Quantifying the vertical transport of $CHBr_3$ and CH_2Br_2 over the Western Pacific Robyn Butler et al

We thank the two anonymous reviewers and to Q. Liang for their constructive comments. These have helped to improve the revised manuscript. Below are our responses to each individual reviewer comment denoted in italics. We apologise for the delay in responses. Some of the comments needed to be addressed with additional model runs. At the end of this document is a track changed version of the manuscript.

Review report 1

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.

RESPONSE COMMON TO REVIEWER 1 and 2

The land tracer only appeared because of the mask we used to define coastal and open ocean sources. Land tracers have been included in the coastal ocean tracer. We have now changed the manuscript so the land tracer does not feature in the discussion.

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 2x2.5 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 land fraction of each of the GEOS-Chem grids with coastal emissions?

We have now added a reference for these data, and made the associated changes to the manuscript. We have also added and changed the text to improve the description of the tracer calculations: "Fractional contributions (R) of tracers are calculated by assigning each 2-minute cell (c) in a model grid box a value of 1 depending on tracer definitions, 0 if it doesn't. These cells are then calculated as a fraction of the total number in each model grid box. $R = \sum N_{c=1}/N_{ctotal}$."

We developed a land mask from the bathymetry data because the coarser GEOS-Chem land mask does not include the local geography where the campaigns were focused (Guam, Palau and Chuuk).

P5;L16: You give global annual totals of CHBr3 and CH2Br2 emissions for the Liang et al. inven-

tory, 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 contribution 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?

We have added regional seasonal totals for the study period.

We thank the reviewer for spotting the inconsistency in the text about the seasonal cycle. The full chemistry GEOS-Chem has an imposed seasonal cycle, but we do not use that information in our tagged simulation. There is no diurnal cycle to the emissions, they remain constant for 24hs. We have modified the text accordingly to clarify this.

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.

First, we thank the reviewer for unit correction.

We included the elevated value because they fell within the open oceanic tracer mask. To address the reviewer concern, we completed a model run that assigned these elevated value into the coastal ocean tracer.

The revised Figure 3 (shown in Figure 1 in this document) below shows elevated coastal contributions over coastal regions in the vertical profile but there remains a dominant contribution from the open ocean emissions for both gases. This revised calculation changes some parts of the discussion of results but the general findings remain the same, e.g. coastal emissions play a larger role at higher altitudes. We have modified the text to reflect these revised calculations.

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?

Following this reviewers recommendation (as described above) we have removed the land tracer from the discussion.

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.

This reviewer's comments are well taken. The purpose of evaluating the model with the NOAA VSLS data was to quantify and report model performance and not intended to provide additional data over the Western Pacific. We will make that explicit in the text. We will also relate our findings about the coastal NOAA data to our analysis of the aircraft data over the western Pacific.

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.

RESPONSE COMMON TO REVIEWER 1 and 2

In Figure 4 (Model Evaluation in the manuscript) we now include a panel describing the relative model error. We find this model error is consistent with altitude for both gases relating to a constant offset in model values. We explicitly mention this result in the manuscript text. We also acknowledge that values outside of the mean value could be indicative of model transport error.

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

The reviewer raises a good point. We now include a statement about this point where we discuss the NOAA station data.

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.

Good point. We have modified Figure 4 (manuscript) so that the top panel shows the vertical distribution of model and observations from campaigns in the top panel, the middle panel show observations vs. model scatter, and the bottom panel shows relative model error over the vertical profile.

Fig. 12: Have you thought on showing as a separate panel the original results without the correctedbias 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.

We believe our revised Figure 4 now addresses this comment.

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.

Agreed. We have changed the abstract to read "and a mean (range) Bry mole fraction of 3.14 (1.81–4.18) pptv from source gases to the upper troposphere".

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.

Agreed. We have now mentioned additional VSLS in the introduction of the MS. "VSLS include gases such as bromoform (CHBr3), dibromomethane (CH2Br2), bromochloromethane (CH2BrCl), dibromochloromethane (CHBr2Cl) and bromodichloromethane (CHBrCl2). Here, we focus on CHBr3 and CH2Br2...".

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.

This comment is comment to both reviewers so we have obviously not described it clearly enough.

Here, we address the reviewer questions and rewrite the confusing text in the manuscript.

The surface boundary condition, B, is effectively a surface VMR of each tracer at its emission source that linearly increases with time. An air mass initially has a VMR that reflect the time it was in contact with B, but get progressively smaller as time progresses due to atmospheric mixing. The scaling factor f is a value that helps relate the increasing tie to the corresponding change in VMR.

CMF is from the meteorological fields. We have included a statement in the description of meteorological fields stating that this is where the CMF and dynamic tropopause height is from.

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.

Agree. In the absence of reliable emission inventories, the age of air simulation allows us to study the role of atmospheric transport on the distribution of trace gases. We have clarified that point in the manuscript. "We use the age of air simulation to understand the role and frequency of rapid convective systems to transport short-lived halogenated compounds to the TTL, independent of emission inventories."

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

This reflect the Table of squared Pearson correlation coefficients.

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.

Following this reviewer's comment we have modified Figure 4 (as described above) to show the relative model error to better quantify model error. Our results show that the median relative model error for both gases does not significantly change with altitude. Variations around these median values suggest model transport errors. We have changed our discussion of model evaluation highlighting a role for atmospheric transport error.

Following the reviewer suggestion, we have changed the x-axis title to say 'Total tagged VSLS / pptv' to indicate that all tracers are included.

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?

Due to the changes in emissions for the tagged tracers following this reviewer's comment, as described above, we have already revised the discussion to address this comment. The missing CH2Br2 is from the open ocean. We have revised the manuscript to clarify this point. "Coastal sources contribute up to 0.1 ppt of CH_2Br_2 in the TTL with the remaining originating from an open ocean source."

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 pro-file"? 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.

We agree that this sentence is vague. We are referring to the influence of emissions prior to the campaign period. The tagged model only represents emissions from the Jan/Feb period of the research campaign, and the tagged CH2Br2 indicates that CAST and CONTRAST measurements are dominated by emissions before Jan/Feb 2014. The 'influence' refers to pre-campaign emissions on the CH2Br2 and CHBr3 campaign profile. Compared with CHBr3, CH2Br2 is influenced by emissions pre-campaign, whereas CHBr3 is mainly influenced by emissions during the campaign due to their different decay profiles. We have modified the manuscript to clarify this point: "The longer lifetime of CH2Br2 results in a greater influence of emissions prior to the campaign period. In contrast, atmospheric CHBr3 is dominated by emissions during the campaign period."

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.

We hope that some of this confusion will be resolved with a better description of the age of air calculation that both reviewers highlighted.

This sentence refers to the VMR of the age calculation.

Referring to the text above, an air mass initially has a VMR that reflect the time it was in contact with the ocean boundary B, but get progressively smaller as time progresses due to atmospheric mixing. Accumulation of near-zero VMRs refers to the oldest air parcels. The statement explains that the older age profile in comparison to the age calculation. In any case, on reflection we felt it did not add to the discussion so we have removed it.

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 GEOSChem did not represent properly the age of air for this coastal areas?

Agreed. This is potentially a resolution issue that we have now acknowledged in the discussion.

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?

This effect has become obsolete with the modified tracers and age of air run. At higher altitudes, this effect is seen and linked to coastal ocean emissions.

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.

Agreed. We simplified the issue assuming that values in the TTL are directly representative of the values at the surface. This is not a valuable assumption. We have removed this part of the discussion.

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.

We refer to this paper in the introduction, but have specifically referenced Navarro et al., 2015, as it is an additional study using this campaign data.

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.

This is relative to the experimental method. Tagged emissions are only tagged from 01/01/2014 therefore the remaining percentage difference between the tagged VSLS tracers and the total VSLS tracer. The total tracer is based on a 12-month spin up from the emission scenario with the 'total ocean' emissions included. The VSLS VMR that is not represented by the tagged tracers will be attributed to 'background' VMR from the spin up file, which represents the VMR from before the campaign. We have clarified this in the method and discussion sections.

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.

Now we have excluded the discussion about SGI from source gases this comment has been deleted from the discussion.

Technical Comments

We agree with all the technical comments and have made the recommended changes.

Review report 2

1) Results in section 4.2 regarding the tagged-VSLS model output depend very strongly on the chosen emission scenario. Most of the information presented here (i.e., the amount of coastal versus open ocean emissions contributing to upper air mixing ratios) could be quite different for another emission scenario. This aspect is not addressed or discussed at all in the manuscript. Given the large differences between the different emission scenarios and existing research investigating those differences and the implications for atmospheric mixing ratios (Hossaini et al., 2013; Hossaini et al., 2016) a proper discussion is required. Ideally, the study should be carried out based on at least one more emissions scenario in order to understand the uncertainties resulting from the assumptions made here.

Agreed. Instead of using different emission scenarios (none of which convincingly reproduce observations) we decided to focus on using the age of air calculation to investigate the influence of ocean emission regions independent of the emission scenario. However, have revised the discussion section to acknowledge different emission scenarios.

2) The choice of the emission scenario is not discussed. Why top-down and not bottom-up? Which scenario is thought to be the most realistic in this region? Why is this scenario used if the simulated surface mixing ratios show large deviations to the observations? Could these deviations be minimized for a different (lower) emission scenario?

