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 inter-comparison 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.

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).

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.

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.
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.
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.

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 et cetera.
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).
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)?
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
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.

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
2. Page 2, line 33: Our study manly focuses …change to … Our study mainly focuses
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
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?
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.
6. Page 6, line 29: The total Bry burden during daylight hours increases from … change to ..
7. During daylight hours, Bry increases from….
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.

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).
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
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.
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.
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.
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.
15. Page 8, line 2, and elsewhere in the text: Stutz et al. (2016) change to … Stutz et al. (2017)
16. Page 8, line 16: Note that the differences …change to … Note that the predicted differences
17. Page 8 line 16: the EP if the independent flights…change to … the EP if individual flights …
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).
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
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), 2. erase … used an O3-scaling technique, since it falls of the context here, 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
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.
22. Page 10, line 6: …on the distribution of the inorganic species .. change to .. on the partitioning of the inorganic species
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.
24. 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.
25. Page 10, line 33: (SAD-ICE) explain the acronym by words.
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.
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?

Additional references:

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