

Interactive comment on “Modelling the Inorganic Bromine Partitioning in the Tropical Tropopause over the Pacific Ocean” by Maria A. Navarro et al.

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Received and published: 16 March 2017

Revised manuscript with changes in lines and supplementary figures has been attached as a supplement PDF file.

Review of: Modelling the Inorganic Bromine Partitioning in the Tropical Tropopause over the Pacific Ocean by Navarro et al.

General Remarks: This paper uses global model stimulations to examine the inorganic bromine (Bry) budget of the TTL, building on the work of Navarro et al. (2015). In that work, the authors (a) presented measured (and modelled) vertical profiles of brominated very short-lived substances (VSLs), such as CHBr₃ and CH₂Br₂, from recent NASA ATTREX flights, and (b) used a model that reproduces the observations well (CAM-Chem), to estimate the contribution of VSLs to Bry in the TTL (highlighting the

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significance of that contribution). In the present work, the same approach is adopted as above, though the focus is more on understanding the modelled Bry speciation in the TTL, the Bry diurnal cycle, and differences between the West and East Pacific (where the ATTREX missions sampled). The model results from this work show that BrO and Br are the most abundant daytime species, while BrCl and BrNO₂ are more important at night. The authors also discuss differences in modelled Bry partitioning between the West and East Pacific, and briefly the sensitivity to heterogeneous processes on ice. Overall, this paper is an interesting case study that provides an (incremental) advance on our understanding of Bry partitioning in the TTL over the Pacific. In the absence of new BrO measurement data being included in the manuscript, this advance is somewhat subtle when viewed alongside the modelling study of Fernandez et al. (2014, ACP) that also used CAM-Chem to look at TTL bromine partitioning, in some detail. I have outlined three major areas below that should be addressed before publication.

Response: We thank the reviewer for the helpful comments and technical corrections. Below we address point-by-point all his/her comments and suggestions.

Major Comments: 1. The authors should ensure that the Introduction clearly sets out which of the broad model findings have come before, in order to help determine what the main motivation and purpose of this paper is. For example, the model results on zones where the Br/BrO ratio is >1 in the UTLS are interesting, though have been discussed previously by Fernandez et al. (2014, ACP) and Saiz-Lopez and Fernandez (2016, GRL). The same can be said about the analysis of the Bry diurnal cycle and Bry speciation in the TTL, and their sensitivity to heterogeneous processes. Is the advance here that this is simply a CAM-Chem case study for the ATTREX campaign period? If so, that is fine, but the measurements of BrO (and NO₂) from ATTREX would very much strengthen the paper and help corroborate the modelled fields. In the first paragraph of Results and Discussion, it is noted that “BrO and NO₂ measurements from the ATTREX mission were still under examination by the time of this analysis”. Is this still the case? It strikes me that it is quite odd that these data are not included here.

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Response: We have amended the text of the introduction to clarify that the main motivation and purpose of this paper is to model the inorganic bromine partitioning derived from the different flights during the ATTREX campaign. A paragraph has been added to page 2 line 33 and now it reads: "Our study mainly focuses on the difference in modelled Bry concentrations in the TTL over the Pacific throughout the ATTREX campaign flight tracks, and examines its temporal and spatial distributions. "Based on the reliable representation of the observed VSLorg by the CAM-Chem model on the study of Navarro et al., 2015, and as a follow up of this investigation regarding the chemistry of bromine tracers in the TTL, we estimated the partitioning of Bry over the tropical eastern and western Pacific during 2013 and 2014, respectively." "From this case study analysis, we also complement the finding of the diurnal Bry speciation in the TTL, and the Br/BrO ratio distribution in the Upper Troposphere-Lower Stratosphere (UTLS) found by Fernandez et al., 2014 and Saiz Lopez and Fernandez, 2016." Regarding to the measurements of BrO (and NO₂) from ATTREX, we agree with the reviewer that it would strengthen the paper and help corroborate the model. However, this model study was running simultaneously with the study published by Navarro et al., 2015, when measurements of BrO and NO₂ were still under examination, as we stated in Results and Discussion section. We clarify this point by adding the following sentence at the beginning of the Results section (page 5 line 28), which now read: "This modelling study was carried out simultaneously with the work published by Navarro et al., 2015. Only ozone and VSLorg abundances were available to validate model performance as BrO and NO₂ measurements from the ATTREX mission, now published by Werner et al., (2017), were still under examination by the time of this analysis. Thus, once the model performance during ATTREX campaign is evaluated in Sect. 3.1, we step into a CAM-Chem modelling case study oriented to determine the Bry partitioning (Sect. 3.2) and efficiency of heterogeneous recycling reactions (Sect- 3.3) on the mostly unexplored eastern and western pacific." To the day, the BrO and NO₂ measurements from ATTREX 2014 (Western Pacific) are still under review. Measurements of BrO and NO₂ from ATTREX 2013 were published on the work of Werner et al., 2017,