FIGURE COMMON TO REVIEWER 2 and 3

Our preliminary work used the alternative Ziska emission scenario. Here we have reported results from the associated analysis. Figure 2 (in this document) shows results from the Liang (left two panels) and the Ziska (right two panels). We decided to use the Liang emissions because they were consistently higher at a similar percentage compared to VSLS, whereas the Ziska emissions are different for each gas at a greater magnitude.

3) What would cause land sources of CHBr3 and CH2Br2? In the introduction, only marine sources are discussed, but later the reader is confronted with the land tagged tracer and its contribution to the observed mixing ratio.

This common to Reviewer 1, which we address above.

4) The discussion of the model evaluation (section 4.1) needs to be improved. How large are the relative deviations between model and observations. If the bias is mostly a result of the emissions used, than the relative differences should stay constant with height. If however, the relative differences increase or decrease with height this would indicate errors introduced by the transport scheme

of the model. Even tough, there are six panels used to discuss the comparison such conclusions are currently not possible.

This common to Reviewer 1, which we address above.

5) Please provide the model resolution. At the moment only the resolution of the meteorological input data is given. Is this the same as the model resolution and the resolution of the output data? How would this quite coarse resolution (2×2.5) impact the results? In particular, how would this impact the model-based analysis of the observations?

We have now included the resolution, which is the same as the driving meteorological data. The model resolution would potentially impact some of the model results, particularly for tagged tracers in coastal regions around the smaller islands. We now include the role of model resolution in our discussion of the CAST and CONTRAST age profiles.

6) Please improve description and discussion of Figures 9, 10 and 11. It is difficult to understand what has been done and why some of the statements are made. See also detailed comments further below.

Agreed. We have clarified the discussion of these Figures.

Minor comments

Page 5, line 4-12. Please explain Figure 2. Are the tagged tracer regions shown or are the tracer regions combined with the emission scenario shown? How do you end up with 20 tagged tracers? Seven for CHBr3 and seven for CH2Br2 and the rest for total and background?

We show tagged regions with emission flux in Figure 2. We have better described the Figure in the caption and main text. We describe the 20 tracers in the tagged model methodology. In addition, to describe the (now) three ocean tracers:

FROM "We assign individual tracers to major islands within the study domain, including Guam (13.5N, 144.8 E), Chuuk (7.5 N, 151.8 E), Palau (7.4 N, 134.5E) and Manus (2.1S, 147.4E). We assume these island land masses account for 100% of a grid box irrespective of whether their area fills the grid box. We have a total of 18 tagged tracers, evenly split between CHBr3 and CH2Br2 including a total tracer and a background tracer"

TO "In addition to the ocean tracers, we assign individual tracers to major islands within the study domain: Guam (13.5N, 144.8 E), Chuuk (7.5 N, 151.8 E), Palau (7.4 N, 134.5E), and Manus (2.1S, 147.4E). We assume these islands account for 100% of a grid box irrespective of whether their area fills the grid box. We have a total of 18 tagged tracers, consisting of the total, background, three ocean tagged tracers, and four island tagged tracers for CHBr3 and CH2Br2."

Page 5, line 15. Please explain what 'de-seasonalized monthly means'? Are you using annual means?

Or interannual anomalies plus mean values?

Deseasonalised monthly means are monthly means with this seasonal cycle removed. We use the same emissions are used throughout the study. "This emission inventory has global annual totals of 425 GgBryr-1 for CHBr3 and 57 GgBryr-1 for CH2Br2 (Parella 2012). Emissions do not have a diurnal cycle and are emitted over a 30 minutes time resolution over the model period."

Page 5, line 26. This sentence makes no sense. You use age of air simulations because you have no reliable emission inventory? But then the other half of the analysis is based on one emission inventory? Furthermore, should this sentence suggest that only the bottom-up inventories are unreliable while the top-down are not?

We agree this is confusing and have modified this statement. Age of air is used to interpret the emission regions independent of the emission scenario. This means that even if the model does not represent observations, the relative influence of emission sources can be investigated over the region. In Section 3.1 describing the tagged model, we acknowledge model evaluation using the Ziska (2013) emission scenario and that it is also unreliable at reproducing observations from this campaign.

"We use the age of air simulation to understand the role and frequency of rapid convective systems to transport short-lived halogenated compounds to the TTL, independent of the emission inventory. The method uses only knowledge of the distribution of emissions, and not the magnitude, so we investigate the influence of emissions source region with respect to respective CHBr₃ and CH₂Br₂ atmospheric e-folding lifetimes."

Page 6, line 21-22. Please explain how the amount of explained variability is estimated. Page 7, line 17. How were those percentage contributions calculated? Transform numbers from Figure 5 into relative numbers and then apply them to the observations? Here and at other places, the methodology is not clear and the reader has to guess what exactly has been done.

We transform the squared Pearson correlation coefficient from Figure 5 into the variability. We have changed the text to read: "From Pearson correlation coefficients, we find that GEOS-Chem reproduces.."

Page 8, line 5. I don't understand how the discussion of Figure 9 (which shows age of air as a function of source region but no emissions or mixing ratios) allows such a statement. Or is here information from other earlier analysis used? Same for line 8.

The discussion of this Figure has now changed due to updated model runs and these lines have been deleted. The text has been clarified to relate the age of air to lifetime of $CHBr_3$ and CH_2Br_2 , with comparisons to mixing ratios being included in discussion of Figure 10 (was Figure 11).

Page 8, line 12. The text says that 53% of what reaches the TTL comes from the open ocean? From other parts of the manuscript, I had the impression that the large majority comes from the open ocean? Please clarify.

These values have now changed due to correcting an error in the age of air model run. In the text, it has been clarified that the percentages relate to the percentage of emissions from source regions. Currently it reads as:

"We find that 76% (92%) of oceanic emissions reach the TTL within 2τ CHBr3 (3τ CHBr3), with 64% (88%) of open ocean emissions and 9% (50%) of coastal emissions reaching the TTL within the same time frame."

Figure 9: Comparing the lines for ocean, open ocean and coastal ocean, I wonder if the coastal and open ocean together should give the ocean age of air? However, the total ocean (blue line) shows the youngest age of all. Please clarify.

I have checked this in the model by summing the open and coastal tracers and they are equal to the total ocean (Figure 3 in this document).

Review report 3 (Q. Liang)

1. The use of Liang et al. (2010) emissions. I don't understand why there were emissions over the land, as the Liang et al. emissions scheme only specifies emissions from Open Ocean and coastal regions. While the original inventory was derived on 2x2.5 horizontal resolution, I provided a refined emissions inventory on 1x1 degree resolution to the GEOS-Chem group. Could it be possible when the 1x1 degree emissions were regrided to 2x2.5, emissions appeared to occur over the island landmasses as a result of coarse resolution? Whatever the reason was, the use of land tagged emissions tracers for CHBr3 and CH2Br2 and the reference of terrestrial sources of these gases throughout the manuscript, in my view, are not accurate and lead to wrong impression that land could be a source of these oceanic-originated compounds. Second, the Liang et al. (2010) emissions inventory was originally derived for stratospheric bromine budget purposes (therefore without much attention to fine-tuning the surface emissions details, e.g. longitudinally invariable and simple treatment of Open Ocean vs. Coasts), with no observations over the western Pacific to constrain surface emissions in that region. As shown by Hossaini et al. (2013), the Ziska bottom-up inventory is a much more skillful and a more appropriate choice of emissions for the Western Pacific region. Quantifying the relative importance of open ocean emissions vs. coastal sources using the Liang et al. (2010) emissions scheme for the Western Pacific region, which is one of the main focus of this paper, does not provide a credible estimate.

This is a comment raised by the other reviewers. The land tagged tracer appeared due to the ocean mask used overlapping with the emission fluxes. The land tracer has been incorporated in to coastal tagged tracer as this is the area that has overlapped.

We find that using the Ziska emissions are not better at representing observations over our study region region. Ziska emissions are more inconsistent in representing CHBr3 and CH2Br2 over our study region. They underestimate CHBr3 by around 40% and overestimate CH2Br2 by 35%. Liang is based high for both gases. On the basis on that result, we decided to use Liang emissions. We now include a justification in the revised manuscript. 2. Page 8, Line 29 – Page 9, Line 9. I have to say I don't see the meaning of the use of modeled profiles of CHBr3 and CH2Br2 by applying a vertical uniform correction of model biases to quantify SGI and PGI. i) First, the estimated injection of PGI based on model corrected profiles is not correct. Why use the model? The model, even after correction, still shows low biases for CHBr3 and CH2Br2 at 10-12 km. In fact, shouldn't the observation-based organic Br be the true PGI value?

We used this method so we could apply it to our model of CHBr3 and CH2Br2 for future scenarios without observations. It is a simplified method for estimating model PGI at these altitudes.

ii) While it was not explained in the text, my guess is that the authors use the difference of Br value at the surface and that at the TTL to calculate PGI. This is not a correct approach in my view. As show in Liang et al. (2010), a significant fraction of the inorganic Br produced from CHBr3 and CH2Br2 degradation are removed by largescale precipitation in the lower troposphere and never makes to the UT.

Agreed. This was a comment raised by another reviewer. It was an oversimplification of the issue and calculation. Consequently, we have decided to remove it from the discussion.

3. Same as the other reviewers, I also find the use of idealized age of air, in particular the results presented in Figure 11, hard to interpret.

As described above in response to the other reviewers, we have revised the definition of age of air and the description of the results in the revised manuscript.



