Replies to reviewer report 1:

We thank the reviewer for the detailed and supportive comments. Below are our point-to-point replies.

This manuscript explores an important topic regarding the recovery of the stratospheric ozone layer, in particular the emission rates of halogenated very short-lived substances (VSLS) at the surface. These compounds can be rapidly transported into the stratosphere, especially over areas of active, deep convection, and affect stratospheric ozone levels, thereby delaying the recovery process. very few observations exist in key areas of the world where VSLS emissions and transport rates can be significant to the stratospheric budget of inorganic bromine, so the availability and use of new aircraft data sets constitutes a unique opportunity to test our models and evaluate our inventories. I will first provide some general comments to the manuscript, followed by some specific ones.

We thank the reviewer for the insightful comments.

General

1. While the topic is of great relevance, it is unclear what the contribution of the manuscript is, as written. Similar flux calculations were done by previous studies (lines 171-173). Is the contribution of this manuscript related to the methodology used, to the new aircraft data set over the tropical Western Pacific, and/or to the new magnitudes of fluxes obtained in this study?

We have applied a MAP approach to inferred $CHBr_3$ and CH_2Br_2 fluxes over tropical Western Pacific from the new CAST / CONTRAST experiments. Currently there are large differences in the distribution and magnitude of between existing $CHBr_3$ /CH_2Br_2 inventories (see, for example, the new Figure 6).

To our knowledge, we are the first to use the MAP approach to infer $CHBr_3$ and CH_2Br_2 surface fluxes over open oceans in tropical Western Pacific region, supported by new data from the CAST/CONTRAST campaigns. Our posterior estimates consistently show systematic deviations from the three independent prior inventories (see new Figure 6). These results have now been emphasized in the discussions (Page 11).

2. The results presented in the manuscript are based on numerous model assumptions (e.g., lines 215–226). Were any sensitivity tests performed on the choice of values used? Are there any references to justify the choice of values used? Paragraphs 4 and 5 in the Introduction highlight how previous studies were based On several (different) assumptions and how those results need to be examined with caution. How can the results from this analysis, along with the assumptions used, be compared against previous studies?

The reviewer is correct that we do introduce several assumptions to help infer surface fluxes from aircraft measurements. As wit other top-down flux inversions, we assume prior knowledge and its uncertainty. In the revised manuscript, we include sensitivity tests to test these assumptions about the magnitude of uncertainty (Lines 223-235), and three different sets of prior fluxes (Figure 6). The results from these tests demonstrate the robustness of our $CHBr_3$ fluxes over the main study domain where observation coverage is relatively dense. Our posterior model simulations at two different spatial resolutions (revised Figure 2) are also in better agreement with observations than those based on prior inventories. However more independent data including the direct flux measurements are needed to fully evaluate our results in particular for CH_2Br_2 fluxes (See discussion).

3. The type of correlation between bromoform and dibromomethane is of importance. What is the rationale for a linear correlation used in several studies published earlier (e.g., lines 103-105)? Given that the new aircraft data set elucidates a different correlation between the two 2 compounds, elaborating some more on this topic will highlight one of the new findings from this study.

Several previous studies have assumed the linear correlation between $CHBr_3$ and CH_2Br_2 based on some observations as well as on the assumption about the shared biogenic sources. However other measurements and model studies suggest a rather complicated correlation between these two species. Our inversions also show no evidence to support such a simple linear relation. But our posteriori flux uncertainties, in particular for CH_2Br_2 (Figure 3), are too large for us to reach a definitive conclusion.

4. There are several instances of missing punctuation marks such as commas and periods throughout the manuscript.

During the revision, we have corrected the punctuation.

5. Some of the listed uncertainties are significant (e.g., line 262, line 342). What is the impact of these uncertainties on the conclusions of this study?

Our current estimates, in particular for CH_2Br_2 still have large uncertainties, limited by the observation quality and coverage, as well as by transport model errors. We believe they will only be addressed by more coordinated fluxes/concentrations measurements.

Specific

6. **Abstract, line 25: An r value of 0.38 does not really qualify as "reasonably consistent" correlation.**

Here the consistence is about the agreement with vertical distributions. We have clarified the text.

7. Abstract, line 36: which a priori inventory was used for the comparison?

It is from Ordonez et al. (2012). We have clarified this in the abstract.

8. Introduction, line 47: "The wide range of … lifetimes allows for …"

Changed the sentence as suggested

9. Introduction, line 55: "There is a wide range of…"

Changed the sentence as suggested

10. Data, paragraph 1: Are there any references available for the CAST and CONTRAST instruments?

See Andrews et al. (2016).

11. Data, lines 146-149: What are "mean absolute percentage errors"? Which data set is higher? Are the differences uniform with height? How is this metric used in the analysis and how does it impact the results?

Their deviations change with altitudes (see Andrews et al 2016). By design, our inversions depend on observed horizontal and vertical gradients in the boundary layer, mainly observed by CAST. Most CONTRAST measurements are at much higher altitudes and hence less sensitive to local sources.

Our sensitivity experiments), in which we introduce a bias between CONTRAST and CAST data that we infer in our inversion, show very similar results to our control run. We have included this in the main text.

12. Data, lines 146-149: The second half of the statement is confusing as stated. WAS refers to the collection method and GC/MS to the analysis technique. Each campaign provided one data set. It might be simpler to state "…between the CAST and CONTRAST instruments", instead.

Good suggestion. We have changed accordingly.

13. Data, line 157-158: Is there a reference available to support the statement?

See Butler et al (2016)

14. Data, lines 163-164: Are the referenced data from NOAA's ground network collected at the surface? Given that this study examines data at higher altitudes as well, are there any model comparisons with data at higher altitudes?

Yes. They are NOAA surface measurements. Unfortunately we cannot find independent aircraft measurements to evaluate our prior or posterior model simulations.

15. Data, line 186-187: Is a 6-month spin - up enough time and seasonally appropriate?

It is appropriate because of the short lifetime (<4 months) of the species. In the inversion, we are also only focused on January and February, 2014.

16. Results, line 248: Even with higher a priori ocean fluxes, the model still depletes bromoform much faster between the surface and 2 km than the observations show. Is this a result of chemistry, transport, and/or something else within the model?

We believe the higher lapse rate is likely related to the issues with model vertical transport, as it has also been found for posterior model simulation (Figure 2) even at finer model resolution.

17. Results, line 274-278: The right panel of Figure 2 shows that the model's vertical distribution of bromoform is practically the same when run at coarse and fine spatial resolutions. This suggests that sub-grid convection, assuming that the model resolves some events at the finer scale used, does not play a significant role in the modeled vertical profile. Is this result expected for a tracer with a relatively short lifetime and over a region of active, deep convection?

The coarse and fine model simulations show different atmospheric lapse rate in the boundary layer for both prior and posterior surface fluxes. Even with our fine-scale model simulation (spatial resolution of ~25 km) there are sub-grid scale processes that are unaccounted. The role of model error is the subject of ongoing work.

18. Results, line 293-294: How were the 50% and 30% chosen? How sensitive are the results of the analysis to these percentage choices?

These percentages are chosen just to demonstrate observation constraints. The error reduction is insensitive to these values. Also, as shown in Figure 6, our inversion results are not sensitive to *a priori* fluxes over regions with proper observation coverage.

19. Figure 1, line 445: Suggest using "15°S–25°N"

Thanks. We have changed the latitude range as suggested.

20. Figure 1 and Figure 2: Are the in situ data shown in these figures an average of both aircraft data sets?

Figure 1 shows the altitudes of the CAST/CONTRAST measurements, and Figure 2 shows the $CHBr_3$ concentrations at the boundary layer, which are mainly observed by CAST.

Reviewer report 2

We thank the reviewer for providing a second round of reviewer comments. Below are our point-to-point responses to the reviewers' comments (denoted in bold). In particular, following the reviewer's suggestion, we have conducted additional inversion experiments using Liang's inventories as our a priori, and include the results to the main text (Section 3 and Section 5). In short, we find that our posterior flux estimates are robust against using different prior emission inventories, subject to data coverage.

General comments

This manuscript describes an inverse modelling study designed to infer biogenic, oceanic emissions of two short-lived bromocarbons (bromoform and dibromomethane- CHBr3 and CH2Br2). The authors use an emission inversion setup consisting of a global chemistry transport model, a priori emission inventories for CHBr3 and CH2Br2, and aircraft measurements from two separate campaigns measuring both compounds over the tropical Western Pacific. The authors also carry out a short observing system simulation experiment to retrieve a set of known idealised emissions as a means of proving the efficacy of their inversion modelling setup. The authors conclude that the a priori emissions of CHBr3 and CH2Br2 are too high over this region, and find the a posteriori emissions of CHBr3 and CH2Br2 to be lower than the a priori emissions by 40% and 20%, respectively. They also conclude that assumptions in previous studies of a correlation in the emissions of CHBr3 and CH2Br2 cannot be supported based on the findings of this work.

The subject matter of the article sits well within the frame of ACP. In addition, the objectives of the scientific study and the design of the experiment (on the whole) mean that this work provides a useful scientific contribution on a topic (i.e. the biogenic, oceanic emissions of bromocarbons) where we have relatively poor understanding. It is welcome to see studies moving away from heuristic methods for inferring CHBr3 and CH2Br2 emissions towards using more robust methods. I therefore find that this paper is a welcome and much needed scientific contribution.

