatures between 350 and 400 K in the TTL …change to…. showed approximately 3 to 5 ppt Bry for potential temperatures between 350 and 400 K in the TTL
Done
2. Page 2, line 33: Our study manly focuses …change to … Our study mainly focuses
Changed to "focuses mainly" as suggested by a native English speaker author.
3. Page 4, lines 6 and 7: … with 90 custome-made stainless change to …. with 90 custom-made stainless…and again from … a custome inlet at 2 to 8 liters .. to .. a custom inlet at 2 to 8 liters
Done
4. Page 4, line 31: …. the modelling estimates of the organic bromine fractions were similar for the entire Pacific (3.84 ± 0.64 and 3.18 ± 1.49 ppt from WP and EP, respectively). I guess here 'bromine tied in very short lived species' is meant?
The phrase very short-lived species was added to the text.
5. Page 6, line 29: Over the EP, BrONO2 dominates the entire range of altitude from 14 to 18 km.

Since this statement is certainly only correct for the inorganic bromine partitioning at night, the sentence should accordingly read. Over the EP, BrONO2 dominates the entire range of altitude from 14 to 18 km at night.

Done

6. Page 6, line 29: The total Bry burden during daylight hours increases from … change to .. During daylight hours, Bry increases from….

Done

8. Page 7, line 8: …. of 2.63 ± 1.04 ppt to 5.11 ± 1.57 ppt as we move upward in the TTL …delete … as we move upward in the TTL.

Done

9. Page 7, line 15: is almost half the value found in the EP ... change to ….. is almost half the concentration predicted for the EP (since a model predicts rather than finds (measures) something).

Done

10. Page 7, line 16: ……………are < 85 pptv in the WP and < 182 for … change to … are < 85 pptv in the
WP and < 182 pptv

Done

11. Page 7, line 19 and elsewhere in the manuscript: … in the western pacific region, … change to … in the western Pacific ... since Pacific is a name and hence needs to be written with a capital letter.

Changed to WP to keep consistency along the text.

12. Page 7, line 23: Figure 5 compares the mean abundances observed ….. change to Figure 5 compares the mean abundances of O3 (measured?), NO2 (modelled), and Cly (modelled)… since your study mostly reports on model results.

Since figure 5 and 6 were added to the manuscript, the text in page 7 line 33 to page 8 line 3 now reads: *"Figures 5 and 6 compare the Br_y partitioning as well as the modelled O_3, NO_2 and Cl_y abundances along all flights in the EP and WP, respectively. Here, it can be clearly observed how the dominant species changes from BrO during daytime, to $BrONO_2$ or BrCl during night-time. Figure 7 shows the mean abundances for all species including all flights in the WP and EP."*

13. Page 7, line 28: As the SZA keeps on increasing, a decrease on photolysis as well as ozone concentrations… change to .... As the SZA is increasing, a decrease in the photolysis as well as ozone concentrations… and delete … as well as ozone concentrations…since there is no reasons why ozone concentrations should decrease with SZA.

Changed to "As the SZA increases, a decrease of photolysis…" as suggested by a native English speaker author.

14. Page 7, line 34: The scenario over the EP is slightly different as levels of NO2 and O3 define a high NOx regime … change to .. The scenario for the EP is slightly different from the WP as concentrations of NO2 and O3 define a high NOx regime there.

Changed to *"The scenario over the EP is slightly different as levels of NO_2 and O_3 are larger, while the Surface Area Density of ice-crystals (SAD-ICE) is reduced (see Section 3.3)."* as explained in major comment 2.

15. Page 8, line 2, and elsewhere in the text: Stutz et al. (2016) change to … Stutz et al. (2017)

Done

16. Page 8, line 16: Note that the differences …change to … Note that the predicted differences

Done

17. Page 8 line 16: the EP if the independent flights…change to … the EP if individual flights …

Done

18. Page 8, line 28: Note, however, that atomic Br abundances surpass BrO mixing ratios at low SZA (close to noontime) and low ozone abundances (below 100 ppb, Fig. 5b and 5d) …. change to …Note, however, that modelled atomic Br abundances surpass BrO mixing ratios at low SZA (close to noontime) and low ozone abundances (below 100 ppb, Fig. 5b and 5d).

Done, and as the number of the figures changed now it reads: *"However, modelled atomic Br abundances surpass BrO mixing ratios at low SZA (close to noontime) and low ozone abundances (below 100 ppb, Fig. 7b and 7d)."*

19. Page 9, line 2: In the EP, Br surpasses BrO mixing ratios at 60º SZA for flights RF04 and RF06, but…. change to … In the EP, modelled Br surpasses BrO mixing ratios at 60º SZA for flights RF04 and RF06, but

Done

20. Page 9, line 8: …. which focused on ATTREX measurements taken exclusively over the EP and used an O3-scaling technique to retrieve their results, our model calculations support the fact that …change to .. which focused on ATTREX measurements taken over the EP, our model calculations indicate Br/BrO ratios (erase 1. exclusively since SF2 and SF5 lead to central Pacific),

Done

2. erase … used an O3-scaling technique, since it falls of the context here,

We have not modified the sentence as we believe that this is actually one of the main differences between Werner et al., 2017 study and ours.

and 3. our model calculations support .. erase the fact that .. since a model can never produce facts but only more or less good predictions et cetera

Word fact changed to prediction.