Figure 1: Comparison of Figure 5 (in the manuscript) using original emission estimates for ocean tracers of $CHBr_3$ (left) with elevated coastal emissions (right). The box denotes the emission scenario and Figure used in the revised manuscript.



Figure 2: Comparison of Figure 4 (in the manuscript using original Liang emission estimates (left) with Ziska emission estimates (right).



Figure 3: Figure 8 (in the manuscript) with the addition of the calculated ocean line from the sum of open and coastal tracers.

Quantifying the vertical transport of CHBr₃ and CH₂Br₂ over the Western Pacific

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Abstract. We use the GEOS-Chem global 3-D atmospheric chemistry transport model to interpret atmospheric observations of bromoform (CHBr₃) and dibromomethane (CH₂Br₂) collected during the CAST and CONTRAST aircraft measurement campaigns over the Western Pacific, January–February, 2014. We use a new linearised, tagged version of CHBr₃ and CH₂Br₂, allowing us to study the influence of emissions from specific geographical regions on observed atmospheric variations. The

- 5 model describes 32%–37% of CHBr₃ observed variability and 15%-45% of CH₂Br₂ observed variability during CAST and CONTRAST, reflecting model errors in vertical model transport. The model has a mean positive bias of 30% that is larger near the surface reflecting errors in the poorly constrained prior emission estimates. We find using the model that observed variability of CHBr₃ and CH₂Br₂ is driven by ocean emissions, particularly by the open ocean above which open ocean emissions where there is deep convection. We find that contributions from coastal oceans and terrestrial sources over the Western Pacific are
- 10 significant above altitudes Atmospheric variability above >6km, but includes a significant contribution from coastal oceans, but it is still dominated by emissions from the open ocean emissions and by air masses transported over longer time lines than the campaign period and by older air masses that originate upwind. In the absence of reliable ocean emission estimates, we use a new physical age of air simulation to determine the relative abundance of halogens delivered by CHBr₃ and CH₂Br₂ to the tropical transition layer (TTL). We find that 676% (4792%) of air masses with halogen released by that originate from
- 15 the ocean reach the TTL within two (three) atmospheric e-folding lifetimes of CHBr₃ and almost all of them reach the TTL within one e-folding lifetime of CH_2Br_2 . We find these gases are delivered to the TTL by a small number of rapid convection events during the study period. Over the duration of CAST and CONTRAST, and over our study region, oceans delivered a mean (range) CHBr₃ and CH₂Br₂ mole fraction of 0.46 (0.13–0.72) and 0.88 (0.71–1.01) pptv, respectively, to the TTL, and a mean (range) Br_y mole fraction of 3.14 (1.81–4.18) pptv from source gases to the upper troposphere. Open ocean emissions

20 are responsible for 75of these values, with only 8from coastal oceans.

1 Introduction

- 5 stratosphere that drives halogen-catalysed ozone loss, as anthropogenic halogenated compounds continue to decline in accordance with international agreements. Quantifying the magnitude and variation of these natural VSLS fluxes to the stratosphere is therefore a research priority for environmental science. We focus on VSLS include a wide range of gases such as bromoform (CHBr₃)and-, dibromomethane (CH₂Br₂), which-bromochloromethane (CH₂BrCl), dibromochloromethane (CHBr₂Cl), and bromodichloromethane (CHBrCl₂). Here we focus on CHBr₃ and CH₂Br₂, which collectively represent >80% of the organic
- ¹⁰ bromine in the marine boundary layer and upper troposphere, and are dominated by marine sources (WMO, 2007). We use aircraft observations of $CHBr_3$ and CH_2Br_2 collected over the western Pacific in January and February 2014 to quantify the regional flux of these compounds to the stratosphere.

The main sources of $CHBr_3$ and CH_2Br_2 include phytoplankton, particularly diatoms, and various species of seaweed (Carpenter and Liss, 2000; Quack and Wallace, 2003; Carpenter et al., 2014). The magnitude and distribution of these emissions

- 15 reflect supersaturation of the compounds and nutrient-rich upwelling waters (Quack et al., 2007). Tropical, subtropical and shelf waters are important sources of CHBr₃ and CH₂Br₂ with high spatial and temporal variability (Ziska et al., 2013). Current emission inventories, informed by sparse ship-borne data, have large uncertainties (Warwick et al., 2006; Liang et al., 2010; Ordóñez et al., 2012; Tegtmeier et al., 2012; Hossaini et al., 2013; Ziska et al., 2013). The atmospheric lifetime of CHBr₃ is ~24 days, determined primarily by photolysis and to a lesser extent by OH oxidation. CH₂Br₂ has an atmospheric lifetime of
- 20 \sim 123 days determined by OH oxidation (Ko and Poulet, 2003).

Ascent-Vertical ascent of CHBr₃ and CH₂Br₂ and their oxidation products to the upper troposphere lower stratosphere (UTLS) represent a source of bromine that acts a catalysts as a catalyst for ozone loss in the stratosphere. Balloon-borne and satellite observations estimate that brominated VSLS and their degradation products contribute 2–8 ppt to stratospheric Br_y (Sinnhuber et al., 2002, 2005; Sioris et al., 2006; Dorf et al., 2008; McLinden et al., 2010; Salawitch et al., 2010). Model

- 25 estimates range between 2 and 7 ppt for this contribution (Aschmann et al., 2009; Hossaini et al., 2010; Liang et al., 2010; Ordóñez et al., 2012; Fernandez et al., 2014). This contribution mainly originates from areas of deep convection over the tropical Indian ocean, Western Pacific, and off the Pacific coast of Mexico (Gettelman et al., 2002; Fueglistaler et al., 2004; Aschmann et al., 2009; Ashfold et al., 2012; Hossaini et al., 2012). The stratospheric community has categorized two methods of delivering VSLS to the stratosphere: 1) source gas injection (SGI), which describes the direct transport of the emitted
- 30 halogenated compounds (e.g., CHBr₃ and CH₂Br₂); and 2) product gas injection (PGI), which refers to the transport of the degradation products of these emitted compounds. Previous model-based calculations (Hossaini et al., 2012; Tegtmeier et al., 2012; Aschmann and Sinnhuber, 2013; Liang et al., 2014) have estimated that 15%-75% of the stratospheric inorganic bromine budget from VSLS is delivered by SGI, with uncertainty of the total Br_y reflecting uncertainty of wet deposition of PGI product gases in the UTLS (Sinnhuber and Folkins, 2006; Liang et al., 2014).

Active biological waters that coincide with regions of strong convection represent the major sources of VSLS to the upper troposphere (UT). The tropical tropopause layer (TTL) represents a gradual transition from the troposphere to the stratosphere (Zhou et al., 2004; Fueglistaler et al., 2009; Pan et al., 2014). It extends over a few kilometres and lies within this area of the UT between within the lapse rate upper troposphere between where the atmospheric lapse rate is at a minimum (~12–13 km) and

- 5 the cold point tropopause (~17 km) (Gettelman and Forster, 2002). A slow transition between the thermodynamic structure of the convectively controlled troposphere to the radiatively controlled stratosphere gives it a smaller lapse rate than a saturated adiabatic up to the cold point. This gives the TTL properties and structure of both the troposphere and the stratosphere, making it the predominant transport pathway of The TTL is the dominant transport pathway for SGI and PGI gases to the lower stratosphere. TTL temperatures vary zonally with the smallest values between 130°–180°E throughout the year. This
- 10 region corresponds, corresponding to the tropical warm pool over the Western Pacific, where convective activity is largest (Gettelman et al., 2002). Estimates of SGI within this region are highly dependent on the strength and spatial variability of source regions, and how they couple with atmospheric transport mechanisms.

We use the GEOS-Chem global 3-D chemistry to estimate the atmospheric flux of CHBr₃ and CH₂Br₂ to the TTL data from two coordinated aircraft campaigns over the western Pacific using measurements collected during two coincident airborne

- 15 campaigns: the Coordinated during 2014, the Co-ordinated Airborne Studies in the Tropics (CAST) and CONvective TRansport , Harris et al. (2016)) and the CONvective Transport of Active Species in the Tropics (CONTRAST), Pan et al. (2016)), to study the emission, vertical transport, and chemical transformation of halogenated gases. The CAST and CONTRAST campaigns measured a suite of trace gases and aerosols centred on the Micronesian region in the western Pacific, including Guam, Chuuk, and Palau during January and February 2014. 2014. We interpret aircraft measurements of CHBr₃ and CH₂Br₂ mole fraction
- 20 using the GEOS-Chem atmospheric chemistry transport model.

In the next section we describe these two campaigns <u>CAST</u> and <u>CONTRAST</u> and the data <u>we</u> used. Section 3 describes the GEOS-Chem model and how it is used to interpret the airborne data. In section 4 we evaluate the model and describe our results. The paper is concluded We conclude the paper in section 5.

2 Observational data

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25 2.1 CAST and CONTRAST CHBr₃ and CH₂Br₂ mole fraction data

We use $CHBr_3$ and CH_2Br_2 mole fractions from the CAST and CONTRAST aircraft campaigns - A comprehensive description of the data collection and analysis procedures used during the campaigns can be found in ; here (Harris et al., 2016; Pan et al., 2016). Here for the sake of brevity we provide only brief details of about the CHBr₃ and CH_2Br_2 data and refer the reader to Andrews et al. (2016) for a more comprehensive description of the data collection and analysis procedures used during the campaigns.