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but were not used in our study as the other manuscript was still under discussion by the time of our submission. However, our NO₂ and BrO estimations are within the ranges observed by the measurements of Werner et al., manuscript. An additional statement have being added to our manuscript on page 7 line 5 and page 7 line 34 to clarify this information. The text now reads: “Our mean vertical distributions for the EP are in the lower edge of the reported ranges of Werner et al. (2017), who reported a measured range for BrO between 0.5 ± 0.5 ppt at the bottom of the TTL and about 5 ppt at $\theta = 400$ K, consistent with an inferred increase of Bry from a mean of 2.63 ± 1.04 ppt to 5.11 ± 1.57 ppt as we move upward in the TTL.” “Our average range of NO₂ mixing ratios is approximately 15 ± 6 ppt at 14 km, with slightly higher values over the tropopause, 22 ± 24 ppt at 17 km. These estimates within 1 standard deviation agree with the NO₂ values presented by Stutz et al. (2016) and Werner et al. (2017) from observations made during ATTREX 2013 over the EP. As they report in their manuscript, their O₃ scaling technique allowed retrieval of NO₂ concentrations of 15 ± 15 ppt in the TTL, and a range of 70 up to 170 ppt in the mid-latitude lower stratosphere.”

2. The most novel aspect of this work is the examination of differences between the W and E Pacific. The discussion of chlorine could be improved in this regard. If differences in Cly between the two regions can impact local Bry partitioning, some discussion on how well constrained the actual Cly simulation over the WP (average up to 84 ppt Cly in daylight) and EP (up to 181 ppt Cly in daylight) is needed. At the very least some more details of the chlorine simulation could be given. More broadly, I would suggest that the title of the paper should reflect that the emphasis of the paper is on the differences between W and E Pacific. Response: We appreciate the reviewer for highlighting this aspect, which has now been strengthened the revised manuscript. Although the sensitivity simulation described in Section 3.3 was introduced to highlight how the different atmospheric conditions between the EP and WP were affecting the bromine partitioning, the original manuscript mainly focused on the changes due to the high/low NO_x regime prevailing in each region. The impact of Cly chemistry is maximized during the night, as the abundance of reservoir bromine species (i.e. BrONO₂,

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HOBr, HBr) maximizes after down, and in the presence of ice-crystals those species can react with HCl (which is the dominant Cly species throughout the troposphere). Thus, the following heterogeneous reacting sequence is amplified in the presence of large Surface Area Densities (SAD) in the TTL. $\text{BrONO}_2 \rightarrow \text{HOBr} + \text{HNO}_3$ $\text{HOCl} + \text{HBr} \rightarrow \text{BrCl} + \text{H}_2\text{O}$ $\text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}$ In order to highlight the large impact that the heterogeneous recycling occurring on ice-crystal has on the nighttime partitioning, as well as validate the Cly abundance in CAM-Chem, we introduced the following sentences. Please note that additional information regarding chlorine chemistry is also given below in the answers to the general comments. Page 7 lines 14: “It is worth noting that even when the maximum inorganic chlorine levels are larger in the EP, BrCl is not the dominant nighttime reservoir, while in the WP, where BrCl dominates, maximum Cly mixing ratio is almost half the value found in the EP (see Table 1). 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). This can be explained considering the faster vertical transport occurring in the western pacific region, which decreases the photochemical decomposition of VSL chlorocarbons (Saiz Lopez and Fernandez, 2016).” Page 8 lines 14: “Note that the differences in Cly abundance can reach factors as much as 5 times larger for the EP if the independent flights are considered (e.g., max. Cly ~500 ppt for RF01, RF03 and RF04 performed in the EP during ATTREX 2013, while max. Cly for all flights except RF07 (< 400 pptv) remain below 100 ppt. However, the night time BrCl abundance is larger in the WP, representing more than 90% of the nighttime Bry partitioning for flights RF02 and RF04 (see Figure S1 & S2 in the Supplement). For these cases, BrCl mixing ratios between 1 and 2 pptv are formed within air parcels with a very low Cly abundance (of the order of 10 ppt). In order to understand this unexpected behavior, we performed a sensitivity simulation neglecting the inter halogen heterogeneous recycling occurring on upper tropospheric ice crystals, see Sect 3.3 below.” Page 10 line 5: “Heterogeneous recycling reactions of reservoir species on ice crystals are relevant at UTLS levels, thus, a sensitivity test

