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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Quantifying the vertical transport of $CHBr_3$ and CH_2Br_2 over the Western Pacific" *by* Robyn Butler et al.

Anonymous Referee #2

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General Comment

The paper presents a modelling experiment oriented to quantify and attribute the location of oceanic CHBr3 and CH2Br2 sources reaching the Upper Troposphere (UT) and Tropical Transition Layer (TTL) within the Western Pacific. GEOS-Chem tagged simulations are performed to determine the extent at which coastal and open ocean geographical regions contribute to the CHBr3 and CH2Br2 mixing ratios at different heights, as well as to determine the physical age of air of the air parcels arising from each of the tagged regions. Experiment results are compared to atmospheric measurements performed during CONTRAST and CAST in Jan-Feb 2014, showing a good agreement when the model bias is removed. Overall, I found the study very interesting and of relevance for ACP. It contributes to understand how oceanic sources of brominates substances are transported to the TTL, a transit region with important strato-

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Discussion paper

spheric injection implications. However, I have some concerns respect to the validity of one of the tagged scenarios and the model validation against NOAA data; and most importantly, I found many of the analysis and discussions given in Sections 4 (Results) and 5 (Discussions and Concluding remarks) very vague and/or requiring stronger evidence that supports them. I suggest being more specific and formal on the explanation of the specific statements highlighted in this review.

Specific Comment I

The emission inventory for CHBr3 and CH2Br2 used in GEOS-Chem is that from Liang et al., 2010, which is based on Warwick et al., 2006. Those emissions scenarios include only oceanic sources (continental emissions are zero), and include a coat-to-ocean enhancement to better fit experimental data. Then, I do not understand why one of your tagged scenarios is for "land", I would have join "land + coastal ocean" into a unique tagged scenario (and compared it to open ocean), as all of the CHBr3 and CH2Br2 prevailing in the land tagged scenario currently belong to emissions from coastal ocean within the Liang et al., 2010 inventory.

P5;L6-8: Please provide a proper reference to the NOAA ETOPO2v2 Global Relief map, and explain how the 2 minute spatial resolution from that database is extrapolated to the 2° x 2.5° horizontal resolution of GEOS-Chem, and how well it compares to the land mask of the model. Also, what is the resolution of the Liang et al., 2010 inventory? "For tracers that spatially overlap we calculate their fractional contribution taking into account the area covered by land or ocean and local emission fluxes". Couldn't it just be done by computing the landfraction of each of the GEOS-Chem grids with coastal emissions?

P5;L16: You give global annual totals of CHBr3 and CH2Br2 emissions for the Liang et al. inventory, but it would be very useful if you could explicitly indicate what fraction of the annual global source is emitted within the modelled region during the Jan-Feb modelled period. Later in the results section there is an explicit reference of the contri-

bution of VSL sources arising from outside the study region, so knowledge of the net emission from the selected region is valuable. Also, here you explicitly mention the imposition of a seasonal cycle, whereas in the Appendix A you state that there is not any seasonal cycle. Please make this point clear. Finally, do you apply any daily profile to the emissions or they are constantly being emitted during the 24 hs of a day?

Fig. 2: The Open Ocean emission includes maximum values above 1.0x10-13 kg m2 s-1 (correct the units on the figure) which are probably related to the coastal particularities. The rest of the open-ocean is quite constant with a latitudinal dependence as in the Liang et al. emissions inventory. Why did you include those large variable hot-spot into the open-ocean tracers? This certainly increases the open ocean contribution to the overall abundance of CHBr3 and CH2Br2.

Note that the coastal ocean age of air profile shown in Fig. 9 is very similar to the land profile. Isn't this indicative that GEOS-Chem represents convective transport similarly for the coastal-ocean and land tagged scenarios? The coastal oceans even shows more aged air-masses that the land? Could you explain this? Could you also explain by how much does the coastal ocean age of air contribute to the whole ocean (open+coastal) profiles?

Specific Comment II

There are some details on the NOAA VSLS validation that should be explicitly stated in the text. From Table 2 and Appendix A, it becomes evident that none of the 14 NOAA stations is located in the Western Pacific, the area of study. Indeed, the pacific stations are located either in Hawaii, Australia or Samoa Island, well outside the study region. P6;L17: "The model generally has less skill at reproducing observations collected at coastal sites close to emission sources". Then, this constitutes an additional factor which must be considered when computing the uncertainties of the "coastal ocean" contribution to the overall CHBr3 and CH2Br2 abundances in the MBL, FT and TTL. This is not explicitly mentioned in the text.