Figure 1 shows the spatial distribution of whole air samples (WAS) collected during CAST and CONTRAST; other non-WAS halocarbon data, not analyzed here, have only recently become available. For CAST, WAS canisters were filled aboard the Facility for Airborne Atmospheric Measurements (FAAM) BAe-146 aircraft. These canisters were analysed for CHBr₃ and

CH₂Br₂ and other trace compounds within 72 hours of collection. The WAS instrument was calibrated using the National Oceanic and Atmospheric Administration (NOAA) 2003 scale for CHBr₃ and the NOAA 2004 scale for CH₂Br₂. For CON-TRAST, a similar WAS system was employed to collect CHBr₃ and CH₂Br₂ measurements on the NSF/NCAR Gulfstream-V HIAPER (High-performance Instrumented Airborne Platform for Environmental Research) aircraft. A working standard was

- 5 used to regularly calibrate the samples, and the that working standard was calibrated using a series of dilutions of high concentration standards that are linked to National Institute of Standards and Technology standards. The mean absolute percentage error for CHBr₃ and CH₂Br₂ measurements between 0-8 km is 7.7% and 2.2%, respectively, representing the combined error between the two WAS systems and two accompanying GC/MS instruments.
- Table 1 shows mean measurement statistics of CHBr₃ and CH₂Br₂ for the CAST and CONTRAST campaigns. CHBr₃ is generally more variable than CH₂Br₂ throughout the study region, reflecting its shorter atmospheric lifetime, so that sampling differences between CAST and CONTRAST will introduce larger differences for this gas. CAST measurements of CHBr₃ are typically lower than for CONTRAST, but CAST recorded the highest and lowest CHBr₃ mole fractions at 0–2 km and 6–8 km, respectively. We define the TTL from 13 km (Pan et al., 2014) to the local tropopause determined from the GMAO-FP GEOS5–FP analysed meteorological fields, as described below. CONTRAST measured a minimum CHBr₃ value indistin-
- 15 guishable from zero just below the TTL at 10–13 km. Measurements of CH_2Br_2 are generally consistent between CAST and CONTRAST at all altitudes. There is only a small vertical gradient for CH_2Br_2 above 2 km with a mean value of ~0.91 pptv. CONTRAST measured the lowest value of 0.21 pptv just below the TTL. Within the TTL, CONTRAST reports mean (maximum) values of 0.42 pptv (0.85 pptv) and 0.84 pptv (1.05 pptv) for CHBr₃ and CH_2Br_2 , respectively, providing some evidence of rapid convection of surface emissions to the upper troposphere.

20 2.2 NOAA ground-based CHBr₃ and CH₂Br₂ measurements

To evaluate our model of atmospheric Table 2 summarises the independent surface measurements of CHBr₃ and CH₂Br₂, described below, we use independent surface measurements of these VSLS collected by the NOAA Earth System Research Laboratory (ERSL) - we have used to evaluate the GEOS-Chem atmospheric chemistry model simulation on a global scale. This evaluation was undertaken to report on model performance and is not used to provide additional data over the Western Provide

25 Pacific.

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Table 2 shows the 14 geographical locations of the measurements we use, which These measurements are part of the ongoing NOAA/ESRL global monitoring program (http://www.esrl.noaa.gov/gmd). CHBr₃ and CH₂Br₂ measurements are obtained using WAS collected approximately weekly in approximately weekly using paired steel flasks, which are then analysed by GC/MS. Further details about their sampling are given in Montzka et al. (2011). In Appendix A, we evaluate the model using mean monthly statistics at each sites from 1st January 2005 to 31 December 2011.

3 The GEOS-Chem Global 3-D Atmospheric Chemistry Transport Model

To interpret CAST and CONTRAST data we use v9.02 of the GEOS-Chem global 3-D atmospheric chemistry transport model (www.geos-chem.org), driven by GMAO-FP-GEOS5-FP analysed meteorological fields from the NASA provided by the Global Modelling and Assimilation Office (GMAO) at NASA Goddard Space Flight Centre. For our ex-

5 periments we degrade the meteorological analyses to a native meteorological fields to a model horizontal spatial resolution of 2° latitude × 2.5° longitude over described on 47 vertical levels., with a top pressure of 0.01 hPa. Dynamic tropopause height and convective mass flux (CMF) from the meteorological fields are given on a 1-hourly and 3-hourly averaging period, respectively.

We describe below two new GEOS-Chem simulations that we developed to interpret observed variations of CHBr₃ and

10 CH₂Br₂ during CAST and CONTRAST airborne campaigns: 1) a tagged simulation of CHBr₃ and CH₂Br₂ to better understand source attribution; and 2) an age of air simulation to improve understanding of the vertical transport of these short-lived halogenated compounds. For both simulations, we sample the model at the time and location of CAST and CONTRAST observations.

3.1 Tagged CHBr₃ and CH₂Br₂ Simulation

15 The purpose of this simulation is to relate observed <u>atmospheric</u> variations to surface emissions from individual sources and/or geographical regions. To achieve this we use pre-computed monthly 3-D fields of OH and photolysis rates for CHBr₃ and CH_2Br_2 from the full-chemistry version of GEOS-Chem, allowing us to linearise the chemistry so that we can isolate the contributions from individual sources and geographical regions.

The structure of the model framework follows closely other tagged simulations within GEOS-Chem (e.g., Jones et al. (2003); Palmer et al. (2003); Finch et al. (2014); Mackie et al. (2016)). We use the following temperature (*T*) dependent reaction rate constants that describe oxidation of CHBr₃ and CH₂Br₂ by the OH OH (Sander et al., 2011): for CHBr₃, $k(T) = 1.35 \times 10^{-12} \exp(-600/T)$ cm³molec⁻¹s⁻¹; and for CH₂Br₂, $k(T) = 2.00 \times 10^{-12} \exp(-840/T)$ cm³molec⁻¹s⁻¹.

Figure 3 shows the land and 2 shows the magnitude and spatial distribution of our prior emissions of $CHBr_3$ and CH_2Br_2 (Liang et al., 2010). These emission estimates were derived from airborne measurements in the troposphere and lower stratosphere

- 25 over the Western Pacific and North America. Liang et al. (2010) has global annual totals of 396 Gg Br yr⁻¹ for CHBr₃ and 57 Gg Br yr⁻¹ for CH₂Br₂. These emissions integrated over the geographical region and duration of the campaign are 3 Gg Br yr⁻¹ and 0.4 Gg Br yr⁻¹ for CHBr₃ and CH₂Br₂, respectively. We temporally distribute emissions every 30 minutes without any diurnal variation. We found that other commonly-used emission inventories for CHBr₃ and CH₂Br₂ (e.g. Ordóñez et al. (2012) and Ziska et al. (2013)) were not noticeably better than Liang et al. (2010) at describing the CAST and
- 30 CONTRAST data (not shown). We chose to use Liang et al. (2010) because it has a consistent bias for CHBr₃ and CH₂Br₂. Figure 3 shows the ocean (open and coastal) ocean tagged tracer regions we use in the GEOS-Chem model. Our These geographical definitions are informed by the NOAA ETOPO2v2 Global Relief map (National Geographic Data Center, NOAA, 2006), which combines topography and ocean depth data at 2 minute spatial resolution: heights above between 0 m are defined

as land; and -200 m < heights < 0 m are defined as coastal oceans; and heights below -200 m are open ocean. For tracers that spatially overlap we calculate their fractional contribution taking into account the area covered by land or ocean and local emission fluxesEach 2 minute cell that falls within a model grid box is assigned a coastal or open ocean. Each model grid box can then be described as fractional contributions (R_{α}) to the open and coastal ocean tagged regions. We have explicitly included

- 5 elevated coastal emissions from the inventory in to the coastal tracer. We assign individual tracers to major islands within the our study domain, including Guam (13.5°N, 144.8°E), Chuuk (7.5°N, 151.8°E), Palau (7.4°N, 134.5 °E), and Manus (2.1 °S, 147.4 °E). We assume these island land masses account for 100% of a grid box irrespective of whether their area fills the grid box. We have This gives a total of 20.18 tagged tracers, evenly split between CHBr₃ and CH₂Br₂ including a total tracer and a background tracer.
- 10 Figure 2 shows the spatial distribution of CHBr₃ and CH_2Br_2 emissions that we use . These emissions are "top-down" estimates derived from airborne measurements in the troposphere and lower stratosphere in the Western Pacific and North America. We use de-seasonalised monthly prior emissions from this inventory, with global annual totals of 425 Gg Br yr⁻¹ for CHBr₃ and 57 Gg Br yr⁻¹ for CH₂Br₂, and impose a monthly seasonal cycle at latitudes >30N, following .
- For For global model evaluation using the NOAA data, described above, we initialize the model model tagged tracers in 15 January 2004 with near-zero values until January 2013 with the first year disearded and run the simulation to January 2013. We diseard the first model year to minimize the impact of the initial conditions. For model evaluation using the CAST/CONTRAST data, we initialize the tagged tracers in January 2014 with near-zero values, and background initial conditions that. Background initial conditions were determined from a 12-month integration of the full-chemistry modelthat are subject only, which are then in the tagged model subject to atmospheric transport and loss processes. This approach minimizes any additional model
- 20 error that has accumulated during the longer model integration. We For model evaluation, we sample at the time and location of each observation. For the NOAA data described above, we calculate monthly mean statistics from 1st January 2005–31 December 2011.