Overall, I find the article to be well written and organised. The scientific ideas are laid out in a clear and logical manner, and consequently one can follow the flow of ideas easily. The article also does quite well at justifying the methodological choices, although there is one major issue here that I will highlight below in the specific comments section. Unfortunately, this issue does have a direct bearing on my recommendation for publication. Separately, and as a more minor issue, I did find that the authors stopped short somewhat of some deeper discussion that I feel would help strengthen the article, and I will explain this in more detail below.

I therefore find that this has the potential to be a very good scientific article. However, I cannot recommend publication until the issues outlined in the specific comments section are addressed.

We thank the reviewer for their supportive comments. We originally chose the dibromomethane and bromoform ocean flux estimates from Ordóñez et al (2012). as our prior because they provided more detailed spatial patterns than Liang et al (2010). As we show in the new Figure 6, using two alternative prior inventories (Ziska et al (2013) and. Liang et al. (2010)) does not significantly impact our results subject to coverage provided by the aircraft data

We broadly agree with previous studies (but for a larger geographical region) that the Ordóñez inventory overestimated bromoform emissions over the Western Tropical Pacific region by nearly 40%. In our study, we also found large differences between open ocean fluxes and coastal (island) sources, contrary to Ordóñez et al, and also different from the simple spatial pattern over open oceans suggested by the inventory from Liang et al. (2010).

However, we agree with the reviewer that additional inversions informed by alternative prior knowledge can further this study. We now present additional experiments that use Ziska's and Liang's prior bromomethane emission inventory. These are included in the main text but summarized below.

Specific comments:

1) The most significant problem I find in this study relates to the choice of Ordonez et al as the sole choice for priori emission inventory for both CH2Br2 and CHBr3 emissions.

a. My first point relates to the CHBr3 a priori emissions. I fully recognise the challenges Ordonez et al. faced in creating an emission inventory using heuristic methods in a global model, and I fully respect the useful contribution Ordonez et al. have made to our understanding of VSLS emissions. However, we now have several studies (including this study and Ordonez et al. itself) that show that the Ordonez et al. CHBr3 emissions in particular are over estimated in the Western Pacific region.

i. In fact Ordonez et al. (2012, ACP) itself in Figure 7 (the PEM-Tropics A, PEM-Tropics B, and TRACE-P panels) shows that their own model over estimates CHBr3 in the Western Pacific region when using their own emissions.

ii. Ashfold et al. (2014, ACP) - another study employing a top-down method to infer VSLS emissions in the tropical Western Pacific - derived lower estimates of CHBr3 emissions in the tropics than Ordonez et al. Similarly, their retrieved

western, northern and southern fringes. Can the authors please discuss how they think this issue affects their results.

We agree that the aircraft observations do not uniformly cover the study domain, but some of these gaps are effectively filled by atmospheric mixing of surface sources. Our inversion system includes scaling factors not only for sources within the study region but also for neighbouring regions that lie outside our study regions and for the initial conditions at the beginning of the study period. Our sensitivity experiments reveal that our results are not sensitive to global priori inventory when the observation constraints are strong such as the for $CHBr_3$ emissions over the study domain between between 130^o—155^{o}E and 0^o—12^{o}N. This is discussed in section 4.

3. Concluding my remarks on point 1), I strongly recommend, and as a condition of acceptance for publication, that in addition to running the emission inversion with Ordonez et al. as the a priori for both compounds, that the authors also run their emission inversion algorithm with Ziska et al. (CHBr3) and Liang et al. (CH2Br2) for the two compounds. Comparing this work to that of Ashfold et al. (2014, ACP), one can see that Ashfold et al. (2014, ACP) undertook a variety of emission inversion experiments (including changing their a priori) to test the setup of their system. These aspects of Ashfold et al. (2014, ACP) strengthened their work, and, similarly, this manuscript would also benefit from a similar effort.

Figure 1 summarizes our results from using different prior inventories. Posterior flux estimates of $CHBr_3$ over the geographical region covered by CAST/CONTRAST aircraft data are remarkably similar. This supports the idea that the data are playing a significant role in determining the posterior flux estimates.

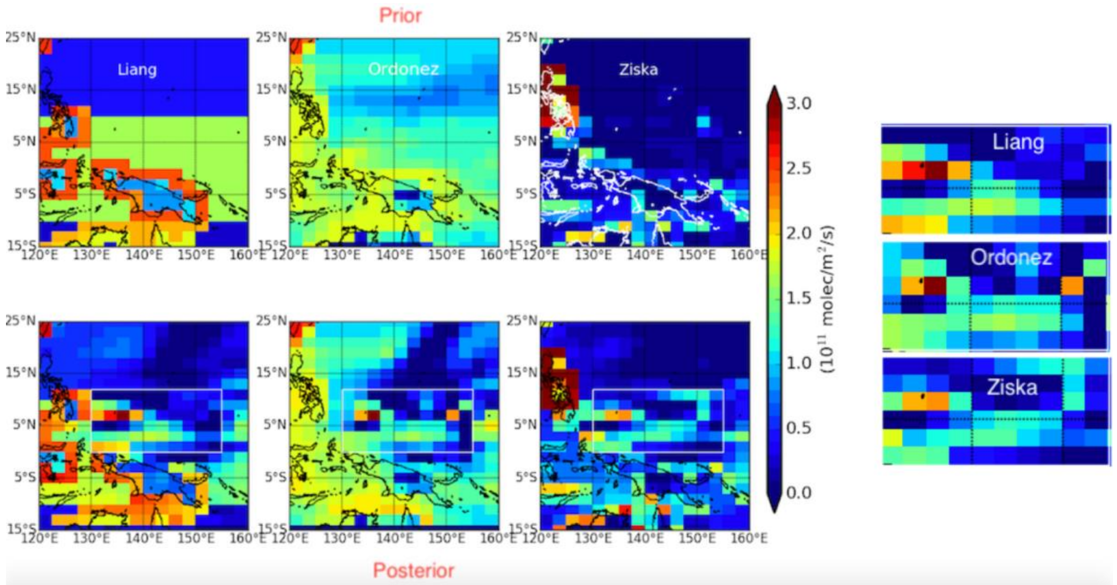

Figure 1: (Left upper panels) Prior and (left lower panels) posterior $CHBr_3$ flux estimates (10^{11} molec/m^2/s) over the study region. The three prior inventories include Liang et al (2010), Ordóñez et al (2012), and. Ziska et al (2013). The right panel is focused on the geographical region between (130°—155°E and 0°—12°N) between where the CAST/CONTRAST had the most information.

2***) Some key discussions seem to be missing including those of limitations of this study.***

a. It would have been nice to see a discussion of the prevailing meteorology during the period of study and an explanation linking this to the error reductions that we see in the OSSE results in Figure 3. Presumably, the error reductions are a function of the location of the observations and the origin of air masses arriving at the observation locations. An analysis similar to what I am suggesting was carried out in Ashfold et al. (2014) in their Figure 2, which allowed them to determine where there inversion setup was able to retrieve emission values. I realise this is perhaps easier in the Lagrangian framework of NAME, but the authors could draw upon the information in their meteorological inputs for GEOS-Chem to create a climatology of the winds and then make a discussion that would add useful context to the results and strengthen the paper.

We agree that it is of great interest to show the origins of airmass, which has been partially investigated by another study (Bulter et al, 2016). However, the complexity of the global CTM and its analyzed meteorological fields and the nature of the aircraft measurements precludes a simple and intuitive summary of the overall sensitivity of the CAST and CONTRAST observation to the underlying surface fluxes. In addition, we have included scaling factor for initial concentrations and for emissions from neighbouring regions, and as a result, the posterior flux estimates are more or less dependent on the difference between modelled and observed internal horizontal and vertical gradients, instead of single concentration values (which has also been revealed by consistency in posterior fluxes when different a priori is used.

b. It would be good to see the authors try to connect the results of the OSSE, i.e., the spatially limited pattern of the error reduction, to the areas in the a posteriori CHBr3 emissions where we see the largest reductions in absolute emission values relative to the a priori. Given the evidence I present in point 1) above, I do not believe that the

similarity in the spatial patterns in the OSSE error reduction and the area of reduced a posteriori emissions is coincidental. I think this implies that with greater spatial coverage in the aircraft observations that we would see reductions in the a posteriori emissions covering a larger spatial area. The authors should discuss this point, and also conclude that the spatial extent of the aircraft observations provides a limitation for this study.

This is an interesting point. Aircraft measurements are sensitive to a wider range of geographical regions than the error reduction suggests, e.g. Figure 2 and Butler et al, 2017. The inversion updates the ocean fluxes over a wide geographical domain but the error reduction is often small because of the low signal (contribution) to noise (observation error and model transport error) ratio.

Further to point b., I do not find the a posteriori CHBr3 emission estimates outside of the region sampled by the observations (towards the N,S, W fringes of the domain) to be credible in light of the large reductions we see in the a posteriori compared to the a priori over the most sampled region. I am working on the assumption that the emissions are spatially correlated. Perhaps some discussion of this point in the context of the previous studies (e.g., those highlighted above in point 1) would help readers gauge the quality of the emission inversion in the areas on the N,S, W extremes of the domain where there is little information from the observations. This might also help readers understand the large gradients we see between the sampled and poorly sampled regions.

See response to previous point.

Figure colours in Figure 4 need greater differentiation. I struggled to differentiate the monochrome orange/brown tones. A set of panels representing the relative differences between the a priori and a posteriori emissions would also be of help.