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was carried out to determine the influence of waterâice aerosols on the distribution of the inorganic species. Equations (1) to (6) shows the chlorine, bromine and inter halogen tropospheric heterogeneous reactions occurring on iceâcrystals (for a complete description of the implementation of heterogeneous reactions in CAM Chem, see Table S1 in supplementary online material of Fernandez et al., 2014). $\text{BrONO}_2 \rightarrow \text{HOBr} + \text{HNO}_3$ (1) $\text{ClONO}_2 \rightarrow \text{HOCl} + \text{HNO}_3$ (2) $\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$ (3) $\text{HOCl} + \text{HBr} \rightarrow \text{BrCl} + \text{H}_2\text{O}$ (4) $\text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}$ (5) $\text{HOBr} + \text{HBr} \rightarrow \text{Br}_2 + \text{H}_2\text{O}$ (6) Page 10 line 28: “Thus, neglecting ice recycling reactions (1) to (6) suspend the heterogeneous conversion of BrONO_2 to BrCl , and gasâphase bromine nitrate (which is formed mainly by the termolecular reaction of $\text{BrO} + \text{NO}_2 + \text{M}$ during twilight) remain as the dominant Br_y species during the night both under a high NO_x regime (i.e., within the EP region) as well as under the low NO_x regime (western pacific). But when the heterogeneous recycling reactions are activated, the model output predicts that the recycling efficiency depends mostly on the total surface area density of ice crystals in the upper troposphere (SAD ICE): even under very low Cl_y concentrations (between 10 and 20 ppt), if SAD ICE is present in the TTL, the nighttime partitioning is displaced in favour to BrCl . Fernandez et al., (2014) found tropospheric SAD ICE levels within the western pacific upper TTL to be the largest of the whole tropical region, suggesting that BrCl abundance should be maximized in this region of the pacific.” Finally, following the advice of the reviewer we change the title of the manuscript to emphasize the difference between W and E pacific. The title now reads: “Modelling the Inorganic Bromine Partitioning in the Tropical Tropopause over the Eastern and Western Pacific Ocean”

3. The writing is quite awkward in many places and the paper would benefit from a very thorough check/read through. In addition, although the paper is compact, it would benefit from some sub-headings, particularly in the Results and Discussion section (e.g. Model-measurement O_3 comparison, Diurnal cycle in Br_y partitioning, or something similar). Response: Following the advice of the reviewer, we have added some sub-headings to the results and discussion section. The text is now separated in the

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following sections: 3.1 CAM-Chem model evaluation 3.2 Bry partitioning 3.2.1 Tropical ring of atomic Br: indications from this case study 3.3 Heterogeneous reactions: impact of water-ice recycling on Bry speciation/distribution

Other points: *Abstract* Sometimes the “E” in Eastern (Pacific) and the “W” in Western (Pacific) are capitalized and sometimes they are not. Please be consistent throughout manuscript (including in figures and captions). This has been corrected in the manuscript. *Introduction* P1, L33: “Bry” is defined early on in the manuscript but “inorganic bromine” is used in numerous places after that. I suggest changing the latter to the former where appropriate throughout the manuscript. Change has been made, although we kept “inorganic bromine” at a few places to facilitate the reading of congested sentences. P3, L2: Struck me that introducing the “proposed tropical ring of atomic bromine” here is odd. Could you not make mention of these papers earlier in the Introduction? A statement has been added to the introduction on page 2 lin 27. Now the text reads: “This study also introduced the concept of the “tropical ring of atomic bromine”, a photochemical phenomenon that extends in the tropics from approximately 15 to 19 km where the abundance of Br atoms is favoured due to low temperatures (<200K) and low O3 abundances(<100 ppb).” P3, L3: “section 3” → “Section 3” Change has been made *Methods* I would separate out Methods into 2.1 Observations and 2.2 Modelling. This section seems quite unstructured in its present form. The Modelling section needs more details as to the ozone precursor emissions that were used in CAM-Chem + some brief information of the chlorine simulation. Change has been made. The methods section has been divided in section 2.1 Observations and 2.2 Modelling. In addition section 2.1 has been separated in 3 other sub-sections to improve the format and structure of the manuscript. Section 2.1 now includes: 2.1.1 ATTREX campaign, where we have added in the paragraphs of P5, L7 as it was suggested in your last comment. 2.1.2 VSLorg Observations, which briefly described the GWAS methodology explained on our previous publication: Navarro et. al., 2015. 2.1.3 O3 Observations, which described the O3 methodology. In addition, we extended the description of the ozone precursor inventory and the bromine and