21. Page 9, line 16: Over the EP, Br/BrO > 1 are observed as discrete masses, particularly at SZA between 40°and local noon … change to … Over the EP, Br/BrO > 1 are predicted (you did not observe it) in distinct air masses, particularly at SZA between 40°and local noon. …..by the way a result not supported by the results of the Werner et al., 2017 study.

Change made. However, comment regarding to comparison with Werner et al., 2017 manuscript has been omitted here as they have been mentioned just a few lines above (page 9, line 21). Once again, we want to emphasis that our modelling paper is not based on how well or not we compare to measurements and TOMCAT/SLIMCAT model results in Werner et al., 2017.

22. Page 10, line 6: …on the distribution of the inorganic species .. change to .. on the partitioning of the inorganic species

Done

23. Page 10, line 24: As explained by Aschmann et al. (2011) the increment in the amount of HBr at high altitude levels could be due to a slowly sedimentation following by evaporation as the adsorbed HBr is not washed out right away. This sentence (as it is) does not really make sense to me, since if HBr is taken-up by particles it should reduce Bry at the condensing altitudes and upon evaporation (of the particles) should release HBr at lower altitudes (and not vice versa). So accordingly correct the sentence.

We have modified the sentence as follows. For a complete description of HBr washout see also the answer to minor comment 5 above.

"HBr is highly soluble and it would be expected that a relative increase in HBr partitioning would imply a more efficient washout. But, as explained by Aschmann et al. (2011) it is possible that a significant part of the adsorbed HBr at high altitude levels can re-evaporate within the TTL (and eventually reach the stratosphere) before being washed out."

25. Page 10, line 33: (SAD-ICE) explain the acronym by words.

SAD-ICE= Surface Area Density of ICE. The acronyms was described before put it between parentheses. We capitalized the initials of the phrase to make it clear.

26. Page 11, line 10: …while BrCl and BrONO2 were found as the night-time dominant species over the WP and EP, respectively. …change to … while BrCl and BrONO2 were predicted to dominate TTL Bry at night-time.

Done

27. Legend Figure 5: 'Average of inorganic bromine species (top panel) and main reactants of the inorganic chemistry (bottom panel) using the entire range of altitudes (14 to 18 km) over the western Pacific (a and b) and eastern Pacific (c and d). Black boxes indicate the percentage of the dominant Bry species for day and night at 17 km.'

First I'm not sure what can be learned from 'averages' for the altitude range 14 – 18 km, when obviously information on the profiles (from the measurements and the model) of the shown quantities is available. Second, I really wonder why these 'averages' somewhat 'oscillate', actually more for the dark than the sun-lit hours. Third, I wonder whether these oscillations are also seen in the measured source gases?

We appreciate the reviewer for addressing the erroneous caption description of old Figure 5, which is now Fig. 7 in the current version. Perhaps it is clearer to interpret now that an equivalent plot for each individual flight has been included in the new main Figures 5 and 6. Each independent panel in Figures 5 and 6 shows the modelled CAM-Chem bromine partitioning sampled at exactly the same times and locations (lat, lon, lev) as the ATTREX measurements. Only results lying between 14 and 18 km are considered. Current Figure 7a and 7b then shows the mean SZA dependence (averaged within ± 5 SZA) for all flights developed in the WP and EP, respectively. We have then modified the text and caption as follows:

"Figure 5 and 6 compares the Br_y partitioning as well as the modelled O_3, NO_2 and Cl_y abundances along all flights in the EP and WP, respectively. Here it can be clearly observed how the dominant species changes from BrO during daytime, to $BrONO_2$ or BrCl during nigh-time. Figure 7 shows the mean abundances for all species including all flights in the WP and EP. Even though the mean results do not simulate differences observed in each flight, they are representative and illustrative of the average state of the tropical upper atmosphere within the EP and WP in the presence and absence of sunlight, and should provide relevant information about the dominant processes occurring in each region." (page 7 line 33 to page 8 line 6)

"The CAM-Chem output along the ATTREX flights, indicates that Br and BrO alternate as the dominant daytime species, indicating a large inhomogeneity for the tropical ring of Br, mainly due to the large ozone/T variability of the air parcels within the convective tropical WP and EP." (page 12, line 14-16)

"Figure 5: Inorganic bromine species and main reactants of the inorganic chemistry sampled at exactly the same times and locations as the ATTREX flights developed over the western Pacific.

Each separate panel show SZA dependent results for flights RF01, RF03, RF04, RF05, RF06, RF07 and RF08. Only output sampled between 14 and 18 km is considered. (page 22, caption)

"Figure 6: Figure 6: Inorganic bromine species and main reactants of the inorganic chemistry sampled at the same times and locations as the ATTREX flights over the eastern Pacific. Each separate panel show SZA dependent results for flights RF01, RF03, RF04, RF05 and RF06. Only output sampled between 14 and 18 km is considered." (page 23, caption)

"Figure 7: Average of inorganic bromine species (top panel) and main reactants of the inorganic chemistry (bottom panel) for all ATTREX flights developed over the western Pacific (a and b) and eastern Pacific (c and d). The output from each flight has been sampled only between 14 and 18 km, and that the average has been performed within ± 5 SZA bins. Black boxes indicate the percentage of the dominant Br_y *species for day and night at 17 km."* (page 24, caption)

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