Agreed. The manuscript (Figure 4) has been amended, accordingly.

4) I think it is necessary for the authors to include a discussion of the conclusions of Russo et al. (2015, ACP). Russo et al. (2015, ACP) made two conclusions relevant to the work in this study:

a) That it is difficult to infer emissions using aircraft measurements and coarse global models in the case where the emission distribution is heterogeneous in regions of strong convective activity.
b). That model resolution can affect the simulated distributions of CHBr3 in cases where the emissions distribution is heterogeneous.
The authors should include some discussion of these points and should explain how they present limitations for the current work, or why this points are not relevant to the conclusions in this manuscript.

The authors should include some discussion of these points and should explain how they present limitations for the current work, or why this points are not relevant to the conclusions in this manuscript.

Certainly, using a finer-scale model resolution would be preferable. Our forward simulation at the native model resolution of 0.25° × 0.3125° confirm that posterior fluxes result in a better agreement with observations than the prior as shown in the revised Figure 2. However, the resolution of estimates fluxes is determined by the quality, quantity, and distribution of available data. In this case, even if we used a finer resolution model it is likely we would need to aggregate model grid values to generate estimates that do not include large spatial correlations. We have included this discussion in the revised manuscript, following the reviewer's recommendation (Page 11).

5) It is important to note that the a posteriori emissions are more heterogeneous than the a priori. Therefore, following from Russo et al. (2015, ACP) and the discussions in point 4) above, the issue of model resolution could affect the simulated distribution of CHBr3 more significantly for the a posteriori emissions than for the a priori emissions. The authors have tested the impact of model resolution on the a priori emissions and found no effect. However, it seems plausible that model resolution could change the distributions of CHBr3 in the atmosphere more significantly for the a posteriori emissions given their greater heterogeneity. I recommend that the authors test this in a separate sensitivity study and present their conclusions.

Good suggestion. We have included such a comparison the revised manuscript (at revised Figure 2), which confirms that the posterior nested simulation at 0.25°×0.3125° is very similar to the run at 2°×2.5°.

6) It isn't clear to me that the mean bias between the mole fractions of observed and modelled CH2Br2 decrease from the a priori to the a posteriori simulations. The paper states this, but as it is written the bias changes from 0.01 +/- 0.14 to -0.1 +/-0.1. Can the authors please explain this result? Is this due to an overcompensation in the a posteriori emissions close the well observed region? According to the forward model section, a large fraction of the CH2Br2 originates from outside of the domain, and I imagine that in this case it is hard/impossible to infer those emissions with any reasonable specificity and overcompensation locally seems therefore to be a plausible explanation.

We agree that it is due to an overcompensation caused by an uneven sensitivity (Jacobian) for measurements at different altitudes, and observation errors that are assumed to be proportional to mole fraction values by two campaigns. See Pages 10 and 11 for more discussions

Technical comments:

Looking at Figure 4, it seems that the Ordonez et al and Ziska et al panels have been mislabelled in the caption whereby the Ziska emissions are described as being the Ordonez emissions and vice versa for the Ordonez emissions. Looking at Hossaini et al. (2013) ACP in figures 1 and 2 (and in fact the emission files themselves), I have checked the spatial patterns, and they seem to confirm this. Please can the authors check this themselves and confirm there is a mislabelling in the Fig. 4 caption? Please can the authors also check other instances of discussion of Ordonez and Ziska and verify that there a) there are no other mix-ups in the naming and b) that this is just a technical naming error.

We are grateful to the reader for spotting this error. We have checked and can confirm that it is just a plot labelling error.

Russo et al. (2015, ACP) is included as a reference but is not cited. Please check for other articles referenced but not cited.

Thanks. We have now checked the reference list and cite Russo et al in the revision (see above).

Surface fluxes of bromoform and dibromomethane over the tropical western Pacific inferred from airborne in situ measurements

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ABSTRACT

We infer surface fluxes of bromoform ($CHBr_3$) and dibromoform (CH_2Br_2) from aircraft observations over the western Pacific using a tagged version of the GEOS-Chem global 3-D atmospheric chemistry model and a Maximum A Posteriori inverse model. Using GEOS-Chem as an intermediary, we find that the distribution of *a priori* ocean emissions of these gases are reasonably consistent with observed atmospheric mole fractions of $CHBr_3$ (r=0.62) and CH_2Br_2 (r=0.38). These *a priori* emissions result in a positive model bias in $CHBr_3$ peaking in the marine boundary layer, but capture observed values of CH_2Br_2 with no significant bias by virtue of its longer atmospheric lifetime. Using GEOS-Chem, we find that observed variations in atmospheric $CHBr_3$ are determined equally by sources over the western Pacific and those outside the study region, but observed variations in CH_2Br_2 are determined mainly by sources outside the western Pacific. Numerical closed-loop experiments show that the spatial and temporal distribution of boundary layer aircraft data have the potential to substantially improve current knowledge of these fluxes, with improvements related to data density. Using the aircraft data, we estimate aggregated regional fluxes of 3.6±0.3x10^8 g/month and 0.7±0.1x10^8 g/month for $CHBr_3$ and CH_2Br_2 over 130°—155°E and 0°—12°N, respectively, which represent reductions of 20—40% of the prior inventories by Ordóñez et al. (2012), and substantial spatial deviations from different *a priori* inventories. We find no evidence to support a robust

linear relationship between $CHBr_3$ and CH_2Br_2 oceanic emissions, as used by previous studies.

1.Introduction

The role of halogens in the catalytic destruction of stratospheric ozone is well established (WMO, 2014). The anthropogenic contribution to the inorganic halogen budget continues to decline in the stratosphere as a result of the Montreal protocol. A consequence of this decline is that very short-lived substances (VSLS), halogenated compounds with e-folding lifetimes typically much less than 6 months, now represent a proportionally greater source of stratospheric halogens. The wide range of VSLS atmospheric lifetimes allows at least some of the emitted material to reach the upper troposphere, particularly over geographical regions where there is rapid, deep convection (Penkett et al., 1998; Yang et al., 2005; Warwick et al., 2006; Levine et al., 2007; Pisso et al., 2010; Hosking et al., 2010; Carpenter et al., 2014; Hossaini et al., 2016a; Butler et al., 2016). Here, we use aircraft observations of bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2) collected over the western Pacific Ocean to infer, using an inverse model, the magnitude and distribution of ocean emissions of these gases.

There is a wide range of VSLS that are beginning to limit the recovery of stratospheric ozone (e.g., Read et al., 2008; Hossaini et al., 2015; Oman et al., 2016). Chlorine VSLS are typically dominated by anthropogenic sources, but the fraction depends on the species (Hossaini et al., 2016b). Their natural sources include biomass burning, phytoplankton production, and soils. Iodine and bromine VSLS have predominately natural sources. Iodine VSLS are mainly from ocean production processes, but with lifetimes of only a few days they are too reactive to be transported out of the marine boundary layer in large quantities. Bromine VSLS are also mainly from natural ocean sources (Gschwend et al., 1985; Manley et al., 1992; Sturges et al., 1992; Tokarczyk et al., 1994; Warwick et al., 2006; Carpenter and Liss, 2000; 2009; Palmer et al., 2009; Quack and Suess, 1999; Quack and Wallace, 2003; Quack et al., 2007; Butler et al., 2007; Leedham et al., 2013). The most abundant bromine VSLS species are $CHBr_3$ and CH_2Br_2. Together they account for about 80% of bromine VSLS in the marine boundary layer (Law and Sturges, 2007; O'Brien et al., 2009; Hossaini et al., 2013). The local atmospheric lifetime for $CHBr_3$, determined by OH oxidation (76 days) and photolysis (36 days), is 24 days. CH_2Br_2 has a longer atmospheric lifetime of about 123 days, determined primarily by OH oxidation (123 days) and to a much lesser extent by photolysis (5000 days). Their lifetimes are sufficiently long that these natural halogenated compounds can be transported to the upper troposphere.

Previous measurement campaigns have reported that bromine VSLS and their degradation products represent 2-8 pptv of stratospheric inorganic bromine (e.g., Dorf et al., 2008; Salawich et al., 2010). Complementary model simulations of atmospheric chemistry and transport, driven by *a priori* ocean emission inventories, report similar values (2-7 pptv) that are determined mainly by localized regions of active ocean biology that coincide with strong convection. Example regions include western Pacific Ocean, tropical Indian Ocean, and off the Pacific coast of Mexico. These model calculations also suggest that 15-75% of the stratospheric bromine budget from bromine VSLS is delivered by the direct transport of the emitted halogenated compounds (Liang et al., 2010; Hossaini et al., 2016a; Aschmann et al., 2009). The large range of values reflects uncertainty in ocean emissions, model transport, and the wet deposition of degradation products in the upper troposphere lower stratosphere.

Current knowledge of ocean emissions of $CHBr_3$ and CH_2Br_2 are poorly constrained by the sparse measurements. Bottom-up and top-down methods have been used to estimate global $CHBr_3$ and CH_2Br_2 emissions. The bottom-up approach assumes local flux estimates are representation of larger spatial scales. Ship-borne air-sea flux observations with limited spatial and temporal coverage are extrapolated over ocean basins (e.g. Quack and Wallace, 2003; Carpenter and Liss, 2000; Butler et al., 2007; Ziska et al., 2013). Poor observation coverage results in fluxes that rely heavily on assumptions used for extrapolation (Stemmler et al, 2015).

