Reviewer #1

1 General comments

The paper presents novel observational data of VSLS from several aircraft campaigns and compares them with modeling results. It extends on and confirms previous findings. Hence, the title does reflect the contents of the paper.

Some scientific methods and assumptions need more thorough outline and proper discussion.
This is a rather general remark, which makes it hard to give a specific answer. We have added some further explanation where specific remarks have been given, especially in section 5 with respect to the derivation of Br_y.

The results are sufficient to support the interpretations and conclusions, but not all results can be repeated based on the information given, e.g. the derivation of the tropopause for the campaigns labeled as "private conversation".
The tropopause information was indeed labelled as "private communication". However, the details and references are given and Michael Sprenger from ETH is acknowledged, therefore the private communication has been deleted.

The authors give proper credit to related work and indicate their own contribution, but they could make it more clear from the start, what the current consensus regarding the emission scenarios is.
This is a good suggestion. We have added the following text in the Introduction describing the conclusion from the most thorough review papers on this by Hossaini et al., after the introduction of the 4 scenarios:
"Hossaini et al. (2013) concluded that the lowest suggested emissions of $CHBr_3$ (Ziska et al., 2013)) and the lowest suggested emissions of CH_2Br_2 (Liang et al., 2014) yielded the overall best agreement in the tropics and thus the most realistic input of stratospheric bromine from VSLS. They also concluded that "Averaged globally, the best agreement between modelled $CHBr_3$ and CH_2Br_2 with long-term surface observations made by NOAA/ESRL is obtained using the top-down emissions proposed by Liang et al. (2010)".

The abstract provides a complete summary, but it does not deliver regarding the WHY unit, e.g. the context and importance of the measurement. It gives the impression of a paper focused on observational data, whereas 2/3 of the figures and text are related to model evaluation. If the point of the paper is to evaluate existing emission scenarios through a new set of data, this should be made more clear.

The main point of the paper is not to evaluate emission scenarios, but rather to show the increase in observed tropopause values with latitude especialld during winter and to discuss how large the differences between our observations and different model setups are. We have added a sentence at the beginning of the abstract explaining the WHY, as suggested by the reviewer:
"These rather short lived gases are an important source of bromine to the stratosphere, where they can lead to depletion of ozone. The measurements have been obtained using an in-situ gas …."

The overall presentation is well structured and clear. The language is fluent. The authors should be more cautious with the usage of the term "significant". Some parts of the paper need editing. In particular, the manuscript does not follow the ACP guidelines in several points:

The term significant has been replaced at several places:

The Asian monsoon has also been named as a possible pathway for transport of bromine from VSLS to the stratosphere: significant changed to possible

The distributions observed during the WISE and the TACTS campaigns show rather high levels of CH_2Br_2: significantly changed to rather high levels.

The average values derived here for the 10 K interval below the extratropical tropopause are significantly larger. Significantly deleted

This is most probably related to the increase in lifetime with latitude, as especially during the wintertime PGS campaign the photolytical breakdown in higher latitudes is significantly slower than in lower latitudes. Significantly deleted

The EMAC model with the Warwick et al. (2006) emissions significantly overestimates both CH2Br2 and CHBr3 in the lowermost stratosphere of the mid latitudes. Significantly changed to substantially

As has been shown in the comparison of the vertical profiles, significant differences between model results and observations are found, especially in the case of the Ziska et al. (2013) emissions in … significant deleted

The deviations between the TOMCAT model using the Ziska et al. (2010) emissions and the EMAC model using the Warwick et al. (2006) emissions are significantly larger. Significantly replaced by substantially

In this case, both CH2Br2 and CHBr3 are overestimated significantly in the lower stratosphere. Significantly deleted

who showed that TOMCAT using the Warwick et al. (2006) emission scenario significantly overestimated HIAPER Pole-to-Pole Observations (HIPPO) in Northern .. significantly deleted

As shown in the previous Section, significant discrepancies exist between the various combinations of models and emission scenarios with respect to our observations, both around the tropopause and in the lower stratosphere. Significant deleted

In contrast, EMAC results using the Warwick et al. (2006) emissions still show significant amounts of CHBr3: significant changed to substantial

Therefore, despite the fact that EMAC still shows significant remaining CHBr3 rather deep into the lowermost stratosphere, this model setup significantly .. first significant replaced by substantial, second deleted.

Interestingly, while the Ziska et al. (2013) emissions in TOMCAT showed some significant differences, in particular of CHBr3 at the tropopause, the differences in total Bry are not as large. Significant removed

.. of the Ziska et al. (2013) scenario with seasonally varying emissions, yielded significantly higher tropopause values. Significantly removed.

However, it is clear from the comparison with the scenario by Warwick et al. (2006), which restricts emissions to latitudes below 50°, that the sources of these short-lived brominated compounds are not only in the tropics, but that significant emissions must also occur in higher latitudes. Significant replaced by substantial

Using simplified assumptions about the fractional distributions, we have shown that there will be significant differences in stratospheric Bry depending on the emission scenario, significant replaced by substantial

As shown in our sensitivity study (Section 5), the assumptions on the relative contribution of the different source regions has a significant impact especially on the Bry produced from CHBr3 in the lowermost stratosphere. Significant replaced by substantial

Southern hemispheric distributions are expected to differ significantly from northern hemispheric distributions.. significantly deleted

• Subsections should be consecutively numbered.
Subsection numbers have been added.

• Figure captions, figures, and tables:
−Usage of full campaign names renders the captions imprecise and utterly unpleasant to read.
Full campaign names have been deleted

−Poor choice of colors (red, green, blue, black, grey) within the line plots (vector graphics!) and the tick labels' font size make the figures hard to read (Fig. 7, Figs. 13-15)
None of the other reviewers seemed to have problems with the colors and also we feel that they are a rather common choice. Colors are unchanged. However, we have increased the tick label fonts and made these consistent throughout all plots. We have also increased the resolution of the plots, which hopefully also increases the readability.

.−The usage of "[ ]" around units in plots is depreciated (→https://www.bipm.org/en/publications/si-brochure/section5-3.html)
This is not a general ACP guideline. Many papers in ACP use exactly the [ ] notation for units. We could change this if the typesetting requires it. Unchanged.