3.2 Physical age of air model calculation

We use the age of air simulation to understand the role and frequency of rapid convective systems to transport how short-lived

- 25 halogenated compounds are transported to the TTL, in the absence of reliable bottom-up independent of emission inventories. The method uses only knowledge of the distribution of emissions, and not the magnitude, so we investigate the influence of emissions source region with respect to respective CHBr₃ and CH₂Br₂ atmospheric e-folding lifetimes. We use the GEOS-Chem model to determine the physical age of air *A*, building on previous studies (Finch et al., 2014), and use a consistent set of geographical regions used in our tagged CHBr₃ and CH₂Br₂ simulations as described above(Figure 3).
- For each model tracer (X_i) we define a surface boundary condition-volume mixing ratio *B* that linearly increases with time *t* so that smaller values correspond to older physical ages: $B = f \times t \times R_x$,

$$\begin{array}{l}
B = f \times t, \\
\end{array} \tag{1}$$

where f is a scaling factor constant $(1 \times 10^{-15} \text{ s}^{-1})$, and B describes a volume mixing ratio of each tracer dependent on their time of emission. Fractional contributions of tracers are calculated based on R_x denotes the fraction of where the finalised B (B_{final}) in the surface boundary condition is calculated using:

$$B_{final} = (B \times R_x) + (1 - R_x \times X) \tag{2}$$

5 where X denotes the mixing ratio of tracer within the grid boxrelevant to a particular tagged tracer. We sample the resulting 3-D field of model tracers at the time and location of CAST and CONTRAST measurements. As time progresses, smaller volume mixing ratios represent older ages that have spent more time away from the surface boundary.

We initialise this model in July 2013 and run for $\frac{6}{5}$ six months until the start of January 2014 so that at least one e-folding lifetime of CH₂Br₂ has been achieved. We then sample the resulting 3-D field of model tracer mixing ratios (X), at the time

10 and location of CAST and CONTRAST measurements. The physical age of a tracer *i* since it first touched a land or *A* since it last came into contact with a ocean surface is calculated as $A_i = t_i - X_i/f$. By using the atmospheric transport model take into account atmospheric dispersion. We do not take into account any chemical loss in this simulation by:

$$\underbrace{A = t - X/f}_{\longleftarrow} \tag{3}$$

We account for atmospheric dispersion by using the GEOS-Chem model, but we do not consider any chemical losses.

- To explicitly evaluate marine convection in GEOS-Chem we also developed a short-lived tagged tracer simulation with an e-folding lifetime of four days, comparable to that of methyl iodide (CH_3I) in the tropics (Carpenter et al., 2014). We emit the tracer with an equilibrium mole fraction of 1 pptv over all oceanic regions described in Figure 3. We initialise the model on 1st January 2014 with an empty 3-D atmospheric field and run for two months until 01/03/2014. Model output is archived every two hours and the model is sampled along the aircraft flight tracks. By comparison our model with CH_3I observations,
- 20 we find that GEOS-Chem captures mean marine convective flow over the study regioncompared to CH₃I observations. It also captures infrequent fast, . We also find that the model captures fast, infrequent large-scale convective transport with that result in upper tropospheric ages of 3–5 days, but misses does not capture small-scale variations due to rapid convection. Results are explained in detail in Appendix B Appendix B includes a more detailed report on the results.

4 Results

25 4.1 Model Evaluation

We evaluate our tagged model of atmospheric $CHBr_3$ and CH_2Br_2 using NOAA surface data, and CAST and CONTRAST aircraft data during January and February 2014.

Evaluation Model evaluation using the NOAA data is described in Appendix A. In brief, the model generally has a positive bias but reproduces 30–60% of the seasonal variation (Pearson correlation coefficients in Table 3), depending on geographi-

30 cal location. Model errors in reproducing the observed seasonal cycle reflect errors in production and loss rates. The model generally has less skill at reproducing observations collected at coastal sites close to emission sources.

Figure 4 compares modelled and observed shows that CAST and CONTRAST observed and model vertical profiles CHBr₃ and CH₂Br₂ . It shows have an inverted 'S' shape (Harris et al., 2016; Pan et al., 2016). The suggests that GEOS-Chem has a 30percentage bias for both gases during CAST and CONTRAST, which we calculate using: $100/N_i \sum_i (model_i - obs_i)/(max(mod_i, obs_i))$ We assume this bias is due primarily to errors in prior emission and remove it from subsequent calculations. We find that

- 5 the model can reproduce skill in describing the the broad-scale atmospheric transport over the study region. From Pearson correlation coefficients, we find that GEOS-Chem reproduces more than 30% of the observed variability of CHBr₃ from CAST and CONTRAST and between 15% (CAST) and 45% (CONTRAST) of the observed variability of CH₂Br₂. In general, GEOS-Chem has poorer skill at reproducing observed near-surface variations, reflecting errors in prior emissions. We find that the frequency distribution of the model minus observation residuals are similar for CAST and CONTRAST but with an offset
- 10 from zero, reflecting a systematic error that Larger differences in the correlations for CH_2Br_2 is likely due to an error in prior emissions. Differences between CAST and CONTRAST reflect the bias towards boundary-layer sampling during CAST where measurements are more sensitive to fresh surface emissions. There are smaller differences between CAST and CONTRAST for differences in the the sampled air masses that have originated far upwind. Figure 4 also shows that GEOS-Chem has a positive model bias of 30% for both campaigns, which we calculate using: $100/N_i\Sigma_i(mod_i - obs_i)/(max(mod_i, obs_i))$. The
- 15 relative model error is reasonably constant with altitude for $CHBr_3$ and CH_2Br_2 . It has a longer chemical lifetime making it comparable with the mean mole fraction associated with the troposphere, suggesting that this bias is representative of prior surface emissions. Consequently, we remove this bias from subsequent calculations. We attribute the variations about the mean bias to errors due to model atmospheric transport.

4.2 Tagged-VSLS model output Model Output

- 20 Figures 5 (Figure 6) show mean land, and open and coastal ocean tagged CHBr₃ (CH₂Br₂) tracers over altitude compared to model convective mass flux. There is Figure 5 and Figure 6 show a strong region of convection south of Chuuk and along the equator that transports gases CHBr₃ and CH₂Br₂ directly from open oceanic emission sources to the mid-troposphere. Above the mid-troposphere (10 km) the mean convective mass fluxes get smaller with gases being dissipated progressively more in the horizontal. As we show below this leads to and advection plays a more important role in distributing the gases. This results in
- an inverted 'S' shape in the vertical profiles of $CHBr_3$ and CH_2Br_2 , which is observed by both campaigns as discussed above. There is also a strong convection region west of Papua New Guinea/north of Australia, elose to land and coastal emissions which transports coastal emissions to the mid and upper-troposphere.

The model shows CHBr₃ Model mean mole fractions of 2CHBr₃ are $\simeq 1.4$ ppt throughout the boundary layer (0–2 km)emitted from, determined by open ocean emissions, but deplete quickly over the vertical profile due to their short atmospheric lifetime.

30 Throughout the TTL fall off rapidly as a function of altitude due to chemical losses. At the TTL over the study domain and during the campaign period, mean CHBr₃ mole fractions range 0.20.4–0.6 ppt over the study domain and campaign period mainly due to open ocean emissions. Coastal emissions are typically much larger than open ocean emissions but they play a much smaller role in observed variations throughout the troposphere despite coinciding with except over the strong convective regions over Papua New Guinea/north of Australia. Prevailing easterly transport of gases over the region is dominated by the

vast area of open ocean sources that appear to weaken the magnitude of spatially limited coastal emissions (Andrews et al., 2016; Pan et al., 2016). Averaged over the campaign, coastal and terrestrial sources of CHBr₃ show little influence above 6 km. The vertical and spatial distribution distributions of CH₂Br₂ mole fractions is are consistent with CHBr₃ although they deplete less rapidly with altitude by virtue of their-its longer atmospheric lifetime. 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 5 and terrestrial sources contribute up to 0.1 ppt of CH_2Br_2 in the TTL with the remaining originating from an open ocean source.

Figure 7 shows percentage contributions of geographical tracers to CAST and CONTRAST CHBr₃ observations. Ocean that ocean emissions provide the largest fractional contribution to CHBr₃ during CAST, typically more than $\frac{7080\%}{1000}$ throughout the low to mid troposphereof which 60-80, with the remainder originating from emissions prior to the campaigns. This is

- dominated by open ocean emissions that range 50–70% is from the open ocean of the total tracer. Coastal ocean and land 10 emissions represent a much smaller contribution to CHBr₃ at lower altitudes, but increase their influence above 6 km in the CONTRAST data with contributions from geographical regions immediately outside the study region reaching that reach a maximum of 2060% of the total CHBr₃ tracer in the TTL. This is represented in the results in an inverted 'S' shape observed over the vertical profile, as mentioned above. This reflects deep convection of air masses over the region, which has only a
- small amount of detrainment in the mid-troposphere followed by advection of these air masses in the upper tropospherewhich 15 is described above. Island land masses generally represent only a minor contribution through to the vertical profile at our model resolution, and we have excluded them from further analysis.