The top-down method, in this application, uses an atmospheric chemistry transport model to describe the relationship between emissions and the atmospheric measurements. The model emissions are fitted to the observations by adjusting their magnitude until the discrepancy between the model and observed atmospheric measurements is minimized. This fitting can be achieved using heuristic techniques or more established Bayesian optimization methods (e.g. Liang et al, 2010; Ordóñez et al., 2012; Ashfold et al., 2014; Russo et al., 2015). The short atmospheric lifetime of $CHBr_3$ poses particular difficulties for the top-down approach because atmospheric mole fractions are highly variable (Ashfold et al., 2014). Some studies have introduced (explicitly or implicitly) a simple linear correlation between $CHBr_3$ and CH_2Br_2 emissions to provide an additional constraint on the $CHBr_3$ flux estimate (e.g. Liang et al., 2010, Ordóñez et al., 2012). This approach, however, is then subject to errors associated with the assumption about the correlation. As with the bottom-up method, the top-down method is subject to errors due to poor spatial and temporal coverage of observations. By virtue of various assumptions made (and justified) by individual studies the resulting bottom-up and top-down $CHBr_3$ and CH_2Br_2 fluxes are significantly different (e.g. Hossaini et al., 2016a). For example, the estimated global $CHBr_3$ annual emissions range from 216 Tg (Ziska et al., 2013) to 530 Tg (Ordóñez et al., 2012).

We use data from two coordinated aircraft campaigns over the western Pacific during 2014 to infer regional emission estimates of $CHBr_3$ and CH_2Br_2 for the campaign period using a Bayesian inverse model. The Co-ordinated Airborne Studies in the Tropics (CAST; Harris et al., 2017), and CONvective Transport of Active Species in the Tropics (CONTRAST; Pan et al., 2016) 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. We interpret aircraft measurements of $CHBr_3$ and CH_2Br_2 mole fraction using the GEOS-Chem atmospheric chemistry transport model and a Maximum A Posteriori (MAP) inverse model approach.

In the next section we describe the CAST and CONTRAST $CHBr_3$ and CH_2Br_2 mole fraction data, the GEOS-Chem atmospheric chemistry transport model used to interpret the data, and the MAP inverse model. In section 3, we report a model comparison with the CAST and CONTRAST atmospheric data, and results from the MAP inversion. We conclude the paper in section 4.

2. Data and Methods

We use $CHBr_3$ and CH_2Br_2 mole fraction determined using GC/MS from whole air sample (WAS) canisters collected during the CAST and CONTRAST aircraft campaigns during January 18th to February 28th, 2014 (Harris et al., 2017; Pan et al., 2016). We refer the reader to Andrews et al. (2016) for a more detailed description of the observation data sets, and to Butler et al (2016) for a statistical analysis of the $CHBr_3$ and CH_2Br_2 mole fraction data. For CAST, WAS canisters were filled aboard the Facility for Airborne Atmospheric Measurements (FAAM) BAe-146 UK Atmospheric Research Aircraft. These canisters were analysed for $CHBr_3$ and CH_2Br_2 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 $CHBr_3$ and the NOAA 2004 scale for CH_2Br_2 (Jones et al., 2011; Andrews et al., 2016). For CONTRAST, a similar WAS system was employed to collect $CHBr_3$ and CH_2Br_2 measurements on the NSF/NCAR Gulfstream-V HIAPER (High-performance Instrumented Airborne Platform for Environmental Research) aircraft. A working standard was used to regularly calibrate the samples, and the 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 $CHBr_3$ and CH_2Br_2 measurements (over the altitude range 0−8 km) is 7.7% and 2.2%, respectively, between the two WAS systems and two accompanying GC/MS instruments used by CAST and CONTRAST.

To interpret these atmospheric data we use the GEOS-Chem global 3-D atmospheric chemistry transport model (v9.03, http://geos-chem.org). We drive the GEOS-Chem model using GEOS-FP meteorological fields, provided by the Global Modeling and Assimilation Office at NASA Goddard, with a horizontal resolution of 2º (latitude) X 2.5º (longitude). We use a tagged version of the model (Butler et al, 2016) in which the atmospheric chemistry is linearized by using pre-computed OH and photolysis loss terms using the same version of the model but with a more complete description of HOx-NOx-Ox and bromine chemistry (Parrelle et al., 2012). Our 3-D OH fields are consistent with the observed methyl chloroform lifetime. We find small (5%) adjustments to these OH fields do not significantly affect our analysis or conclusions (not shown). For the purpose of our calculations we pre-compute these loss terms every three hours during the campaign. This tagged modelling approach greatly simplifies the calculation of the Jacobian matrix used by the inverse model to determine surface flux estimates, as described below. We have previously evaluated this version of the model using $CHBr_3$ and CH_2Br_2 mole fraction data from NOAA/ESRL (Butler et al, 2016), and showed a level of agreement with *in situ* observations that is comparable to the ensemble of models reported by Hossaini et al (2016a).

We use *a priori* emissions of $CHBr_3$ and CH_2Br_2 from the Ordóñez et al (2012) inventory, which is based on the top-down methodology using aircraft observations from 1996 to 2006. This represents one of three commonly used inventories, which were recently evaluated in a multi-model inter-comparison study (Hossaini et al, 2016a). Liang et al (2010) also employed a top-down methodology to infer $CHBr_3$ and CH_2Br_2 fluxes, but Ziska et al. (2013) inferred these fluxes from a database of surface ocean observations collected from 1989 to 2011. We find no single inventory is best at reproducing observations of both gases. Ordóñez et al (2012) assumed a linear relationship between tropical $CHBr_3$ and CH_2Br_2 emissions and monthly fields of chlorophyll-a, a proxy for ocean biological activity, to help fill in the spatial and temporal gaps left by the aircraft data. This approach strongly links the distributions of these two gases in the *a priori* inventory, an assumption we examine below. We primarily use Ordóñez et al. (2012) but also show the results from other inventories. For our study period, these aggregated regional fluxes are 6.2×10^8 g/month and $0.9\pm0.2\times10^8$ g/month for $CHBr_3$ and CH_2Br_2 over 130º—155ºE and 0º—12ºN, respectively.

Figure 1 shows the geographical regions considered in this study. We divide the world into 605 basis functions: 1) a nested domain of 600 grid-scale tagged regions over the tropical western Pacific (105º—165ºE, 15ºS—25ºN); 2) a lateral boundary of 15º surrounding the nested domain, described by four tagged regions; and 3) the rest of the world. We spin-up the model using *a priori* inventories (Ordóñez et al., 2012) from July 1st 2013 to January 18th 2014, reducing the impact of initial conditions.

We use the MAP approach to infer $CHBr_3$ and CH_2Br_2 surface fluxes from atmospheric mole fraction measurements taken by CAST and CONTRAST aircraft campaigns. We infer regional monthly mean surface fluxes, *f*, of $CHBr_3$ and CH_2Br_2:

$$f_p^g(x) = f_0^g(x) + \sum_i c_i^g BF_i^g(x), \tag{1}$$

where superscript *g* denotes trace gas, and the subscripts 0 and *p* denote the *a priori* and *a posteriori* state vector, respectively We describe the regional fluxes as a product of a basis function set $BF_i^g(x)$, representing distributions of monthly mean fluxes of the study gases over 605 pre-defined geographic regions (Figure 1) over the duration of the CAST and CONTRAST aircraft experiments, and scalar coefficients c_i^g that are fitted to the data.

We include all the coefficients c_i^g for the pre-defined 605 basis functions into the state vector **c** that describes the $CHBr_3$ and CH_2Br_2 fluxes, which we fit to the observations**.** We take into account the uncertainty of the model spin-up by including a scaling factor into the state vector to adjust the background (initial) field, assuming that the model describes the background vertical structure over the study domain. As a result the state vector **c** has a total of 606 elements. We optimally estimate the state vector ***c*** by minimizing the associated cost function *J*(***c***):

$$J(\boldsymbol{c}) = \frac{1}{2}[\boldsymbol{c} - \boldsymbol{c}_0]^{\mathrm{T}}\mathbf{B}^{-1}[\boldsymbol{c} - \boldsymbol{c}_0] \quad + \frac{1}{2}\left(\mathbf{y}_{obs} - H(\mathbf{c})\right)^{\mathrm{T}}\mathbf{R}^{-1}\left(\mathbf{y}_{obs} - H(\boldsymbol{c})\right), \tag{2}$$

where the superscripts T and -1 denote the matrix transpose and inverse operations, respectively; $\boldsymbol{c}_0$ represents the *a priori* estimates; and $\mathbf{B}$ represents the *a priori* error covariance matrix**.** The measurement vector, including the CAST/CONTRAST $CHBr_3$ and CH_2Br_2 mole fraction data, is denoted by $\mathbf{y}_{obs}$, and $\mathbf{R}$ is the measurement error covariance matrix. The forward model *H* projects the state vector (scalar coefficients) into observation space (3-D mole fractions), and includes the GEOS-Chem atmospheric chemistry and transport model that is sampled at the time and location of each observation.

We assume a 60% uncertainty for fluxes within the nested domain and a 50% uncertainty for fluxes in the lateral boundary and the rest of the world regions, guided by the discrepancy between the top-down and bottom-up inventories and their limited spatial and temporal variation. We also assume that the *a priori* errors within the nested domain are correlated over a distance of 400 km, corresponding to approximately the width of two adjacent grid boxes.