• Some white spaces seem odd.
We have deleted white spaces that seemed odd; if there are more than this could be solved during the typesetting process.

• Equations are not properly set, e.g. usage of "*" as indicator for multiplication.
** has been changed to* ·

The number and quality of references are appropriate.

2 specific comments

• P4L33:"It is clearly visible that the halocarbons correlate [...]"Can you quantify this?

We are not sure if a quantification of this would really provide additional information, as it would be unclear to which degree a spread around a correlation function is due to instrumental issues and to atmospheric conditions. Also some model (linear/polynomial) would be needed. We have chosen not to explore this in further depth.

• P5L40-P6L1:"Only bins which contain at least five data points [...]"What criterion led to this choice? (See comment to Fig. 4 below.)

This number has been chosen arbitrarily, but with the intention of assuring that one single measurement should not influence the mean too much, yet still having a reasonable latitude/altitude coverage. We feel that this needs no further explanation in the paper.

• P6L21-22:"[...] the variability averaged over the four lowest stratospheric bins was always lower when using $\Delta\theta$ as a coordinate. "Can you elaborate on this? Why does the variability in the four lowermost stratospheric bins change in response to the transformation of coordinates $\Delta\theta$ (relative to the tropopause)? Am I right to assume that this is due to bins with mixed tropospheric/stratospheric data? If that is the case, "four lowest stratospheric bins" is misleading. Please elaborate on this.

Ideally (if the tropopause attribution were perfect) such mixed bins would exist only in θ and not in $\Delta\theta$ coordinates. The variability in the stratosphere decreases when using tropopause-centred $\Delta\theta$ co-ordinates instead of θ coordinates, due to the elimination of mixing of tropospheric and stratospheric data to a large degree. We have made this clearer by explicitly stating:
"For all campaigns, the variability averaged over the four lowest stratospheric bins when using $\Delta\theta$, was always lower than in the 4 lowest bins above the climatological tropopause using θ as a coordinate(see Tables 3 and 4). This shows that using the tropopause centered coordinate system $\Delta\theta$ reduces the variability and that this coordinate system is thus best suited to derive typical distributions."

• P7L5-7:"The data have been binned in5◦latitude and 5 K intervals of potential temperature. As expected, the distributions closely follow the tropopause (indicated by the dashed line), with values decreasing with distance to the tropopause and also with increasing equivalent latitude. "In the previous section the authors used"[o]nly bins which contain at least five data points [...]"in a much coarser binning. From the sampling frequency, one ought to assume that the shown averaged VSLS concentrations per bin are based on similarly sized numbers of entries, but this neither emerges from the text nor the figures (Fig. 5, Figs. 9-12). Furthermore, earlier in the manuscript the authors find that $\Delta\theta$ is the coordinate of choice for this study, but they don't use it in these figures. If it was possible to show the data in relative coordinates, this would strengthen their point ("closely follow the tropopause"). The authors should elaborate on this.

Thank you for pointing this out. Indeed we used our modified potential temperature coordinate (as stated in the beginning of section 3.2. and in the Figure caption and on the axis of Figure 5). We have modified the text here to explain this more clearly:
"The data have been binned in 5° latitude and 5 K intervals of the modified potential temperature coordinate θ^*."

As with respect to the narrower sampling in this representation: the reason for this is, that this is only used for a graphical comparison, while the sampling of the vertical profiles is used for quantitative comparisons. Therefore the idea was to have a more robust sampling for the quantitative comparison and to use larger ranges of $\Delta\theta$.

• P7L7-9:"The distributions observed during the WISE and the TACTS campaigns show significant amounts ofCH_2Br_2[...]"What purpose does "significant" serve in this context? Elaborate on the actual significance or drop the word.

See general comment above: changed and quantified to
rather high levels of CH2Br2, in the lower stratosphere, with a depletion of only about 35% at 40-50 K above the tropopause

• P7L10-16:"[...] the most stratospheric air [...]"and"[...] very high mean age of air [...]"If the authors' point is to state that the amount of VSLS in the stratosphere is a function of its residence time there, they should make this more clear.

We changed the sentence introducing the mean age to:
"This stratospheric character is in agreement .."

• P7L28-29:"[...] are significantly larger [...]"Can you quantify this? Else drop the term "significantly".

Deleted significantly.

• P7L36-38:“[...] significantly slower [...]”Same as above.

Deleted significantly.

• P8L10-12:“[...] has been extended from the ESCiMo simulations to cover our campaign time period (see Section 2).”The authors give little detail about the extent of this extension. In Section 2, this “extension” of the specified dynamics simulation from the original ESCiMO simulations is not even mentioned at all. The authors refer to Jöckel et al. (2016) for the description of the set-up used. However, Jöckel et al. (2016) give at least 4 simulation set-ups (e.g. RC1SD-base-07/10/10a, RC2-base-04) on which this extension might be based. Presuming this extension includes the time span 2014-2017, it is not clear which prescribed tracer emissions were used. The authors need to provide more details.

Specified:
“The SC1SD-base-01 run which has been used here has been branched off from RC1SD-base-10 (see Jöckel et al., 2016) at January 1, 2000 using the RCP8.5 emissions and greenhouse gas scenario.”

• P8L25-28:“As no direct tropopause information was available for the TOMCAT output [...] ”Refering to Section 2 the authors state: “Local tropopause information for the flights with HALO have been derived from ERA-interim data [...] ”Could the tropopause information from ERA interim, with which the CTM was driven, be derived?• P8L29:“[...] EMAC tropopause and the climatological tropopause differed by less than 3 K [...]”How is the EMAC tropopause defined? How does it differ from the WMO/PV definition? In principle, they are comparing a “modeled” tropopause in EMAC, which has been nudged to ERA interim, with a tropopause climatology directly derived from ERA interim. They do not discuss that fact. What is the point here? Temporal and spatial stability of the tropopause in the time frame of interest?

The point is that we are comparing our measurements to the model in tropopause-relative coordinates. It is therefore important to show that the average tropopauses used for this show good agreement, otherwise discrepancies could also be due to inconsistent vertical attribution. A sentence has been added to explain this:
“As we are comparing our observations to the models in tropopause relative coordinates, we have also compared this climatological tropopause with the tropopause derived from the EMAC model results for the time of our campaigns.”