Figure ?? shows the same as Figure 7 but for CH₂Br₂. The The ocean, in particular the open ocean, represents the largest contributions to total CH_2Br_2 over the campaign periodare from the oceans, particularly from the open ocean. They typically

represent 20% of the total CH_2Br_2 and reaching a maximum of 3428% in the TTL for the CONTRAST measurements. Max-20 imum contributions of coastal emission sources peak at 515% of total CH₂Br₂ tracer in the TTL, much less than for CHBr₃. The remaining contributions are representative of emissions before prior to the campaign period. The longer lifetime of

Different CHBr₃ and CH₂Br₂ mean that these mole fractions have a greater influence over the campaign profile compared to CHBr₃emission scenarios (Ordóñez et al., 2012; Ziska et al., 2013) vary with spatial distribution and magnitude of coastal

and open ocean emissions, leading to uncertainties of atmospheric mixing ratios (Hossaini et al., 2013, 2016). This would 25 have implications for results presented here, as source region mixing ratios will vary dependent on emission scenario used. We developed the age of air calculation to ascertain the influence of ocean emission regions independent of emission scenarios.

4.3 **Physical Age of Air**

Figure 8 shows how the probability density of the age of air, A, from different geographical tracers changes over altitude. The age of air has a bi-modal distribution peaking at approximately 60 days and 200 days. The younger age distribution is 30 dominated by air that the air masses lofted over the open ocean, while the older age distribution is dominated by air lofted over the land and coastal oceans study domain are responsible for the youngest air throughout the troposphere. Coastal ocean contributions are only present in the younger age profile up to 4 km. At progressively higher altitude regions the distributions generally agealtitudes the probability distribution shifts towards older ages, as expected, but above the boundary layer the median values of both modes remain relatively constant at approximately 70 days and 210 days, respectively. The older peak is representative of emission sources have been imported into the study region from outside the study domain. Contributions from coastal ocean and terrestrial emissions are small compared to the contribution from the larger area of open ocean emissions. The oldest ages, which approach the time of the study period, reflect the accumulation of near-zero mole fractions. At higher

- 5 altitudes we find that the probability distributions become less smooth, reflecting more variation in ages. At these altitudes we also find a progressively larger (but still minor) contribution from coastal emissions. We corresponding to longer periods from the point of contact with the surface. However, at 10–13 km we see a noticeable shift towards younger ages, reflecting the peak of the convective outflow of surface air. Within the TTL, mean age increases to a value greater than the e-folding lifetime of atmospheric CHBr₃. However, we find using our CH₃I-like tracer I-like tracer (mean lifetime of approximately four days) that
- air masses can be transported to the TTL within 3–5 days but these are infrequent events so are not easily observed (Appendix B).

Assuming an indicative e-folding atmospheric lifetime τ of 24 days for CHBr₃ and 123 days for CH₂Br₂ we find calculate that the majority of air lofted over the ocean has an age within $3\tau_{CHBr_3}$ and $1\tau_{CH_2Br_2}$. We find that 1176% (5292%) of oceanic emissions reach the TTL within $2\tau_{CHBr_3}$ ($3\tau_{CHBr_3}$) of which 53.6, with 64% (34.988%) are from the open oceans.

- 15 Contributions from the land and coastal oceans are negligible as they dominate the older age profile throughout the vertical. Coastal based emissions show some influence at higher altitudes due to the difference in entire ocean and open ocean age profiles, but they have no strength as an individual geographical tracerof open ocean emissions and 9% (50%) of coastal emissions being transported in the same time frames. The corresponding statistics for CH₂Br₂ are 9599% of air lofted over the ocean reaches the TTL within $1\tau_{CH_2Br_2}$ of which 88, and 99% is lofted over the open (97%) of air emitted from the open
- 20 (coastal) ocean.

Figure 9 is the same as Figure 8 but sampled along CAST and CONTRAST flight tracks. The shows that the atmospheric sampling adopted by the CAST and CONTRAST campaigns capture the bi-modal captures a similar distribution of physical ages discussed above. CAST represents a profile dominated within the boundary layer, with CONTRAST more representative of age profiles outside of the boundary layer that reflects its more extensive horizontal and vertical sampling domain. Despite

25 intensive measurements around coastal land masses of the region, CAST did not very well capture coastal emissions. We also find that CONTRAST generally better samples both modes of the distribution, reflecting the more extensive horizontal and vertical sampling domain and the larger number of collected measurements This is reflective of a model resolution that is too coarse to capture such localised effects on a sub-model-gridscale.

Figure 10 is the distribution of oceanic shows mixing ratios of CHBr₃ mixing ratios in the troposphere, in all systems and 30 in only the highest convective systems compared with associated age . Throughout the tropospheredecreasing with altitude, but remaining fairly constant with increasing age within each altitude range. Coastal emissions are associated with the highest surface emissions but they also subjected to slow ascent rates and consequently greater photochemical losses. In contrast, open ocean emissions are lower than coastal emissions but are convected more rapidly and subject to less chemical loss. Consequently, CHBr₃ mole fractions generally decrease with age. The only exception is at the near-surface where land

35 emissions dominate the older age profile appears to be insensitive to age. From our analysis, we found that CHBr₃ values

are determined mainly by younger air masses from the open ocean (Figure 8). Within the TTL, the highest CHBr₃ higher median mole fractions are associated with the youngest age of air (24–48 days), but this represents only 5of the air transported to the TTL highest model convective mass flux in each age bin. The peak frequency for the mean age of air in the TTL is 48– 72 days, corresponding to $3\tau_{CHBr_3}$ and median values of 0.5 pptv CHBr₃ from oceanic emission sources. The highest values

5 of model convective mass flux do not account for all the high CHBr₃ mole fractions within the TTL. Less, and 0.6 ppty in high convective systems. However, less than 0.5% (2%) of air being transported to the TTL within 20–40-24–48 (48–72) days of emission are associated with high convection events. Weaker, mean convection plays an important role in more consistently transporting large mole fractions to the free troposphere that is then transported more slowly to the TTL.

To estimate the mean observed transport of $CHBr_3$ and CH_2Br_2 to the TTL we remove the calculated model bias as described

- 10 above in section 4.1(section 4.1), assuming this bias reflects errors in surface emissions. Figure 11 shows the resulting corrected mean vertical profiles. We calculate the uncertainties using the upper and lower limits of the bias correction, which are based on CHBr₃ and CH₂Br₂ data that are ± 2 mean absolute deviations from the observed mean mole fractions. For CHBr₃ and CH₂Br₂ we find biases that range -8%–80% and 19%–43%, respectively, which we then apply to the model values throughout the atmosphere over the campaign period. We find that resulting mean model values underestimate observed CHBr₃ and
- 15 CH_2Br_2 between 9–12 km, above the main region of convective outflow, with the observations inside the model uncertainty with the exception of CH_2Br_2 . Mean model values within the TTL (above 13 km and below the local tropopause) reproduce mean observations. Based on this bias correction approach we infer a mean mole fraction and range of 0.46 (0.13–0.72) ppt and 0.88 (0.71–1.01) ppt of CHBr₃ and CH_2Br_2 being transported to the TTL during January and February, 2014. This is consistent with a contribution of 3.14 (1.81–4.18) pptv of Br to the TTL Br_y budget over the region of the campaign campaign.
- 20 region. This is consistent with Navarro et al. (2015) which estimates who estimate VSLS contribution over the Pacific from observations in 2013 and 2014. It estimates 3.27 ± 0.47 pptv of bromine from CHBr₃, CH₂Br₂ and other minor VSLS sources at the tropopause level (17 km).

Based on average observed surface values of CHBr₃ (1.13 ppt) and CH₂Br₂ (1.02 ppt) over the campaign we infer that 40and 86of these emitted gases, respectively, are directly injected into the TTL over our study domain. The larger percentage

- 25 for CH_2Br_2 is consistent with its longer lifetime. Our value of 40for the $CHBr_3$ SGI falls within previously reported values that range 15–76(median \simeq 50), but is lower than the associated median value. One possible reason for the negative bias in our SGI estimate for $CHBr_3$ is the bias correction approach we adopted for our analysis. Our bias correction is simple but not does take account for vertical variations in atmospheric transport. We calculated a mean atmospheric bias, but clearly the model bias is much larger at lower altitudes, reflecting errors in emission estimates. However, we find that model bias at altitudes >10 km
- 30 (29) is comparable to the bias calculated using all data (31). There is much less vertical variation in bias for CH_2Br_2 because of its longer atmospheric lifetime.

Discussion and Concluding Remarks 5

We used the GEOS-Chem chemistry transport model to interpret mole fraction measurements of CHBr₃ and CH₂Br₂ over the Western Pacific during the CAST and CONTRAST campaigns, January-February 2014. We found that the model reproduced 30% of CHBr₃ measurements and 15% (45%) CAST (CONTRAST) CH₂Br₂, but had a mean positive bias of 30% for both

5 compounds. CAST mainly sampled the marine boundary layer (70% of observations) so that biases in prior surface emissions have a greater influence on CAST than CONTRAST, which sampled throughout the troposphere.

To interpret the CAST and CONTRAST measurements of CHBr₃ and CH₂Br₂ we developed two new GEOS-Chem model simulations: 1) a linearised tagged simulation so that we could attribute observed changes to individual sources and geographical regions, and 2) an age of air simulation to improve understanding of the vertical transport of these compounds,

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acknowledging that more conventional photochemical clocks are difficult to use without more accurate boundary conditions provided by surface emission inventories.