We assume the initial conditions for the mole fractions have a 30% uncertainty. We assume individual observations of $CHBr_3$ and CH_2Br_2 have errors of 20% and 10%, respectively, and are uncorrelated. These conservative values are guided by an analysis of data collected from different instruments during CAST and CONTRAST (Andrews et al, 2016). We assume that the observation error covariance $\mathbf{R}$ is diagonal, which also includes model error, such as the representation error and the errors in modelling atmospheric transport and chemistry processes, with an assumed value of 20%. Our results over the geographical regions with dense observation coverage are insensitive to different assumptions about *a priori* uncertainty and observation errors. For example, our changing the *a priori* emission uncertainty by ± 20%, results in changes in the aggregated *a posteriori* $CHBr_3$ emission (130°—155°E and 0°—12°N) of typically less than 10%.

The Jacobian matrix describes the sensitivity of atmospheric $CHBr_3$ and CH_2Br_2 CAST and CONTRAST measurements to changes in geographical surface emissions and the initial value on January 18th 2014. We construct it by scaling the tagged tracers originating from a specific geographical region by surface fluxes from that region.

To avoid negative flux estimates due to, for example, an uneven distribution of observations we use value-dependent *a priori* uncertainties for grid point flux estimates. We assume a functional form for the uncertainty of the flux coefficient c_i (equation 1):

$$\sigma(c_i) = \begin{cases} 0.8, c_i > -0.6 \\ 0.8 - 2(-0.6 - c_i)e^{k(1.0+c_i)},\ c_i < -0.6, \end{cases} \tag{3}$$

where k (=3) is a pre-chosen factor that defines the gradient of the uncertainty with respect to the change of c_i. Using this approach, the *a priori* uncertainty decreases rapidly towards zero when c_i becomes smaller than -0.6 (i.e., when the flux estimate is smaller than 40% of the *a priori*). We find that using different parameters (e.g. changing the threshold from -0.6 to -0.8) does not significantly change our flux estimates.

3 Results

Forward Model Analysis

Figure 2 shows that the model overestimates the $CHBr_3$ concentrations by 0.1—0.7 pptv at altitudes from 0.5 to 12.5 km, with the largest values near the surface that reflects errors in *a priori* ocean fluxes (Hossaini et al., 2016a; Butler et al, 2016). The model has reasonable skill at reproducing the mean observed vertical gradient (r=0.62) but has a positive model bias of 0.46±0.39 pptv. We find that vertical variations in $CHBr_3$ are determined approximately equally by sources over the western Pacific study region (Figure 1) and by sources immediately outside of the nested domain and further afield (Butler et al, 2016). These contributions show different vertical structures. The contribution from fresher sources over the western Pacific has a steeper atmospheric lapse rate from the boundary layer to the free troposphere than the air masses from neighbouring regions. Both contributions are approximately uniform above the free troposphere, with the exception of a peak at 10-12 km from the air being transported into the nested domain (Butler et al, 2016). These differences in vertical structure help the inversion system identify the origin of $CHBr_3$ at different vertical levels.

The model reproduces some of the observed CH_2Br_2 variation (r=0.38) but with a small mean bias (0.01±0.14 pptv). Figure 2 shows that the CH_2Br_2 source outside the nested domain represent more than 60% (0.7—0.9 pptv) of the values sampled over the western Pacific, and almost invariant with altitude. This is due to weaker surface emissions over the western Pacific and the longer atmospheric lifetime of CH_2Br_2 compared to $CHBr_3$. Ocean emissions from the western Pacific and from the immediate neighbouring regions each contribute only 0.1—0.3 pptv to CH_2Br_2. This highlights the difficulties of inferring ocean fluxes of CH_2Br_2 only using atmospheric CH_2Br_2 data collected over the western Pacific and considering this region in isolation.

To examine model transport errors associated with using a relatively coarse model spatial resolution (2°×2.5°), we ran a short, high-resolution (0.25°×0.3125°) simulation of $CHBr_3$ over a limited spatial domain centred on the western Pacific and compared that against the CAST/CONTRAST data. We acknowledge that we could still miss rapid, sub-grid scale convective events using this model that has a factor-of-eight improvement in spatial resolution. However, we find that differences between the two model runs are much smaller than the differences between the individual model runs and the observations (Figure 2). Figure 2 also shows that the global and nested GEOS-Chem simulations of $CHBr_3$ and CH_2Br_2 mole fractions, corresponding to our the *a posteriori* flux estimates (Figure 4), are more consistent with the observations that *a priori* fluxes. This result demonstrates that the *a priori* model bias can be explained by, in principle, errors in ocean sources.

Closed-Loop Numerical Experiments

In the absence of independent observations to evaluate our *a posteriori* ocean fluxes we use closed-loop numerical experiments to understand what we can theoretically achieve from CAST and CONTRAST data, accounting for a realistic description of model and measurement errors. These calculations, often called observing system simulation experiment (OSSEs), provide an upper boundary on the ability of available data to infer the true state.

First, we generate synthetic observations at the time and location of the CAST and CONTRAST data by sampling 3-D model fields of $CHBr_3$ and CH_2Br_2 mole fraction driven by the *a priori* inventories, which we regard as the ‘true' emissions. We consider these sample mole fraction values as the instrument observation after we superimpose instrument (unbiased) noise, informed by realistic observation uncertainty. Second, we enlarge the ('true') *a priori* emissions to generate the *a priori* estimate for the OSSEs: by 50% for emissions over the western Pacific and by 30% for emissions from the neighbouring region. The resulting atmospheric mole fractions represent our model *a priori* concentrations. With perfect coverage of the atmosphere with perfect data (i.e. infinitesimal noise levels) fitting model emissions to the true observations would result in estimating the true ocean emissions. We describe our results as the difference between the *a posteriori* and true fluxes using a metric (Palmer et al, 2000; Feng et al, 2009) that describes the error reduction $\gamma = 1 - \sigma_a/\sigma_f$, where σ_a and σ_f denote the *a posteriori* and *a priori* uncertainties, respectively, ignoring the correlation between state vector elements. The closer the value of γ is to unity the larger reduction in uncertainty.

Figure 3 shows that the CAST/CONTRAST CH_2Br_2 and $CHBr_3$ measurements can reproduce the true fluxes, mainly between 130-155^{o}E and 3S^0-15^{o}N, by reducing the inflated *a priori* flux estimate. *A posteriori* fluxes in several grid boxes are lower than the true value, which is a result of regions overcompensating for other regions that have insufficient data to estimate their emissions. Regions influenced with fewer measurements (Figure 1) generally have smaller reductions in error, as expected. The error reductions for $CHBr_3$ range from 0.1 to 0.6 over the study domain, reflecting the widespread sensitivity of the CAST and CONTRAST observations to emissions from the tropical western Pacific region. The mean and median *a posteriori* fluxes are approximately a factor of three closer than the *a priori* to the true fluxes, with a 40% improvement in the uncertainties. In contrast, for CH_2Br_2, the error reduction is much smaller, with values greater than 0.3 only over a small geographical region where the data density is greatest. There is a factor-of-two improvement in the discrepancy of the fluxes with the 'true', and a 30% improvement in the uncertainties. This large improvement in the knowledge of flux estimates is partly due to our simple description of the difference between the true and *a priori* field.

Ocean Emissions of $CHBr_3$ and CH_2Br_2 Inferred from CAST/CONTRAST data

We now examine the fluxes inferred from the CAST and CONTRAST measurements. Figure 4 shows elevated *a posteriori* $CHBr_3$ emissions surrounding small islands north of the tropics, such as Palau (7.4^{0}N, 134.5^{0}E) and Chuuk (7° 25′ N, 151° 47′ E). However, we find that emissions surrounding Guam (13.5^{0}N, 144.8^{0}E) are not significantly different from the adjacent open ocean. This reflects the distribution of boundary layer measurements (altitudes <2.5 km) of $CHBr_3$ observed during CAST and CONTRAST flights (Figure 1). We find that through sensitivity experiments (described below) that the *a posteriori* emissions are inferred by data and not via spatial correlations in the *a priori* emission inventory. Our *a posteriori* $CHBr_3$ emissions are generally higher than the bottom-up estimates from Ziska et al (2013), particularly over north of tropics.

We find that our *a posteriori* CH_2Br_2 emission estimates are lower than *a priori* estimates over open oceans north of 5^{0}N. We also find elevated fluxes around islands and part of open oceans south of 5^{0}N. Similar to $CHBr_3$, these elevated fluxes coincide with large boundary layer measurements from CAST and CONTRAST.

Over the study domain (130^o—155^{o}E and 0^o—12^{o}N) our *a posteriori* fluxes are $3.6\pm0.3\text{x}10^8$ g/month and $0.7\pm0.1\text{x}10^8$ g/month for $CHBr_3$ and CH_2Br_2, respectively. These represent reductions of 40% and 20% relative to the *a priori* values, respectively. We find that our flux estimates are largely insensitive to small changes in the assumed observation and *a priori* errors. The corresponding *a posteriori* mole fractions of $CHBr_3$ and CH_2Br_2 (not shown) have smaller mean biases (-0.03±0.22 pptv, -0.1±0.11 pptv) and improved correlations (r=0.74, r=0.56) than the *a priori* values compared to the observations. The small negative bias of -0.03 pptv in our *a posteriori* model simulation mainly reflects values in to the upper troposphere (Figure 2), where measurements are less sensitive to local surface fluxes.