• P9L10-18: The authors are referring a sensitivity study conducted within the EMAC framework’s quasi chemistry-transport model (QCTM) mode (Graf 2017). Four different emission scenarios for VSLS are compared therein. They conclude their qualitative comparison of Figs. 7, 8 with the conclusion: “It is therefore clear that the observed differences are not primarily caused by the model but rather by the emission scenarios. ”With respect to the shape of the vertical VSLS concentration profiles, this may actually be true. But this statement does not hold if one takes a closer look at, e.g. the VSLS concentrations at the tropopause between EMAC and TOMCAT. On the back of an envelop – normalize the EMAC QCTM sensitivity studies (Fig. 8) with respect to the Warwick scenario and compare, e.g. Ziska scenarios, with TOMCAT in Figure 7. One finds that TOMCAT mixing ratios of CH_2Br_2 at the tropopause seem to be about 0.3 ppt higher than in EMAC. The spread between the scenarios is roughly 0.5 ppt (0.2 ppt if the Warwick scenario is excluded). Hence, there seems to be a substantial difference between the models, too.

We thank the reviewer for pointing towards this. Indeed differences between the models cannot be excluded as an additional point. However, no direct comparisons are possible, as Figure 8 is based simulation with EMAC,for a different time period. We only state that the differences are not primarily caused by the models, which is still valid. However, we have rephrased the statement to emphasize that a similar picture arises when comparing the 4 scenarios in one model, in particular with respect to the order of the scenarios (highest CH2Br2 in the Warwick scenario and lowest vertical gradient in the stratosphere for CHBr3 in the Warwick scenario):
“Differences between the different models are certainly a factor in the explanation of model-observation differences. However, it is clear that the pattern when comparing all scenarios in the EMAC model is similar to that described above and that differences in the emission scenarios are the main driver of model-observation differences.”

• Section 5: The authors describe a “simplified approach” to estimate total and inorganic bromine from VSLS in the extratropical stratosphere. They assume a linear mixing of two air masses, wherein the fraction of bromine with tropical origin increases linearly with increasing $\Delta\theta$. The bromine mixing ratios are only evaluated once, at the tropical (TTP) and extratropical tropopause (ExTTP). This ansatz completely neglects the actual transport (horizontal as well as vertical) and therefore the further photochemical transformation (depletion) which VSLS undergo. Based on kinetics, one would expect the concentration of any of the VSLS (let’s call it [A] for ‘any’) at the tropopause ([A](0,0)) to follow a power law:$[A](t,\theta) = [A](0,0)\cdot e^{-k\cdot(t(\theta)-t_0)}$,(1)with e.g.,$k \propto J_a + k_A(T)[OH]$. If we look at [A] at $\Delta\theta$ and a time t' and assume the same linear superposition of air masses as the authors: $[A](t',\delta\theta)$ =

$(f_{ex-trop}-1)[A]_{TTP}\cdot e^{-k\cdot\Delta t_a(\Delta\theta)}+ (f_{ex-trop})[A]_{ExTTP}\cdot e^{-k\cdot\Delta t_b(\Delta\theta)}$ (2) Although the authors state"[...] for models it is necessary to have a realistic representation not only of chemistry but also of transport in the lowermost stratosphere.", this is not discussed, e.g. in a critical evaluation of the approach itself. Consulting Figure 4, the linear approach seems to be justified for [CH_2Br_2], whereas [$CHBr_3$] clearly follows a powerlaw. This is not discussed properly in the manuscript. The authors should reevaluate their approach and change it (if possible) or at least discuss it more thoroughly.

We are not convinced that we have completely understood the point that the reviewer is making, why our ansatz should yield a linear relation between e.g. [CH2Br2] fraction and $\Delta\theta$. The linear approach is only made for the ***total Bromine*** *(sum of inorganic and organic bromine). For the organic part (which we measure, see also Fig. 4) no such linear relation is expected or made: First, there is no linear relationship between $\Delta\theta$ and transit time t', second, we assume two different input mixing ratios for tropical and extratropical fractions and third, the chemical lifetime is extremely dependant on the surroundings (photolysis rates, OH radical concentrations and temperature). As we believe that the reviewer (and also reviewer #3) may not have completely understood that our linear ansatz is only restricted to the total bromine, we have reworked the explanation:*

To make the approach clearer we have added in the introduction to section 5:

"The inorganic bromine from SGI can be derived as the difference between the organic bromine in the source region (tropopause) and the organic bromine still observed or modelled at a certain stratospheric location."

And a little further down the same paragraph to motivate that we need some sort of assumptions on the relative importance of both source regions:

"As both regions show different levels or organic bromine source gases, the relative contribution of these source regions needs to be known to derive total bromine which entered the stratosphere and thus also inorganic bromine from SGI."

• Figure 4: It is not clear whether the shown error bars refer to the standard deviation (σ) in each bin or to its standard error ($s=\sigma/\sqrt{N}$). Latter is a more reasonable choice. In any case, displaying data in such way does only make sense as long as the distribution in each bin is Gaussian. Otherwise, a violin plot may be more valid. Have the authors checked their distributions?

The error bars given should be understood as a variability range, not as an uncertainty range. Therefore, we have not used standard errors, as we want to show the variability range of the observations. We also note that a violin plot would make this Figure (and others) unreadable, as a separate violin would be needed at each altitude interval. While, as most observational data, our data are not strictly Gaussian, we thus prefer to stay with the simple uncertainty ranges. We have removed some extreme outliers before the calculation, which are believed to be from contamination, therefore the data are not influenced by some extreme outliers. This has been checked also by comparting means and medians, which we found to differ by less than 5%, showing that the distributions are rather symmetrical. Therefore we have not changed the Figures, but we have added an explanation in section 3.1.

"We have checked the validity of using means to represent the data, by comparing means and medians. Differences were always below 5% of the mean tropopause values. We have thus chosen to use means throughout this paper. The uncertainties given in all Figures are 1 sigma standard deviations of these means."

• Figure 7: Caption L11:"[...] extremely high values [...]"What is "extreme" in this context? Which exclusion criterion has been used? The manuscript doesn't provide any further information on this. Please elaborate on this matter in the appropriate section.