We have three main conclusions. First, we found that open ocean emissions of $CHBr_3$ and CH_2Br_2 are primarily responsible for observed atmospheric mole fractions of these gases over the Western Pacific. Emissions from open ocean sources represent up to 7570% of total CHBr₃, with the largest fractional contribution in the lower troposphere. Coastal ocean and terrestrial

- sources typically contribute 720% to total atmospheric CHBr₃ but reach a maximum of 2060% in the TTL due to advection 15 of air masses convected from areas outside the study region. Based on this model interpretation, we infer that CAST observations of CHBr₃, which are mainly in the lower troposphere, are dominated by open ocean sources. In contrast, CONTRAST measurements have a mix of sources, including a progressively larger contribution from coastal ocean and terrestrial sources in the upper troposphere. Tropospheric measurements of CH_2Br_2 , which has a longer atmospheric lifetime than $CHBr_3$, are
- dominated by sources from before the campaign. The open ocean source typically represents only $\frac{2015\%}{2015\%}$ of the observed 20 variations of CH₂Br₂ emitted during the campaign region throughout the troposphere.

Second, using our age of air simulation, we find that the highest majority of CHBr₃ and CH₂Br₂ mole fractions in the TTL correspond to the youngest air masses being transported from open oceanic sources, predominantly the open ocean with coastal oceans representing older air masses. Within the TTL, the highest CHBr₃ mole fractions are associated with the youngest

25 age of air (24 - 48 days) strongest convective mass flux events, but this represents only 52% of the air transported to the TTL. Weaker, slower convection processes are responsible for consistently transporting higher mole fractions to the UT and TTL. The majority of air (4092%) is being transported to the TTL is within $3\tau_{CHBr_3}$ (48–72 days) corresponding to lower mole fractions and the majority of weaker convection events.

And third, we estimated the flux of CHBr₃ and CH_2Br_2 to the TTL using model data that have been corrected for bias. We calculated a mean and range of values 0.46 (0.13–0.72) pptv and 0.88 (0.71–1.01) pptv for CHBr₃ and CH₂Br₂, respectively, 30 which represent 40and 86 of estimated surface emissions. Together, they correspond to a total of 3.14 (1.81–4.18) pptv Br to the TTL. Our flux estimate for CHBr₃ is lower than previous studies that have reported values closer to 50.

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- 10 The NOAA surface data is available at http://www.esrl.noaa.gov/gmd/dv/ftpdata.html.

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Table 1. Mean measurement statistics for CHBr₃ and CH₂Br₂ mole fraction data as a function of altitude for CAST and CONTRAST aircraft campaigns. \bar{x} , σ , and n denote the mean value, the standard deviation, and the number of data points used to determine the statistics.

Altitude	СН	Br ₃	CH ₂ Br ₂		
	CAST CONTRAST		CAST	CONTRAST	
km	\overline{x} , 1 σ , & range [ppt]; n	\overline{x} , 1 σ , & range [ppt]; n	\overline{x} , 1 σ , & range [ppt]	\overline{x} , 1 σ , & range [ppt]	
0-2	0.95, 0.45, 0.42-3.00; 502	0.89, 0.23, 0.51–1.55; 75	1.01, 0.13, 0.72-1.64	1.07, 0.11, 0.83-1.27	
2-4	0.61, 0.16, 0.29–0.98; 147	0.62, 0.18, 0.29–1.24; 48	0.91, 0.05, 0.73-1.06	0.94, 0.09, 0.78-1.13	
4-6	0.44, 0.17, 0.03–0.79; 59	0.56, 0.18, 0.20-1.12; 65	0.88, 0.06, 0.69-1.00	0.91, 0.09, 0.73-1.12	
6-8	0.38, 0.25, 0.02-0.81, 53	0.60, 0.20, 0.24-1.01; 43	0.85, 0.11, 0.63-1.06	0.90, 0.10, 0.70-1.06	
8-10	0.48, 0.34, 0.14–0.82; 2	0.62, 0.17, 0.24–1.00; 43	0.90, 0.13, 0.77-1.03	0.93, 0.09, 0.72-1.07	
10-13	_	0.59, 0.25, 0.00-1.38; 130	_	0.87, 0.19, 0.21–1.10	
TTL	-	0.48, 0.16, 0.18–1.17; 280	-	0.86, 0.08, 0.64–1.06	

Table 2. Location and code of NOAA/ESRL ground-based stations. All located at the surface with exceptions of SUM (3210 m), MLO (3397 m) and SPO (2810 m).

Station	Name	Lat	Lon
ALT	Alert, NW Territories, Canada	82.5°N	62.3°W
SUM	Summit, Greenland	72.6°N	38.4°W
BRW	Pt. Barrow, Alaska, USA	71.3°N	156.6°W
MHD	Mace Head, Ireland	53.0°N	$10.0^{\circ}W$
LEF	Wisconsin, USA	45.6°N	90.2°W
HFM	Massachusetts, USA	42.5°N	72.2°W
THD	Trinidad Head, USA	41.0°N	$124.0^{\circ}W$
NWR	Niwot Ridge, Colorado, USA	$40.1^{\circ}N$	$105.6^{\circ}W$
KUM	Cape Kumukahi, Hawaii, USA	19.5°N	$154.8^{\circ}W$
MLO	Mauna Loa, Hawaii, USA	19.5°N	$155.6^{\circ}W$
SMO	Cape Matatula, American Samoa	14.3°S	$170.6^{\circ}W$
CGO	Cape Grim, Tasmania, Australia	$40.7^{\circ}S$	177.8°E
PSA	Palmer Station, Antarctica	64.6°S	$64.0^{\circ}W$
SPO	South Pole	90.0°N	-

	CHBr ₃				$ m CH_2Br_2$		
	DJF	MAM	JJA	SON	DJF	MAM	JJA
Station	r ² , %bias	r ² , %bias	r ² , %bias	r ² , %bias			
ALT	0.00, 3.8	0.55, 0.1	0.05, 5.5	0.43, 19.3	0.09, 12.4	0.21, 0.0	0.23, 10.0
SUM	0.05, 25.1	0.01, -17.1 - <u>17.1</u>	0.23, -12.0 - <u>12.0</u>	0.54, 20.6	0.06, -2.7 <u>2.7</u>	0.15, -13.0 - <u>13.0</u>	0.15, 4.8
BRW	0.00, -41.3-41.3	0.52, -30.2 - <u>30.2</u>	0.13, -26.5 - <u>26.5</u>	0.80, -26.5 - <u>26.5</u>	0.15, 9.5	0.07, 8.7 <u>8.7</u>	0.00, -4.4-4
MHD	0.00, -40.8 -40.8	0.18, -72.4 -72.4	0.04, 80.6 <u>80.6</u>	0.08, -61.2 - <u>61.2</u>	0.05, -20.5 -20.5	0.11, -35.9 - <u>35.9</u>	0.14, -42.7 -4
LEF	0.03, 45.7	0.01, 15.5	0.03, 39.3	0.73, 51.2	0.17, 13.4	0.25, 3.1	0.44, 18.2
HFM	0.06, 52.2	0.01, 30.1	0.15, 46.9	0.38, 52.3	0.03, 20.0	0.06, 9.3	0.22, 27.1
THD	0.19, 55.3	0.15, 15.8	0.36, 11.7	0.17, 40.2	0.09, 16.9	0.06, 0.9	0.01, 8.6
NWR	0.02, 43.3	0.49, 25.9	0.01, 21.8	0.31, 38.7	0.20, 2.3	0.55, 4.9	0.40, 11.9
KUM	0.00, 20.2	0.37, -1.9 - <u>1.9</u>	0.05, 0.9	0.01, 6.8	0.25, 0.3 <u>0.3</u>	0.50, 4.4	0.47, 15.6
MLO	0.18, 61.9	0.60, 60.3	0.02, 65.1	0.58, 64.7	0.14, 14.8	0.32, 15.2	0.21, 22.8
SMO	0.23, 8.2	0.02, -4.9 -4.9	0.04, 3.0	0.11, 4.7	0.39, 6.9	0.38, 0.9 <u>0.9</u>	0.19, 0.2 0
CGO	0.23, -39.0 - <u>39.0</u>	0.01, -12.8 - <u>12.8</u>	0.05, 7.7	0.00, -19.6 - <u>19.6</u>	0.13, 8.7 <u>8.7</u>	0.13, -1.6 - <u>1.6</u>	0.04, -1.4 - <u>1</u>
PSA	0.19, -13.9 - <u>13.9</u>	0.25, 26.4	0.01, 31.7	0.05, -1.9 - <u>1.9</u>	0.00, -1.7 - <u>1.7</u>	0.29, 11.7	0.15, 10.3
SPO	0.50, 6.6	0.12, 6.7	0.07, 19.2	0.11, -7.3 - <u>7.3</u>	0.01, 4.8	0.06, 4.6	0.11, 3.7

Table 3. Seasonal break down of mean statistics for NOAA ground station sites (Table 2) showing Pearson correlations, r^2 correlations, between observed and climatological monthly mean CHBr₃ and CH₂Br₂ mole fraction data, and corresponding model bias values biases.



Figure 1. Distribution of measurements Measurement distribution of CHBr₃ and CH₂Br₂ mole fractions from the CAST (left) and CON-TRAST (right) aircraft campaigns as a function of altitude (km). Relevant island waypoints are shown inset: Guam (G), Palau (P), and Chuuk (C).

Flux of CHBr₃ from land and ocean, the latter separated in to its open and coastal ocean tracers. Guam (G), Palau (P), Chuuk (C) and Manus (M).



Figure 2. Surface emissions of CHBr₃ (10^{13} kg/m²/s) and CH₂Br₂ (10^{14} kg/m²/s) taken from Liang et al. (2010) for the time and region study domain of the CAST and CONTRAST campaigns.