This model bias may reflect unaccounted atmospheric model transport error, particularly because we use a relatively coarse atmospheric transport compared to the data resolution. Previous studies have highlighted similar issues (e.g. Russo et al, 2015). Figure 3 shows, however, that CAST and CONTRAST data can only reduce flux uncertainties by about 10—60% over the study regions at this coarse model resolution, limited by the density and coverage of the available data. Using a consistent model simulation but run at a higher spatial resolution (0.25^o×0.3125^o) we find significant improvement in model performance (Figure 2). This provides some evidence that our *a posteriori* emission estimates are robust against the resolution of the meteorological input data. We also find that using this high-resolution model does not significantly reduce the small bias above 8 km. This may point to a small offset between CAST (mostly at lower altitudes<8 km) and CONTRAST measurements (more at higher altitudes) (Andrews et al., 2016). Systematic errors between CAST and CONTRAST data are difficult to fully quantify, but any possible small offset between CAST and CONTRAST data is unlikely to affect our results significantly. Our sensitivity experiments (not shown), in which we introduce a bias between CONTRAST and CAST data that we infer in our inversion, show similar results to our control experiment configuration.

The spatial gradient we find in our *a posteriori* $CHBr_3$ emissions between the coasts of Palaua and Chuuk and the surrounding open oceans is not present in our *a priori* emission inventory (Ordóñez et al, 2012). It is, however, qualitatively consistent with observations (e.g., O'Brien et al., 2009; Quack et al., 2007) and bottom-up estimates (e.g., Ziska et al., 2013 and Simmerler et al., 2015). These elevated coastal emissions also improve the fit to CAST and CONTRAST observation particularly between 6-10 km. Figure 4 shows that the spatial distribution of *a priori* and *a posteriori* CH_2Br_2 emissions from the open ocean is different from the climatological bottom-up emissions (Ziska et al, 2013), particularly south of 5^oN. This is surprising because studies have shown that tropical ocean emissions of CH_2Br_2 are correlated with the distribution of chlorophyll-a (e.g., Liu et al., 2013), but differences may reflect inter-annual changes in ocean biology.

Figure 5 shows the *a priori* and *a posteriori* $CHBr_3:CH_2Br_2$ flux ratios. The top down inventory of Ordóñez et al (2012) use a linear model to describe emissions from these two gases, but the bottom-up inventory by Ziska et al, (2013) develop the emissions independently using a database of ocean observations. This discrepancy between the two inventories is why we chose not to exploit this linear relationship in our MAP inversion. Our *a posteriori* emissions for $CHBr_3$ and CH_2Br_2 appear to be linearly related at low emissions but larger values appear to follow a more complicated relationship, which may reflect differences in the responsible ocean biological processes.

To examine the sensitivity of our results to the *a priori* inventories, we use the same MAP approach to infer $CHBr_3$ flux from CAST and CONTRAST measurements for three different prior inventories (Figure 6): (a) Ziska et al (2013); (b) Liang et al (2010); and (c) Ordóñez et al (2012). For simplicity, we assume the same *a priori* error covariance for the 600 grid boxes over the tropical western Pacific (Figure 1) when the three different priori inventories are used. Figure 6 shows that despite a large *a priori* discrepancy, the three sets of *a posteriori* flux estimates (Figure 6) show similar features over our study domain between 130^o—155^oE and 0^o—12^oN (as denoted by white rectangles). Despite their being a large discrepancy between $CHBr_3$ ocean emission estimates over our study region from Ziska et al., (2013) (0.73×10^8 g/month) and Liang et al., (2010) (6.9×10^8 g/month) inventories, we infer similar aggregated *a posteriori* emissions of 3.0×10^8 g/month and 3.5×10^8 g/month from Ziska et al., (2013) and Liang et al., (2010), respectively. This suggests that the choice of *a priori* plays only a small role in determining the *a posteriori* solution. These *a posteriori* estimates are also comparable with fluxes from our control experiment ($3.6 \pm 0.3 \times 10^8$ g/month) that uses *a priori* emissions from Ordóñez et al., (2012). We find that outside our study domain, the discrepancies in posterior fluxes are still very large, in particular over coastal regions, due to the limited observation coverage by CAST and CONTRAST experiments.

4. Summary and Concluding Remarks

Very short-lived brominated gases have predominately natural sources, and therefore cannot be regulated by international agreements (Oman et al., 2016; Butler et al., 2007). Current understanding of these natural sources is poor due to the infrequent and incomplete measurements of ocean fluxes that vary in space and time. Past studies have relied on developing bottom up inventories using a database of ship-borne measurements or an heuristic top down method that adjusted *a priori* emissions to match tropospheric and lower stratospheric measurements of a range of gases, including of $CHBr_3$ and CH_2Br_2. As a consequence of the uncertainties associated with the modelling and data, the resulting inventories adopt simple distributions and are not necessarily consistent with each other on regional spatial scales.

Here, we used an *a priori* inventory to reproduce observed atmospheric boundary layer variations of $CHBr_3$ and CH_2Br_2 over a small geographical region encompassing Guam, Palau and Chuuk over the western Pacific. The measurements were collected as part of the CAST and CONTRAST aircraft campaigns during January and February 2014. We use the GEOS-Chem atmospheric chemistry model to relate the *a priori* emissions to the atmospheric concentrations, and develop a MAP inverse model to infer the ocean fluxes that correspond with the aircraft measurements.

First, using a small number of closed-loop numerical experiments we showed that the aircraft data could in theory, using assumptions about their uncertainties, improve knowledge of ocean fluxes. Improvements in knowledge are generally related to the density of measurements, as expected.

Using the aircraft data we find substantial spatial variations in fluxes of both gases that differ significantly from the *a priori* inventory. We find that aggregated regional *a posteriori* fluxes of $CHBr_3$ ($3.6 \pm 0.3 \times 10^8$ g/month) and CH_2Br_2 ($0.7 \pm 0.1 \times 10^8$ g/month) are 40% and 20% lower than the *a priori* fluxes over the main study domain (130^{o}—155^{o}E and 0^{o}—12^{o}N). Using the model we find that observed variations of $CHBr_3$ are determined mainly by the open ocean while CH_2Br_2 has a large influence from outside the immediate study region. *A posteriori* fluxes significantly improve the mean observed vertical gradient of both gases, particularly in the free troposphere. We also find no evidence to suggest a robust linear relationship between the emissions of these two gases over the study region, unlike one of the top-down *a priori* inventories. This discrepancy may reflect differences in the analysis of data over different spatial scales, or the construction of the *a priori* inventory using data in the free and upper troposphere where observed air masses originating from disparate surface sources have time to mix.

The MAP approach we used fits *a posteriori* fluxes to minimize the discrepancy between model and observed atmospheric mole fractions. Any discrepancy in atmospheric data may result from errors in surface fluxes (emissions minus uptake), atmospheric chemistry, and atmospheric transport. Where observation coverage is denser, our inversion results are less sensitive to the assumed *a priori* inventories, as expected. The next most likely source of error is atmospheric transport, particularly sub-grid scale vertical mixing. Sensitivity tests that crudely account for model errors suggest that the *a posteriori* fluxes are robust.

Our paper highlights the value of using atmospheric data to improve the magnitude and distribution of ocean emissions of halogenated gases, but also shows some of the difficulties associated with interpreting these data even with the aid of an atmospheric transport model. Future scientific progress in quantitatively understanding the role of natural emissions of halogens in the catalytic destruction of stratospheric ozone is hampered by the lack of available observations.

Author contributions.

L.F, P.I.P and R.B designed the computational experiments; P.I.P. and L.F. wrote the paper; all authors provided input on data analysis shown in the paper; the CAST and CONTRAST team provided access to $CHBr_3$ and CH_2Br_2 data.