These same data have also been omitted in other Figures and tables. We have therefore deleted this explanation in the caption of Figure 7 and added a statement in section 2.1 where the observational data are introduced:
"For this combined data set, some observations from the TACTS campaign have been omitted, where some extremely high values of VSLS (up to a factor of 10 above typical tropospheric values) were observed in the UTLS which are suspected of being contaminated. The source of the contamination is, however, unknown"

3 technical corrections
3.1 General
Typesetting of the name "Ordóñez" in citations is not coherent and incorrect at times.

We searched the entire document and made the spelling consistent.

3.2 Specific

• P1L22:“Distributions [...] below the tropopause shows [...]”→“show”

changed

• P1L26:“A scenario which has emissions most strongly concentrated to low latitudes [...]”. This sentence needs rephrasing – maybe: “A scenario with emissions mainly confined to low latitudes [...]”

Changed as suggested

• P3L8-10:“Two pathways for input of halogens from short-lived gases are dis-cussed: Source Gas Injection (SGI),where the halogen is transported to the stratosphere in the form of the source gases; and Product Gas Injection,where photochemical breakdown products of source gases are transported into the stratosphere, usually in inorganic form (i.e. Bry).”This sentence is not concise. Please rephrase.

We have rephrased and broken up into two sentences:

“Halogen atoms can be transported to the stratosphere in the form of the organic source gas (Source Gas Injection (SGI)) or in the inorganic form as photochemical breakdown products of source gases (Product Gas Injection (PGI))”

• P3L11-12:“While halogens transported into the stratosphere due to PGI are usually directly in a form available for catalytic ozone depletion reactions, halogens from source gases must first be released in the stratosphere photochemically.”You may rephrase this along the lines: “Halogenes from product gases are readily available for catalytic ozone depletion reaction. Source gases have to undergo a photochemical transformation first.”

Nice formulation; we have adapted it as is.

• P3L23:“The main source of brominated VSLS is believed to be[...]”Although orally excepted, one should refrain from the usage of “believe” in a scientific context. Please rephrase. You may use, e.g., “most likely” or “observations indicate”.

Rephrased to:

“Observations indicate that the main source of brominated VSLS is from oceans and in particular from coastal regions.”

• P3L41-43 and P4L1-3:“These observations are compared [...]”and“[...] these observations are [...] presented [...] and compared [...]”. These sentences are almost identical. You may merge them into the latter.

First sentence has been deleted and merged into second sentence, which now includes a mentioning of the different emission scenarios:

“Typical distributions of brominated VSLS derived from these observations are then presented in Section 3 and compared to model output from two different atmospheric models run with the different emission scenarios mentioned above in Section 4.”

• P4L7-11:“An isothermal channel uses [...]”and “The second channel [...] uses [...]”You may rephrase these in passive voice.

Changed to passive voice: “An Electron Capture Detector (ECD) is used in an isothermal channel, in a similar set-up as used during the SPURT campaign (Boenisch et al., 2009;Boenisch et al., 2008;Engel et al., 2006) to measure SF_6 and CFC-12 with a time resolution of one minute.”

• P4L31,33:“mean age”. Supposedly “mean age of air” as used later on in the manuscript.

Yes, “of air” has been added

Section 2: The authors only mention the spatial resolution of their models. It might be worth to mention the temporal resolution of the model output, too.•

Added in the model description:

"The EMAC SD-simulations with 90 vertical levels, as described in detail by Jöckel et al. (2016), were integrated with an internal model time step length of 12 minutes and the data has been output every 10 hours from which the monthly averages on pressure levels have been derived."

And:

"The TOMCAT (Toulouse Off-line Model of Chemistry And Transport) model (Chipperfield, 2006;Monks et al., 2017) is driven by analyzed wind and temperature fields taken 6-hourly from the ECMWF ERA-Interim product. Here, the model was run with T42 horizontal resolution (2.8° by 2.8°) and with 60 vertical levels, extending from the surface to ~60 km. The internal model timestep was 30 minutes and tracers were output as monthly means."

P6L28:"As in previous work [...]"→"works"•

We think that previous work is correct here, as it used in a general way. However, we will be happy to modify this based on suggestions during the typesetting process. Unchanged

P6L28-33: First of all, most of this is a repetition of the text written in the beginning of section 3 and can be dropped. "As in previous work [...]"and "However, we propose a somewhat different approach [...]"These two sentences are slightly contradicting. They can and should be merged along the lines: "We slightly diverge from approaches in previous works [...]"

We have modified according to the suggestion:

"We slightly diverge from the coordinate system used to present zonal mean latitude-altitude distributions used in in previous work (e.g. Boenisch et al., 2011;Engel et al., 2006), where equivalent latitude and potential temperature where used as horizontal and vertical coordinates. We use equivalent latitude as a horizontal coordinate …. "*

• P6L36-38:"In order to ensure that this tropopause value is representative [...]"This sentence is too long and might be grammatically incorrect ("[...] when we have observations [...]"). Please rephrase.

Split up into two sentences:

"In order to ensure that this tropopause value is representative also for the period of our observations, we compare the potential temperature of the campaign-based tropopause with the climatological tropopause. The campaign based tropopause has been calculated by averaging the tropopause at all locations for which observations are available during the campaign."

• P7L7-9:"[...] which has a rather long lifetime in the cold upper troposphere and lower stratosphere (Hossaini et al., 2010) even quite deep into the stratosphere."This sentence is quite unclear and needs rephrasing.

Rephrased and quantified:

"The distributions observed during the WISE and the TACTS campaigns show rather high levels of CH2Br2 in the lower stratosphere, with a depletion of only about 35% at 40-50 K above the tropopause. This is consistent with the rather long lifetime of CH2Br2 in the cold upper troposphere and lower stratosphere (Hossaini et al., 2010)."

• P7L9-10:"[...] is strongly depleted [...]"Can you quantify this statement?

Quantified to "The shorter-lived CHBr3 is depleted by about 85% already at 20-30 K above the tropopause during the winter campaign PGS."

• P7L10-12:"[...] flight levels [...]"You may refer to "flight altitudes" instead.

Changed as suggested

• P7L36-38:"This is most likely [...]"The authors may rephrase this sentence into two. The natural breakpoint would be"[...] with latitude. As [...]".

We looked at this sentence and considered splitting it up. However, there is a causality in here, which would make it awkward to split this into two sentences. Unchanged.