Figure 3. Comparisons Flux of CHBr₃ from total, open, and coastal ocean tracers. Relevant island waypoints are shown inset: Guam (G), Palau (P), and Chuuk (C).



Figure 4. Comparison of model and observed (left panels) CHBr₃ (ppty) and (right panels) CH₂Br₂ (ppty) mole fractions from the fraction data for CAST (denoted by blue) CAST and CONTRAST (denoted by red)CONTRAST aircraft campaigns. The top, middle and bottom rows display Top panels describe the comparison between model (dotted line) and observed (solid line) values as a seatter box and whiskers plot (with on 2-km altitude bins. The middle panel describes the model and data comparison as a scatterplot. Pearson correlation correlations (r²) and percentage biases are shown inset. Black, linear best-fit red, and blue dashed lines denote the 1:1 line, and percentage biase inset); a frequency distribution of the model minus observed values; best fit linear models for CONTRAST and CAST, respectively. The bottom panel show the relative model error, described as a box and whiskers plot on 2-km altitude bins. The vertical profile of box-and-whiskers of dashed line denote the model minus observed values; corror line.



Figure 5. Model mole fractions (pptv) of CHBr₃ over the study domain as a function of altitude, averaged between 18/01/14 and 28/02/14, from the <u>land_total</u> (column 1), open <u>ocean</u> (column 2) and coastal ocean (column 3) tagged tracers. The corresponding mean model convective mass flux (kg/m²/s) is shown in column 4. Tagged tracers are averaged from 2-hour fields and convective mass fluxes are averaged from daily fields.



Figure 6. As Figure 5 but for CH_2Br_2 (ppty).



Figure 7. The percentage contributions from total ocean, expressed as a box and whiskers plotopen oceans, from land and ocean sources coastal oceans to total CHBr₃ sampled throughout the troposphere during (bluetop) CAST CHBr₃ and (redbottom) CONTRAST eampaignsCH₂Br₂ described as a box and whiskers plot on 1-km altitude bins.



Figure 8. Frequency distributions of probability Probability density function functions of the age of air *A* for (orange) land, (blue) entire total ocean, and (green) open oceans, and (black) coastal ocean tracersin 2 km, described as 2-km altitude regions up from the surface to the TTL (13 km to the tropopause) averaged over the whole study domain between 18/01/2014–28/02/2014.

As Figure 7 but for CH₂Br₂.



Figure 9. As Figure 8 but sampled along CAST and CONTRAST flight tracks.



Figure 10. Box and whiskers plot of model CHBr₃ mole fractions from the entire ocean tracer as a function of 2 km altitude intervals and a nominal 24-day e-folding lifetime (τ). Data are averaged over 18/01/2014–28/02/2014 and over 10°S-30°N, 125-175°E. All-Blue values correspond to results determined by all available dataare shown in blue, and data corresponding red values correspond to results determined by convective mass fluxes >95th percentileare show in red. Solid lines denotes the percentage of occurrence rate over the period and region denoted above. Percentage of occurrence rate refers to how often air masses fall within the specified age range.



Figure 11. Observed (solid circles) and model (dashed-dot line) mean mole fractions of $CHBr_3$ (blue) and CH_2Br_2 (red) as a function of altitude, January–February 2014. The <u>solid</u> horizontal lines associated with each mean observation denotes the range about that mean. The coloured envelopes associated with the model denote the uncertainty based on the bias correction as described in the main text. The black horizontal dashed line denotes the mean model tropopause of 16.5 km.

Appendix A: Model Evaluation Using NOAA Surface Mole Fraction Measurements

Figure A.1 is the mean annual percentage bias and associated r^2 values betweens modelled and observed CHBr₃ and CH₂Br₂ at stations in table2. The shows that the majority of station sites have a positive model bias with magnitude varying depending on location. Mid-latitude stations (LEF–NWR) have similar bias values of 30–40% (10–20%) for CHBr₃ (CH₂Br₂). At the

- 5 tropical sites, which are comparable with the campaign region, the model bias varies strongly depending on location. This variability will represent the large variability of convective events over the region, as well as the aforementioned errors in model emissions. KUM and MLO both sit on Hawaii, with KUM and SMO being a near surface coastal station and MLO sitting at an elevated altitude of 3397 m. Model bias calculated for MLO (60%) is much greater than the other two near surface sites ($\leq 10\%$), however it gives the strongest annual correlation with r^2 values of 0.75 (0.55) for CHBr₃ (CH₂Br₂). All coastal
- 10 sites (with exception of ALT) near emission sources have low r^2 values (<<0.4) suggesting the model does not capture local variations in emissions well. This is also representative of the variation of convection events over the tropical region being represented within the model.

Seasonal variations within model bias and correlations of CHBr₃ and CH₂Br₂ are shown in Table 3. The campaign season of DJF is poorly constrained within the model at all sites with an $r^2 < 0.5$ for both gases. The annual correlation at sites appears

15 to be dominated by other seasons. Within the tropical stations, model bias increases from the annual at KUM to around 20% with no correlation to observed values. MLO and SMO show a similar seasonal bias to the annual indicating the effect to be local to the KUM station site.

Figure A.2 is the observed modelled and seasonal cycle at the tropical station sites (KUM, MLO and SMO) for CHBr₃ and CH₂Br₂. The model is able to reproduce shows that the model reproduces the seasonal cycle well at all three sites. The

- 20 emissions at these sites are not scaled seasonally, the phase is representative of the chemistry at these sites. The shorter lived $CHBr_3$ profile is dominates by its loss from photolysis whereas the CH_2Br_2 cycle is dominated by oxidation with OH. The amplitude of the seasonal cycle is overestimated in $CHBr_3$ at MLO, and to a lesser extent KUM. This can be indicative of local biases within photolysis loss rates and/or emissions. The same effect is not shown within the CH_2Br_2 suggesting there is not a similar problem associated with OH fields. This is concurrent with a recent multi-decadal analysis of carbon monoxide
- 25 (Mackie et al., 2016) at higher northern latitudes does not support a major problem with similar monthly 3-D fields of OH.



Figure A.1. Mean annual percentage model bias (blue) calculated at NOAA ground station sites (Table 2) for CHBr₃ (dots) and CH₂Br₂ (crosses). The horizontal dashed line denotes zero bias. The right-hand-side y axis describes the ability of the model to reproduce observed variations (r^2) (red). The vertical dotted lines define the tropical stations.



Figure A.2. Observed (green) and model (blue) mole fractions of (a) CHBr₃ and (b) CH₂Br₂ at tropical NOAA sites. The seasonal cycle is shown as the climatological monthly mean anomaly calculated by subtracting the annual mean from the climatological monthly mean (pptv). Horizontal bars on observed values denote $\pm 1\sigma$.

Appendix B: Evaluation of Model Convection

To evaluate model convection over the marine environment during the CAST and CONTRAST campaigns, we developed a short-lived tagged tracer simulation with an e-folding lifetime comparable to CH_3I , as described in section 3.

We emitted CH₃I at an equilibrium mole fraction of 1 pptv over ocean regions and applied an atmospheric e-folding lifetime of four days similar to that CH₃I in the tropics (Carpenter et al., 2014). We can then use the model mole fraction to determine the effective mean age of air parcels throughout the troposphere, and to compare the qualitatively to observed CH₃I values collected during the CONTRAST campaign.

Figure B.1 is a comparison of observed CH_3I to our CH_3I -like tracer. The shows that the model can generally reproduce the quantitative vertical distribution of CH_3I : a decrease from the surface source up to an altitude of 10–11 km. Above this, there

10 is a 1-2 km altitude region where values are higher than those in the free troposphere, suggestive of outflow from convection.

As expected, the youngest air masses are close to the surface with the ages as young as 5–6 days in the upper troposphere. These ages are indicative of fast convective transport but they are not as young as would be expected from some of the highest observed mole fractions, which are likely due to faster, sub-grid scale, convective transport.

Figure B.2 is the probability distribution of the age of the simulated CH₃I-like tracer between 10–15 km altitude. The shows

- 5 that the model captures infrequent fast, large-scale convective transport over the study domain, with ages as young as 3– 4 days reaching the upper troposphere. One metric to describe the convective transport is the marine convection index (MCI), following Bell et al. (2002): the ratio of mean upper tropospheric CH_3I (8–12 km) to lower tropospheric CH_3I (0–2.5 km). The CONTRAST observations have an MCI of 0.38 and the corresponding model MCI sampled for these observations is 0.19. The MCI for the model domain for the duration of CONTRAST is 0.28. These values are consistent with those found in Bell et al.
- 10 (2002) over a similar Pacific regions.

Overall, we find that the model describes the mean convective flow over the region and can capture instances of rapid, largescale convective transport. Differences in the MCI suggest a significant role for rapid, sub-grid scale vertical transport that are not captured by our coarse model resolution.



Figure B.1. Vertical profiles of observed (blue) and synthetic (coloured as a function of age) CH₃I mole fraction data collected by sampled along flight tracks corresponding to AWAS samples collected during **CONTRAIL** CONTRAST as a function of altitude.



Figure B.2. Probability distribution of the physical age of CH₃I for the 3-D study domain (solid line) and as sampled by the aircraft (dashed line) between 11–15 km during CONTRAST, 18th January–28th February, 2014. The dotted line indicates $1\tau_{CH_3I}$ of 4 days.