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Figures

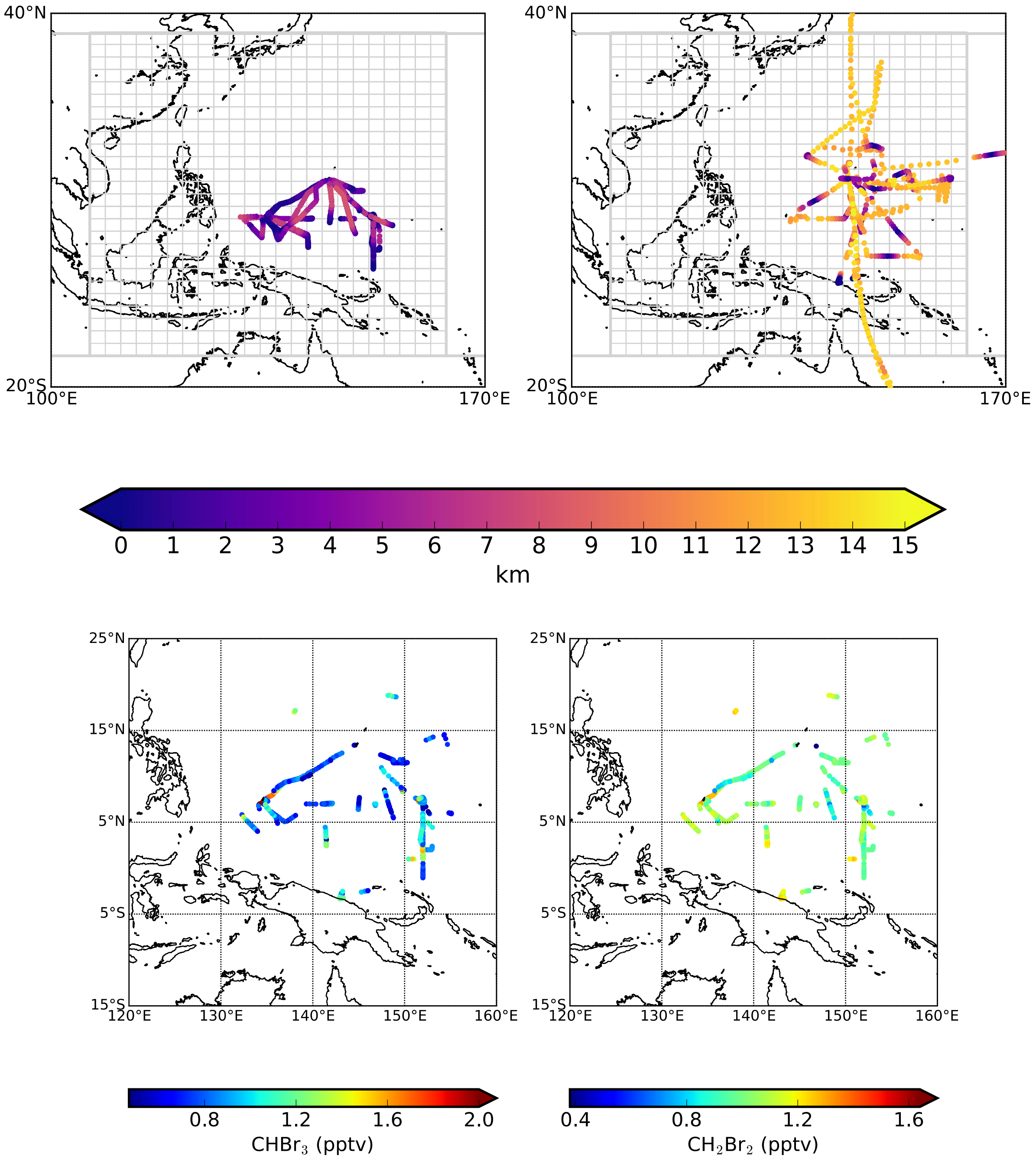

Figure 1 Distributions of data from the (left) CAST and (right) CONTRAST aircraft campaigns during January and February 2014. Data are described on 2° (latitude) X 2.5° (longitude)

GEOS-Chem grid boxes. The top panels show the altitude of data collected by both campaigns. We superimpose the flux inversion domain (grey lattice), consisting of 600 grid boxes between 105°—165°E and 15S°—25°N, four larger neighbouring regions, and the rest of world. The bottom panels show the distributions of boundary layer (less than 2.5 km) $CHBr_3$ (pptv) and CH_2Br_2 (pptv) mole fraction data.

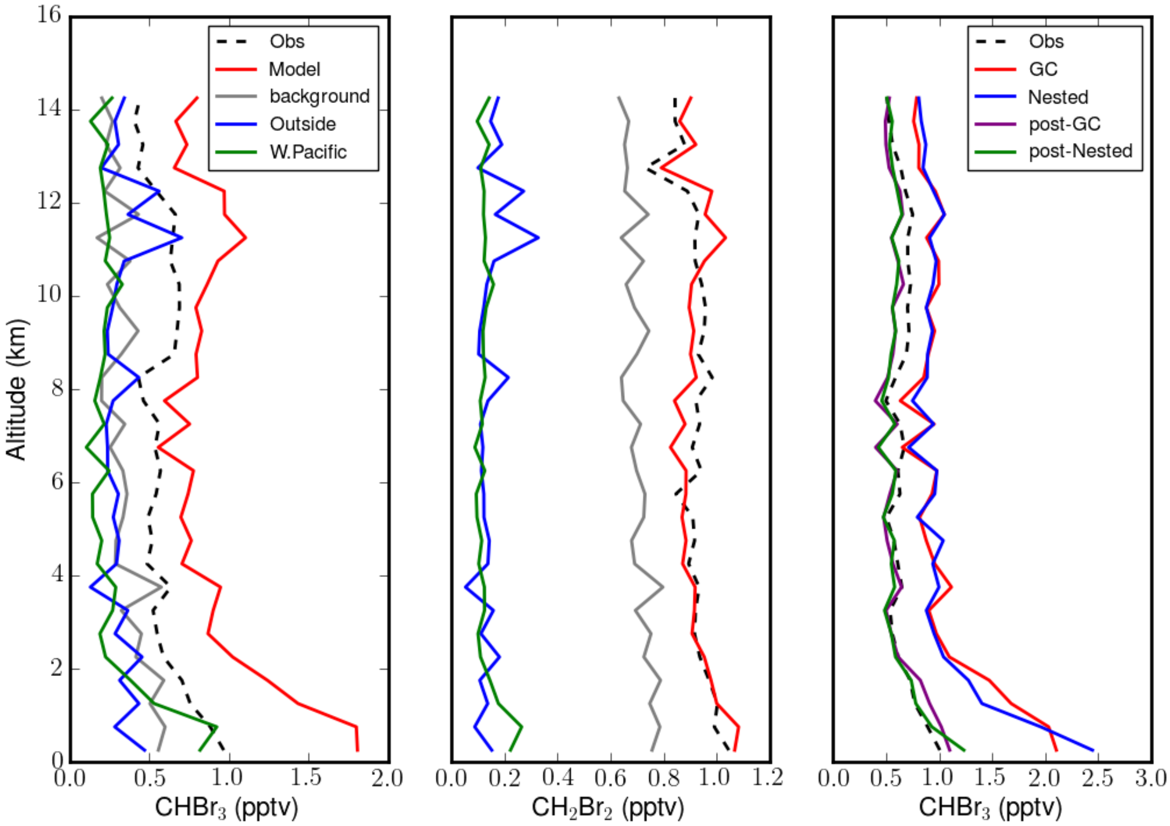

Figure 2: Observed and model mean vertical profiles of (left) $CHBr_3$ (pptv) and (middle) CH_2Br_2 (pptv) from the CAST and CONTRAST campaigns, described on a 1 km resolution grid. Model values have been sampled at the time and location of each observation. Also shown are the model contributions to these gases from within the Western Pacific study region, immediately outside the study region, and further afield which we denote as background values. The right panel compares CAST/CONTRAST observations of $CHBr_3$ with GEOS-Chem model simulations using the standard (2.0°×2.5°) and nested (0.25°×0.3125°) spatial resolutions from January 18th to February 13th, 2014. The two model runs (red and blue lines) use the same emission inventories (Ordóñez et al., 2012). For comparison, we also

present posterior model simulations (purple and green lines). based on the posterior fluxes inferred from CAST/CONTRAST observations (Figure 4).

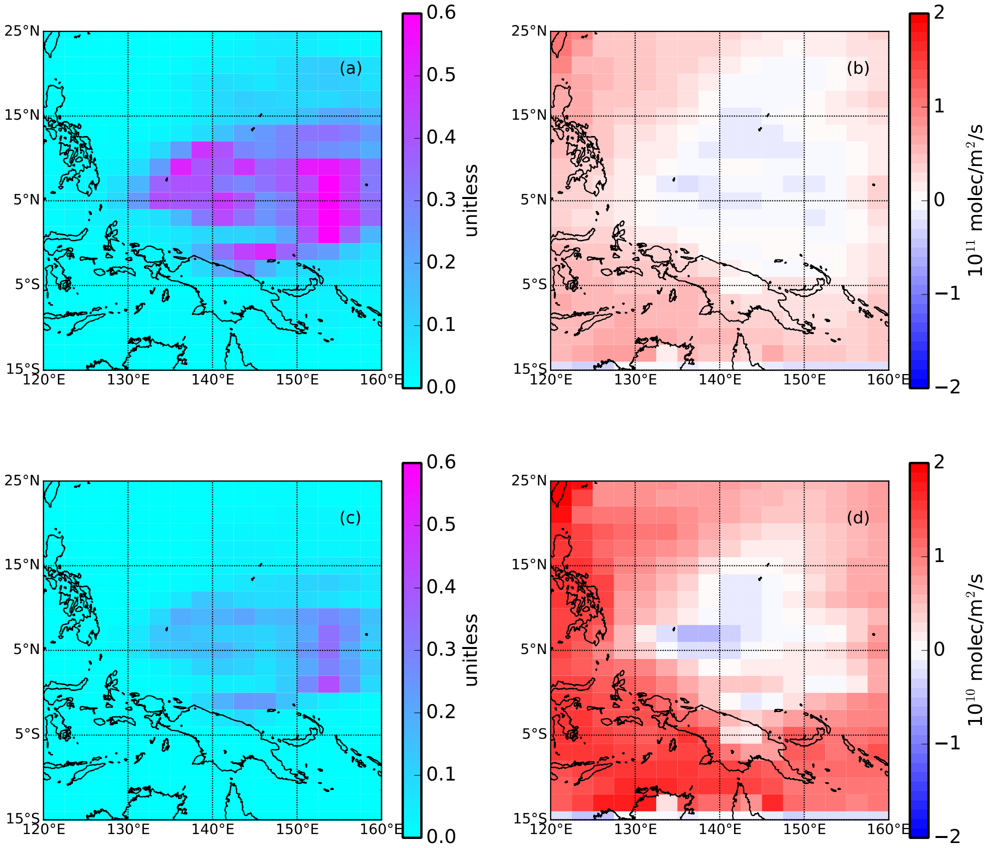

Figure 3: Simulated error reductions (unitless) and *a posteriori* flux error distributions (10^{10} molec/m^2/s) of (top) $CHBr_3$ and (bottom) CH_2Br_2 based on the theoretical potential to recover true fluxes using the time and location of CAST and CONTRAST data.