• P8L6-7:"[...] are based on the emission scenario by Warwick et al (2006) [...]was run with different emission scenarios (Ordoñez et al., 2012;Ziska et al.,2013;Liang et al., 2010)."The authors should mention which or the 8 scenarios by Warwick et al (2006) and which of the three by Liang et al. (2010) they have used.

We have specified that scenario # 5 from Warwick and scenario A from Liang have been used in the model description.

• P8L36:“overestaimtion”→overestimation: *changed*

• P9L4-6:“Because of the different chemical lifetimes [...] above 20 K above the tropopause [...]”This sentence might need some rephrasing. The authors may use$\Delta\theta$>20 K.

Good suggestion: we have rephrased as suggested:

“Because of the different chemical lifetimes of the two species, this results in a wrong vertical distribution of Bry with too high mixing ratios at $\Delta\theta$>20 K in winter and a much steeper vertical gradient in late summer.”

• P9L10-12:“In Order to [...] ”This sentence is too long and not concise. Please rephrase.

Rephrased to: “We additionally compare model data from EMAC simulations using all four emission scenarios (Graf, 2017) in order to investigate if the large deviation of the Warwick et al. (2006) emission scenario is due to the EMAC model or due to the specific emission scenario.”

• P9L12-13:“Note that these simulations [...]”You may drop “Note that”

dropped

• P9L23-24:“Again, we use equivalent latitude*[...]”This has been stated several times by now. As the authors indicated by using“[a]gain [...]”. They should consider dropping the whole sentence or the “again” therein.

In order to make it clear that slightly different vertical coordinates are used for observations and models we rephrased as follows:

“While we use equivalent latitude as the latitudinal coordinate for the observations and θ* as vertical coordinate, the zonal mean data are displayed as function of latitude and potential temperature θ for the model results.”*

• P9L39:“The direct comparison of the distributions between the different model data sets is also interesting.”This statement is redundant. Please rephrase, e.g.“We will have a look at [...]”

We have deleted this sentence.

• P11L8:“In this Section [...]”Add a comma after “section”. *done*

• P11L33: The indent of the equation number is incorrect. The authors may reduce the equation to$Br_{tot}(\Delta\theta) = Br_{y}(\Delta\theta) + Br_{org}(\Delta\theta)$

changed

• P12L20:“Figure 14 compares [...]”There is a grammatically issue here. A figure cannot compare anything. Please rephrase using passive voice.

Changed to passive voice.

• P13L18:“have e a”→Remove the “e” in between. *removed*

• P13L30:“[...] a large dataset [...]”Can you quantify this?

Changed to “We present a large dataset of around 4000 in-situ measurements of five brominated VSLS”

• P13L36:“[...] which is line [...]”→“which is in line” *changed*

• P13L40:“in high latitudes”→“at high latitudes” *changed*

• P14L3:“[...] with large differences produced by the different emissions. ”It maybe better to use “caused” in this sentence.

Changed to caused

• P14L3-5:“Overall, for CH_2Br_2[...]”Please consider rephrasing this sentence.

• Figure 1: The figure is too wide. Would it be possible to color code the different flights temporally?

We suppose the Figure size could be reduced during the final typesetting. With respect to colour coding, this would mean also including a legend, which would make the Figure too busy. Not changed.

• Figure 2: Is it possible to highlight the flight path displayed in Figure 3?

As the flight shown in Figure 3 is rather arbitrary, we believe that colour coding it would give no additional information. Not changed.

• Figure 4: Caption L8:“dotted”→“dashed”

done

• Figure 7: Referred to choice of colors under “general”. Caption L10:“bene”→“been”•

Bene has been changed to been; colours unchanged (see reply to general comment above)

Figure 14: Please include the information given in L1 of the caption also in the legend of the plots.

Including this information in the legend would actually make the legend very busy. We have instead changed the heading of the plots and included “dashed” in parentheses behind the total bromine to make this clear.

• Figure 15: The x-axis label of the lowermost panel seems to be incorrect (compared to the others in the figure)→“Br total and Bry from VSLS”.

We suppose this comment refers to Figure 14; corrected.

Caption L1:“[...] at$\Delta\theta$of 40 K [...]”→“at$\Delta\theta$= 40K”

done

Reviewer #2, Rafael Fernandez

The paper presents a complete set of carbon-bonded VSLS source gases (SGs) measurements performed in the Northern Hemisphere mid-latitudes using a GC-MS instrument on board an aircraft, as well as a comprehensive comparison of the observations with a complete set of model simulations oriented to evaluate the contribution of tropical and extra-tropical injection of VSLS to the lowermost stratosphere. The main results of the work are: i) the troposphere-to-lowermost-stratosphere transport of VSLS SGs through the extra-tropical tropopause is larger than that occurring within the tropical tropopause; ii) the contribution of both tropical and extra-tropical VSLS injection must be considered in order to reproduce the VSLS abundance within the mid-latitudes lower stratosphere below 400 K; and iii) the models and inventories used in this work show certain limitations in reproducing the VSLS reactive transport and estimate the release of inorganic bromine (Bry) in the NH lower stratosphere. The paper also includes a seasonal, latitudinal and vertical analysis of VSLS abundance in the UTLS.I found the paper very interesting and very well organized, presenting results in a clear and comprehensive format, and including interesting and constructive discussions. It is worth noting that even when the altitude/latitude-dependent observations itself would be worthwhile to be published, the authors have decided to go forward and present a comprehensive model-observation inter-comparison, which contributes to improves the general understanding of the reactive-transport efficiency of VSLS species within the UTLS. In particular, I found very descriptive and intuitive

the vertical coordinate system (△θ and θ*) they used to represent all results relative to the altitude of the tropopause, which allows a consistent description of the vertical and latitudinal decay of VSLS once they are injected to the stratosphere. At the very end of the paper, a simplified approach(eq. 4) is used to estimate the total amount of inorganic bromine (Bry) released byVSLS within the mid-latitude lower stratosphere, highlighting the major importance ofproperly reproducing these Bry levels in model simulations oriented to determine the ozone impact of VSLS. Having said this, I believe that the manuscript posses a handful set of specific issues and many technical details (including figures and tables captions) that must be corrected before final publication.