P1;L7: “The model has a mean positive bias of 30% that is larger near the surface reflecting errors in the poorly constrained prior emission estimates”. P6;L23 “In general, GEOS-Chem has poorer skill at reproducing observed near-surface variations, reflecting errors in prior emissions”. There must be other factors affecting the model results: if only a bias on VSL sources exist, then the bias should remain constant in height. How do you relate these statements with the fact that the CONTRAST and CAST campaigns occur within a region of large coastal areas, so results for coastal ocean tags might not be so reliable.

P30;L4: “At the tropical sites, which are comparable with the campaign region, the model bias varies strongly depending on location”. This could be indicative of the large variability of convective events within the tropical sites, besides the mentioned errors on prior emissions.

Specific Comment III

The vertical profile of modelled and measured CHBr3 and CH2Br2 abundances is not given until the very last figure (Fig. 12). Many panels showing the vertical variation of the model bias, as well as the percentage contribution of each of the tagged scenarios, are shown before the absolute vertical profile is given. I imagine Fig. 12 is shown at the very end of the paper because the authors preferred to present it after all the analysis of sources, uncertainties and associated bias has been described, buy It would be very useful to have it placed early in the text, so the reader has an absolute value in mind when all differences, bias and percentages are computed. Additionally, many of the initial comments, such as the “S” shape profile for CHBr3, could be visualized at first glance.

Fig. 12: Have you thought on showing as a separate panel the original results without the corrected-bias procedure (and perhaps showing the model standard deviation within the WP region). This would help to visualize how well does the model in reproducing the observed values of CAST/CONTRAST or any other campaign. The Bias

correction is helpful to improve the estimation of the VSL burden in the TTL and it impacts on stratospheric injection, but the procedure is still dependent on the model capability on reproducing the measured data.

Further Comments:

P1;L17 (abstract): “and a mean (range) Bry mole fraction of 3.14 (1.81–4.18) pptv to the upper troposphere”. This sentence in the abstract gives the impression that you have quantified both Source Gas and Product Gas bromine, whereas you have only presented results for carbon-bonded source gases. This confusion is only clarified when reading the conclusions. Please rephrase in the abstract to make it clear.

I was surprised the MS does not give any single mention of the contribution of minor VSLS (such as CH2BrCl, CHBr2Cl, etc.) to the atmosphere. Even when minor VSLS are not included in the model experiments and no experimental data is presented, at least a mention of their relevance should be given in the MS.

The description of the Age of Air (A) computation is quite confusing. What magnitude of the surface boundary condition increases linearly with time? Is it the area B, or the vmr of the tracer within the transported air-mass? Also, Is there any physical interpretation for the scaling factor and its value? Note that a fraction of the final sentences of the paragraph describing the CH3I tracer belongs to the Results section. Please also briefly explain how the Convective Mass Flux (CMF) is computed in the model.

P5;L27: you mentioned that the usage of age of air is useful “in the absence of reliable bottom-up emissions inventories”. In my opinion, the use of age of air simulations helps to understand the rapid convection independently of the existence (or not) of bottom-up inventories. Please note that Ziska et al., (2013) presented a bottom-up inventory for VSL species.

P6;L15: How do you compute the 30-60% value of the seasonal variation?

Fig. 4 shows there is a larger bias for CHBr3 at the surface, but for CH2Br2 the bias

is larger at higher heights. This is not explained in detail. Also, why Figure 4 x-axis title indicates "tagged model vs. observed VSL". Isn't this comparison considering all oceanic (coastal + open) plus land sources altogether? If any specific tagged region is considered, that should be explained in the text.

P7;L13-L16: "Averaged over the campaign, coastal and terrestrial sources of CHBr3 show little influence above 6 km". Then, what is controlling CHBr3 abundance over 6 km. Only Open ocean? Also, "At the TTL, averaged over the campaign study, CH2Br2 mole fractions range 0.1–0.3 ppt mainly due to smaller magnitude of ocean emissions compared to CHBr3. Coastal and terrestrial sources contribute up to 0.1 ppt of CH2Br2 in the TTL". And the remaining CH2Br2 in the TTL, where does it comes from?