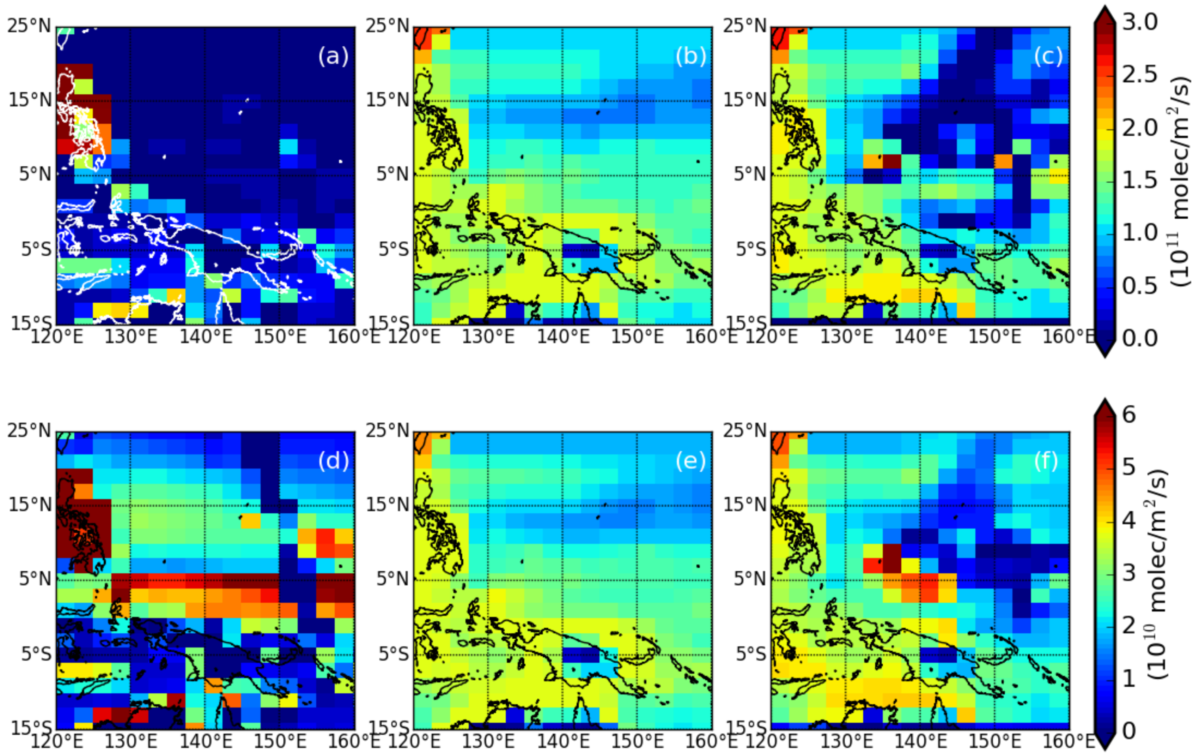

Figure 4: *A priori* and *a posteriori* (top) $CHBr_3$ (10^{11} molec/m^2/s) and (bottom) CH_2Br_2 (10^{10} molec/m^2/s) surface fluxes over the Western Pacific study region. The middle panels show the *a priori* fluxes we use in our MAP inversion (Ordóñez et al., 2012); the left panels shows an alternative bottom-up emission inventory (Ziska et al, 2013); and the right panels show our *a posteriori* flux estimates inferred from CAST and CONTRAST data.

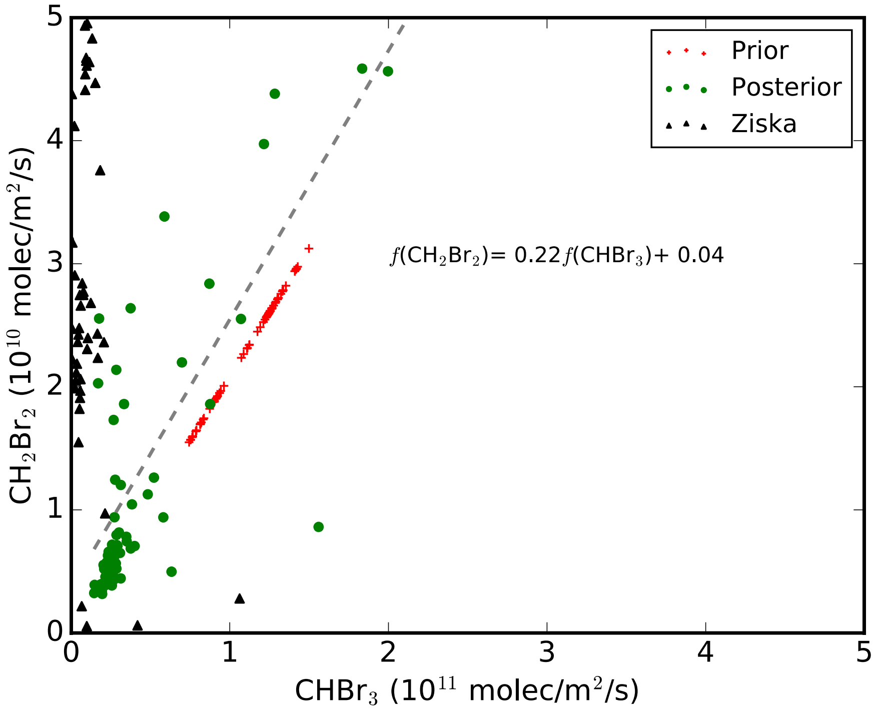

Figure 5: Scatterplot between *a priori* and *a posteriori* $CHBr_3$ and CH_2Br_2 fluxes described on 2° (latitude) X 2.5° (longitude) grid boxes over a sub-region (130°—155°E and 0°—12°N) of the study region (Figure 1), where observations are most dense. Red crosses represent values from Ordóñez et al., 2012 that we use for our *a priori*; black triangles represent values from an alternative bottom-up inventory (Ziska et al, 2013); and green circles denote our *a posteriori* values. *A posteriori* fluxes of $CHBr_3$ and CH_2Br_2 have a Pearson correlation of 0.86. The best-fit linear model for the *a posteriori* fluxes is shown inset.

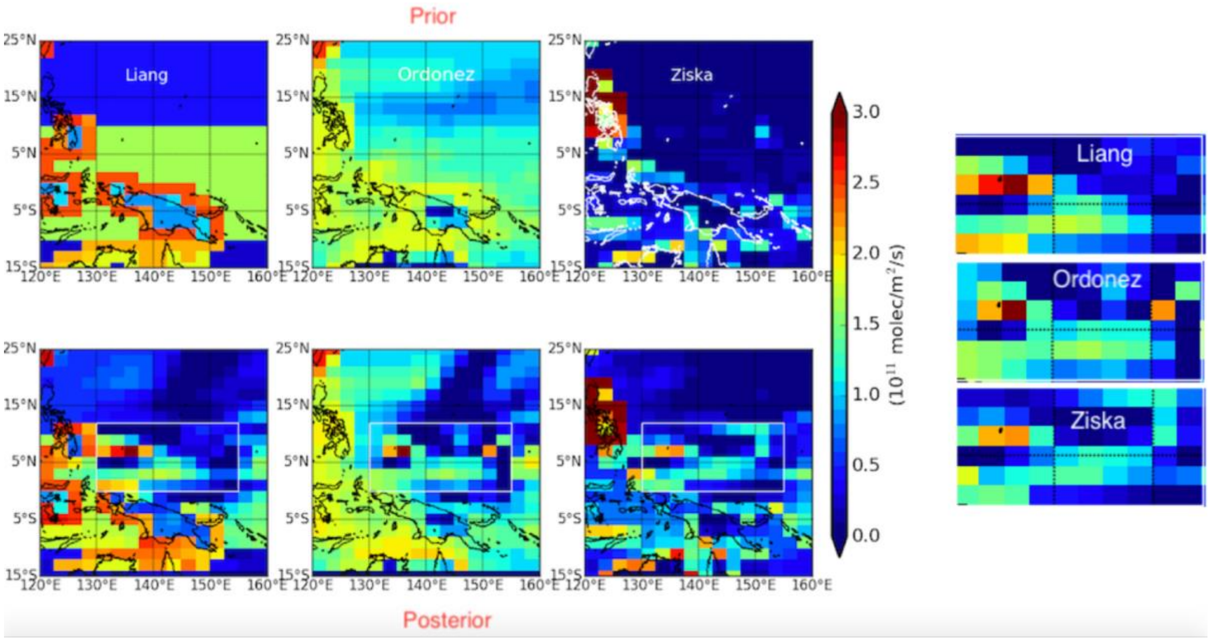

Figure 6: *A priori* (left upper panels) and *a posteriori* (left lower panels) CHBr$_3$ flux estimates (10^{11} molec/m^2/s) over the study region. The three *a priori* inventories include Liang et al (2010), Ordóñez et al (2012), and. Ziska et al (2013). The right panel is focused on the geographical region 130^o—155^{o}E and 0^0—12^{o}N where CAST/CONTRAST data density was highest.

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