Major Concerns:

1. I would like to start mentioning that most of the "important questions" that came to my mind while I was reading the manuscript had already been responded (i.e., as I moved forward with the lecture and reached Section 5). Even when this should be taken as a mainly positive comment, it also implies that some of the analysis/discussions given at the end could be (at least partially) shifted to earlier sections, to help the reading and support the analysis. For example: Sections 3 is concentrated on carbon-bonded VSLS mixing ratios close and above the tropopause in the lower stratosphere, but there is only a brief mention and sideway comparison with the SGI values compiled in the last WMO report (P7,L27). The reader needs to wait until Table 5 is presented (Section 5, P12) to reach a complete discussion and comparison with WMO values, and it is only at this point that the importance of the model-observation inter-comparison (presented in Section 4) becomes evident. In doing so, note that Table 5, which provides values for VSLS SGs within the tropics and extra-tropics, is introduced in the only section of the paper focused on PGs (Section 5).

We have referenced Table 5 already in section 3.3. and 4.3. where we point to the tropical values from the WMO 2018 report. We have also, as mentioned by Rafael Fernandez in a specific comment included the tropical values from WMO 2018 in Figure 6 and also in Figure 13. We hope that this brings forward the point that extratropical values, in particular during winter are higher than tropical values.

Added the following in the text in section 3.3. (latitudinal gradients) after introducing the tropical WMO values.:

"These upper TTL values have also been included as reference Figure 6 (see also Table 5)."

Added/modified the following in section 4.3.:

"In order to investigate if the models are able to represent the latitudinal gradient in upper tropospheric mole fractions, we compare the observed extratropical mole fractions of the brominated VSLS in the upper troposphere (section 3.3) and compiled tropical observations (Engel and Rigby, 2018) with those determined from the different model setups."

And referenced Table 5 in section 4.3.

2. Observations from TACTS and WISE campaigns have been merged into a unique dataset (WISE_TACTS) because they were performed during the same seasons. Even though I found this procedure correct, I wonder if the authors have analyzed this data separately to evaluate if there is at least any glimpse of VSLS SGs trend within the NH-UTLS (there are~5 years between both campaigns). The authors declare they combined both dataset based on „general" observational evidence (P3,L29), but I think they should justify this procedure by evaluating specifically their unique and novel dataset (P4,L29).

We have not analysed the data set with respect to a possible trend, as we believe that there are too many uncertainties associated with this and that the variability is far too high to detect trends, which are expected to be very small. However, we have decided to add an appendix to the paper, which contains plots of the observations (eq. to Figures 4, 5 and 6) for the WISE and TACTS campaign separately.

3. Authors should be really careful and consistent when using the wording "total bromine". Until Section 5 is reached, only carbon-bonded (i.e., organic) bromine is considered, and total bromine is referred as the sum of CH2Br2 + CHBr3 + minor VSLS(P6,L2; P8,L15). But later on Sections 5 and 6, "total bromine" points out to the sum of Br_org + Br_inorg (P11, Eq. 1). Please, be consistent and refer to "total organic bromine" and/or "total bromine" whenever appropriate.

The reviewer is absolutely correct in this statement. We have gone through the manuscript and have made sure that when total refers to the sum of bromine from all 5 species, we always include organic (total organic bromine) or inorganic (total inorganic bromine) with it, in order to separate it from total bromine as the sum of organic and inorganic bromine.

4. Although the vertical profiles for CH2Br2 and CHBr3 are analyzed in detail, there are no mentions regarding the "error bars" presented in the figures (e.g., P6,L20; Fig.4 caption). Do the error bars correspond to 1-sigma or 2-sigma? Besides this, the authors should explain why the vertical error bars for △θ are not the same for the different bins, as well as why the error bars for CHBr3 are larger than for CH2Br2? Is this only due to the shorter lifetime of CHBr3, which shows quite different vertical profiles de-ending on the exact latitude within the 40-60◦bin (as observed in the latitude-altitude cross-sections), or could this also be attributed to differences in their regional source strengths? Note that the variability is only considered in (P7,L34; Fig. 6) when addressing how the VSLS tropopause abundance changes with latitude, but I think that a more complete comparison of this latitudinal and vertical variation within the 20-40◦N bin should be provided (at least the two major VSLS).

The error bars denote 1 sigma variability. The reason for the much larger uncertainty range in CHBr3 is indeed the shorter lifetime, which implies stronger gradients and overall larger variability.

The meaning of the error bars (vertical and horizontal) is now explained in the manuscript in section 3.1, also in relation to a remark by reviewer #1 with respect to using sigma (Gaussian distribution):

We have checked the validity of using means to represent the data, by comparing means and medians. Differences were always below 5% of the mean tropopause values. We have thus chosen to use means throughout this paper. The uncertainties given in all Figures are 1 sigma standard deviations of these means, both for the vertical and horizontal error bars.

With respect to the larger relative uncertainties for CHBr3 and also the different vertical error ranges we have explained towards the end of section 3.1.:

The short lifetime and strong vertical gradient of CHBr3 is also reflected I the largest relative variability (see Tables 3 and 4).

5. P8,L18: "The contribution from these mixed bromochlorocarbons to total VSLS bromine are typically on the order of 20%, while about 80% of total VSLS bromine in the upper troposphere and lower stratosphere is due to CH2Br2 and CHBr3".→Are this percentages computed using WISE_TACTS and PSG data? Have you compared this findings with other studies (i.e., Fernandez et al., 2014)? Have you thought about presenting combined results of your observations of the sum of these minor_VSLS into a figure or table? (currently only results for the sum of CH2Br2 + CHBr3 + minor_VSLSare given)? As minor_VSLS posses in some cases lifetimes larger than CH2Br2, this information could be useful for future studies. The importance of the minor VSL contribution becomes also evident in Section 5 (P13,L11) when the overall contribution from longer-lived VSLS to Bry is discussed.

The mean values just below the tropopause and also at 30-40 K above the tropopause are given for all 5 VSLS species in Tables 3 and 4. We have added the plots as for Figures 4 and 7 for the minor VSLS in the appendix. The 20% contribution of minor VSLS is consistently derived from our observations and from the WMO 2018 compilation (Table 5). This is now stated in the text:
"This relative contribution of 20% from minor VSLS is found in our observations (Tables 3 and 4) as well as in the values compiled in Engel and Rigby (2018) (see Table 5) and is slightly larger than that derived e.g. in Fernandez et al. (2014)."