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chlorine emissions as follow (page 5 line 9): “The current setup is based on the bromo-carbon emission inventory of Ordoñez et al., (2012), which includes time dependent geographically distributed sources of CHBr_3 , CH_2Br_2 , CH_2BrCl , CHBr_2Cl , CHBrCl_2 and CH_2IBr . Even when we do not consider here other chloro carbon sources like CH_2Cl_2 and C_2Cl_4 , those species live long enough to be injected almost entirely as source gases to the stratosphere and do not contribute to the tropospheric inorganic chlorine (Cly) loading [Hossaini et al., 2015]. Additional Bry and Cly sources from sea-salt heterogeneous dehalogenation in the lower troposphere are parameterized (Ordoñez et al., 2012; Fernandez et al, 2014). Prescribed surface volume mixing ratios of long lived chlorofluorocarbons (CFCs) and halons, as well as surface concentration of anthropogenic CO_2 , CH_4 , N_2O and other ozone precursors are based on the long-lived inventory of Meinshausen et al. (2011).” P3, L12: Has “very short-lived organic substances” not already been defined as VSLorg? Also, as the focus of this work is on VLSL, it would be better if some of the gases listed (e.g. CHBr_3 etc.) are actually referred to earlier in the Introduction (maybe around line 31). Changes have been made, and now page 1 line 31 reads: “Many of these discuss the contribution of brominated very short-lived organic substances (VSLorg) like bromoform (CHBr_3), dibromomethane (CH_2Br_2) and/or bromochlorocarbons such as (CH_2BrCl , CHBr_2Cl , CHBrCl_2 , etc.), in addition to long-lived halons and methyl bromide (CH_3Br), as an important source of stratospheric bromine.” P3, L17: The two sentences beginning “At the tropopause level” seems out of place. Is this not motivation/background for the present study and should it not appear in the Introduction? We believe that the phrase “At the tropopause level” may still be correct. As we mentioned before, this study is based on the previous publication of Navarro et. al., 2015 and the model results of the organic and inorganic bromine composition were found simultaneously. The study of Navarro et al., 2015 showed the organic bromine composition at the tropopause level ($\sim 17\text{km}$). To clarify this point, we added a sentence on the introduction page 2 line 34 which now reads: “Based on the reliable representation of the observed VSLorg by the CAM-Chem model on the study of Navarro et al., 2015, and as a follow up of

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this investigation regarding the chemistry of bromine tracers in the TTL, we estimated the partitioning of Bry over the tropical eastern and western Pacific during 2013 and 2014, respectively". P4, L4: CAM-Chem has already been defined. Change has been made P4, L21: "for both, the WP and EP respectively" → "for both the WP and EP". Change has been made P5, L7, Sentence beginning "During ATTREX" to the end of the paragraph. This text describes the different sampling times/paths of the observations/flights and would be better placed in Section 2. In the current location it disrupts the flow of results. Similarly, consider moving Figure 3 to the Measurements section. Changes have been made

References: Fernandez, R., Salawitch, R., Kinnison, D., Lamarque, J.-F., and Saiz-Lopez, A.: Bromine partitioning in the tropical tropopause layer: implications for stratospheric injection, *Atmospheric Chemistry and Physics*, 14, 13391-13410, 2014. Navarro, M. A., Atlas, E. L., Saiz-Lopez, A., Rodriguez-Lloveras, X., Kinnison, D. E., Lamarque, J.-F., Tilmes, S., Filus, M., Harris, N. R., and Meneguz, E.: Airborne measurements of organic bromine compounds in the Pacific tropical tropopause layer, *Proceedings of the National Academy of Sciences*, 112, 13789-13793, 2015. Saiz-Lopez, A., and Fernandez, R. P.: On the formation of tropical rings of atomic halogens: Causes and implications, *Geophysical Research Letters*, 43, 2928-2935, 2016. Werner, B., Stutz, J., Spolaor, M., Scalone, L., Raecke, R., Festa, J., Colosimo, F., Cheung, R., Tsai, C., R.Hossaini, Chipperfield, M. P., Taverna, G. S., Feng, W., Elkins, J. W., Fahey, D. W., Gao, R.-S., Hints, E. J., Thornberry, T. D., Moore, F. L., Navarro, M. A., Atlas, E., Daube, B., Pittman, J., Wofsy, S., and Pfeilsticker, K.: Probing the subtropical lowermost stratosphere, tropical upper troposphere, and tropopause layer for inorganic bromine, *Atmos. Chem. Phys.*, submitted, 2016.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/acp-2016-1031/acp-2016-1031-AC2-supplement.pdf>

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