P7;L30: "The longer lifetime of CH2Br2 mean that these mole fractions have a greater influence over the campaign profile compared to CHBr3." I found this statement very vague or unspecific. What do you mean by "greater influence over the campaign profile"? Do you mean the profile does not decay so rapidly? The campaign profile for each species certainly depends on the lifetime, but I do not understand how the "influence" of the lifetimes from one species to the other can be quantified.

P8;L6: "The oldest ages, which approach the time of the study period, reflect the accumulation of near-zero mole fractions." I do not understand the meaning nor the implications of this sentence.

P8;L19: "Despite intensive measurements around coastal land masses of the region, CAST did not very well capture coastal emissions." Couldn't it be possible that GEOS-Chem did not represent properly the age of air for this coastal areas?

P8;L24: "The only exception is at the near-surface where land emissions dominate the older age profile." Wouldn't coastal emissions also be contributing to the aged profile near the surface?

P9;L9-L10: "Based on average observed surface values of CHBr3 (1.13 ppt) and

CH2Br2 (1.02 ppt) over the campaign we infer that 40% and 86% of these emitted gases, respectively, are directly injected into the TTL over our study domain". I completely disagree with this statement and found it inconsistent to what is being described above. As we move upward in the troposphere, a larger fraction of the VSLS abundance cannot be explained without considering the contribution from source regions "outside" the study domain. Thus, is expected that from the 0.46/1.13 and 0.88/1.02 ratios of TTL/Surface vmr, there is a contribution in the numerator arising from other sources outside the domain . . . thus less than that percentage is directly being transported to the TTL within the study domain.

P9;L9-13: Fernandez et al., 2014, also performed different sensitivity studies including only CHBr3, only CH2BR2 and other minor VSLS in a CTM, and determined the amount of CHBr3 and CH2Br2 being decomposed before reaching the TTL within the global tropics and the WP.

P10;L5: "Tropospheric measurements of CH2Br2,. . ., are dominated by sources from before the campaign". P7;L25: "The remaining contributions are representative of emissions before the campaign period". How do you attribute those values to emissions before the campaign period?. Although it is expected that the species with longer lifetime will have a longer-lasting contribution until its final decay, the statement should be based on any of the results presented in the text.

P10L16: "Our flux estimate for CHBr3 is lower than previous studies that have reported values closer to 50%." 50% of what? Of the overall inorganic bromine burden or respect to the Surface CHBr3 abundance.

Technical Comments

P1;L6: "32%–37% of CHBr3 observed variability and 15%-45% of CH2Br2 observed variability". Rephrase to use only observed variability only once.

P2;L23, and elsewhere in the MS: Whenever many references are being cited, they

should be ordered chronologically.

P3;L21: “other non-WAS halocarbon data, not analyzed here, have only recently become available”. If you include this type of statement, then you should properly reference it.

P3;L29, “between the two WAS systems and two accompanying GC/MS instruments” it is not clear if the percentage error applies to CHBr3 and CH2Br2 species or to the WAS and GC/MS instruments.

P4;L2: You should indicate what the GMAO-FP Office is for the people not familiar with meteorological data, and properly reference it.

P4;L9, correct the subtitle with “and” between species.

P4;L21: What is the top model pressure and or height?

P5;L1: “. . .the following temperature (T) . . .by OH (Sander et al., 2011)

P6;L19: The Equation used for computing the bias uses model_i and mod_i as variables, which I do understand belongs to the same value

P7;L14: by virtue of its longer atmospheric lifetime.

P7;L26: “Figure 8 shows the same as Figure 7 but for CH2Br2.” Please, rephrase.

P8;L9: “We using our CH3I-like tracer that air masses can be transported to the TTL within 3–5 days but these are infrequent events (Appendix B).” rephrase.

P8;L28: replace 20-40 to 24-48

P9;L7: They estimated. . .

P9;L14: but does not take

Appendix B. Indicate if Figure B.1 includes data sampled only at the same times and locations as the CONTRAST (not CONTRAIL) flight tracks, or if the whole study domain

has been considered.

Fig. 1 and Fig 3: M (Manus) is not included in these figures but it is on the others.

Fig.2: replace “in to” by “into”

Fig. 9: Indicate whether the values were averaged within the whole study domain or only the flight tracks.

Fig.10: What is the “percentage of occurrence rate”? rate of what?

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