Specific Comments:
1. Title and Abstract: Shouldn't the title be more specific on the extra-tropical (or the"tropical vs. extra-tropical") contribution of VSLS bromine to the UTLS?? In addition, the abstract has an excessive focus on the results obtained with the different models and emissions scenarios (including specific statements for some of the scenarios giving the best and worst agreement). I would expect the abstract to focus on the contribution of tropical vs. extra-tropical contribution to SGI, and in any case to provide a rough estimate of the relative contribution of each of these two pathways to the over-all organic and inorganic lower stratospheric bromine (and providing only a general mention to the similarities and discrepancies between models and observations and its dependence on latitude and season).

We added extratropical in the title and slightly modified the abstract to include and explanation of the importance of the measurements ("Why aspect mentioned by reviewer #1). We believe that the aspect of tropical vs. extratropical SGI is already mentioned in the abstract: "Distributions of the five source gases and total organic bromine just below the tropopause show an increase in mixing ratio with latitude, in particular during polar winter. This increase in mixing ratio is explained by increasing lifetimes at higher latitudes during winter. As the mixing ratio at the extratropical tropopause are generally higher than those derived for the tropical tropopause, extratropical troposphere-to-stratosphere transport will result in elevated levels of organic bromine in comparison to air transported over the tropical tropopause." Therefore we did not add anything here, but hope that the explanation of Why added more context. The issue of fractional contribution of tropical and extratropical air masses is only treated as a sensitivity study. We have pronounced these issues more specifically in the abstract now:

"In a sensitivity study we find maximum differences of a factor 2 in inorganic bromine in the lowermost stratosphere from source gas injection derived from observations and model outputs. The discrepancies depend on the emission scenarios and the assumed contributions from different source regions. Using better emission scenarios and reasonable assumptions on fractional contribution from the different source regions, the differences in inorganic bromine from source gas injection between model and observations is usually on the order of 1 ppt or less."

2. Section 3 (P5): The first paragraph of section 3 describes the spatial and vertical coordinates used for representing measured and modeled data. In my opinion, the selection of θ, △θ and θ* variables really improves the analysis and interpretation of the results. However, I believe the initial description of how these variables are computed is not clear enough, and the reader needs to go back and forth between figures and text to completely catch up the difference among them. For example: a) △θ is mostly used for vertical profiles figures, whereas θ* is used for latitude-altitude cross-sections (which is not clearly mentioned in the text); b) there are at least 2 or 3 places where △θandθ* vertical coordinates are defined, and in some cases slight differences on the definitions are observed (P5,L31 and P6,L32). In particular specify if the vertical coordinate is computed above the "local" tropopause "for each latitude" and how is it added to the "climatological" tropopause.

The use of θ in the latitude altitude cross sections is now clearly mentioned in the text and also we have deleted the additional explanation of θ* given in section 3.2. and referenced the definition of θ* at the beginning of section 3. We also specified that the local tropopause is the reference for △θ at the beginning of section 3. In addition we have explained at the beginning of the last paragraph of section 3.2. again that θ* is used here (it just stated potential temperature before).*

Explanation of the different vertical coordinates at the beginning of section 3:

"These are potential temperature θ, potential temperature above the local tropopause $\Delta\theta$, and finally a coordinate we refer to as θ^*, which is calculated by adding the potential temperature of the mean tropopause to $\Delta\theta$."

End of section 3.2., explanation of the coordinates used:

"The data have been binned in 5° latitude and 5 K intervals of the modified potential temperature coordinate θ^*."

3. P11,L2-5: "Most importantly, the overall levels, especially in the low latitudes, are much higher than our observations and also much higher than the tropical observations compiled in the WMO report (Engel and Rigby, 2018). This will result in too much VSLS bromine being simulated in the stratosphere, and therefore also in a misrepresentation of the input to the lowermost stratosphere via the different pathways".→In addition to the general description focused on the 340-400 K range, I found interesting that poleward of 40◦and below 320 K (see Fig. 9-10) there is a negative model bias for CH2Br2 mixing ratio exactly at the extra-tropical tropopause, while at the same time there is a positive model bias for CHBr3. This is not mentioned nor explained in the text.

We thank Rafael Fernandez for pointing towards this feature. We have no good explanation for this, with the exception that for the models, the tropopause sometimes seems to be more "penetrable" than for the observations. It can also not be excluded that this is somehow related to the way that the models have been averaged. We decided to add this feature, without trying to explain it. This may indeed be an interesting aspect for further studies.
Added text at the end of section 4:
"We also note that poleward of 40°N and below 320 K (see Figures 9 and 10) there is a small negative model bias for CH2Br2 at the extratropical tropopause when using the scenarios by (Liang et al., 2010) and (Ordóñez et al., 2012). At the same time the model simulations using these two scenarios yield a substantial positive bias for CHBr3 in the same region. This will result in a misrepresentation of the input of brominated VSLS source gases to the lowermost stratosphere via the different pathways."

4. P11,L28: The simplified approach considering fext-trop and ftrop" is very intuitive and helps to visualize the contribution from tropical vs extra-tropical bromine from VSLS, but it would be useful to provide at the end a conclusive sentence of which are the most probable fractional contributions from tropics and extra-tropics to the overall bromine in the UTLS. Certainly, concurrent Bry measurements would be required to close the whole bromine budget, but at least from Figure 15 (△θ= 40 K) it seems that fext-trop values close to 20-40% produce the closest agreement between model and observations. However, on the analysis presented for Figure 14, fext-trop is 60% at this height, isn't it? I suggest to expand the analysis and discussion of fext-trop and ftrop" (you only dedicate a few lines to this subject at the end of Section 5). Finally, why are not equivalent results for WISE_TACTS provided in Fig. 15?

Firstly, Rafael Fernandez is correct in pointing out that concurrent Bry measurements might be a valuable tool in investigating this. This could potentially form the basis for further studies. We would like to emphasize again, that this is a sensitivity study, and that a good agreement with the model may not be interpreted as the right fractional contribution, as it is more likely that several errors may balance each other. We would thus not use this to discuss the right fractional input.

With respect to the WISE TACTS campaign: Similar Figures to Figure 14 and 15 are now available in an appendix.

5. P12,L28-29: "The larger Bry derived in the model calculations above 60 K is caused by the higher total bromine values from CH2Br2, which are caused by the higher CH2Br2 levels at the tropical tropopause in comparison to the observations." P12,L32-33: "In the lower part the discrepancy is more due to higher simulated CH2Br2 in the lowermost stratosphere than found in the observations"→This could "partially" be the reason, but it could also be due to using an improper fext-trop value at this specific vertical level and/or due to the simplified linear approach used. Please elaborate on this.

The text is a discussion of the differences under these assumptions. Different assumptions would yield different results, as discussed in the sensitivity study in Figure 15. We have made this clearer by rephrasing:
"Under the given assumptions about fractional input, the larger Br_y derived in the model calculations above 60 K is caused by the higher total bromine values from CH_2Br_2, which are caused by the higher CH_2Br_2 levels at the tropical tropopause in comparison to the observations."
"Under the given assumptions about fractional input, the discrepancy in the lower part is more due to higher simulated CH_2Br_2 in the lowermost stratosphere than found in the observations."

6. P14,L29: "we have shown that there will be significant differences in stratospheric Bry depending on the emission scenario, which can be as high as 2 ppt, corresponding to a difference of a factor 2 relative to observation-derived values".→Being this sentence included in the conclusions (and also mentioned in the original abstract), I suggest informing not only the largest (i.e., worst) difference, but also the minimum model-observation differences, as well as the range of model bias results for the models which show a better performance.

It is rather difficult to explicitly state the best agreement, as by coincidence, this may be close to 0 at some places. The reason that this value was given is simply to mention the order of magnitude of possible biases. We have restricted the statement of the 2 ppt to Warwick et al. (2006) and added:
"Typical differences in Br_y when using the other scenarios are on the order of 1 ppt."

Technical Corrections:
P1,L17: "The instrument is extremely sensitive due to the use of chemical ionisation,allowing detection limits in the lower parts per quadrillion (10 -15) range".→Is this information of major importance to be included on the abstract? Consider also including the GS-MS acronym in the preceding sentence.

We would like to keep the sentence on the high sensitivity, as the use of chemical ionisation in GC-MS is rather special. We have included the acronym GC-MS in the first sentence.

P1,L35: "Depending on the underlying emission scenario, differences of a factor 2 in reactive bromine derived from observations and model outputs are found for the lowermost stratosphere, based on source gas injection."→Consider rephrasing, and also mentioning the range of agreement of models (see comment above).
Rephrased to:
"Depending on the underlying emission scenario, maximum differences of a factor 2 in inorganic bromine from source gas injection derived from observations and model outputs are found for the lowermost stratosphere."
And added the following to the abstract:
"Using better emission scenarios, the differences in inorganic bromine from source gas injection between model and observations is usually on the order of 1 ppt or less".

P3,L30: "A further future increase has been projected"→A future increase of VSLS emissions has been suggested"

changed to suggested

P3,L38: "In order to investigate the regional variability of bromine input into the lowermost stratosphere and the inorganic bromine loading of the extratropical lowermost stratosphere, we have performed a range of airborne measurement campaigns ..."→You explicitly mention "inorganic bromine" but not "organic bromine" in a sentence focused on the novel measurements dataset. Consider revising, as you've only measured carbon-bonded species, and only inferred inorganic bromine.

The part of the sentence mentioning inorganic bromine has been deleted.

P3,L42;P4,L3: Please specify which are "the implications" you are pointing at.

Changed from implications to differences

P4,L5: Consider changing the subtitle to “Instrumentation and Observations”

Changed as suggested

P4,L22: Check for consistency between the year of the TACTS campaign between the text (2011) and table 2 (2012).

It’s 2012; corrected

P4,L29: “covered a similar time period and latitude range”→you mean same seasons, consider rephrasing.

Changed from time period to time of the year.

P5, L2: “ESCiMo (Earth System Chemistry ntegrated Modelling)”→Integrated
corrected

P5,L12: TOMCAT acronym already defined above (P5,L2). *Deleted*

P5,L7;P5,L13: If both EMAC and TOMCAT are driven by exactly the same ECMWF ERA-Interim reanalysis data, this should be mentioned explicitly. This will help to override additional uncertainties regarding differences between models. Also, although EMAC can be run as a CCM model, it should also be clear that for the current SD simulations, the model behaves like a CTM.

We added the following:
“For the results presented in this paper, EMAC was operated in the so-called specific dynamics mode, in which the synoptic scale meteorology is relaxed towards meteorological reanalysis data.”

P5,L17: “Emitted VSLS (CHBr3, CH2Br2, CH2BrCl, CHBr2Cl and CHBrCl2) are destroyed by reaction with OH and photolysis in the model”→I assume this is also the case for the EMAC model described in the preceding paragraph. You should explicitly mention this to avoid confusion.

This is of course true; the main reason for this sentence was to point towards the source of the kinetical data used in TOMCAT. We have rephrased as follows:
“Chemical breakdown by reaction with OH and photolysis in the model for all VSLS ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$ and $CHBrCl_2$) are calculated using the relevant kinetic data from Burkholder et al. (2015).”

P5,L24: Although the paper reads perfectly well using the θ vertical coordinate, it
should be mentioned at least during the model description which are the equivalent altitude/pressure values for the tropical/extratropical tropopause θ levels used in this work.

As we are using potential temperature in the entire manuscript, we think that adding an altitude information in km would actually link to a vertical coordinate which is not used in the paper at all. Therefore we have not derived this information and not included it.

P5,L36: “we have also binned the data in potential temperature in 10 K potential tem-perature intervals”→repetitive

No, this is not repetitive, as the second phrase explains the potential temperature binning. We have rephrased for more clarity:
“For potential temperature binning, the 10 K bins have been chosen ranging from 40 K below the mean tropopause to 100 K above the mean tropopause.”

P5,L38 and elsewhere: “relative to the mean tropopause observed during the cam-paigns”→in many places the authors make reference to “the campaigns” in a general meaning, when I understand they are pointing out to “each dataset” obtained during the campaign, and not the campaign itself.

We have replaced campaign by measurements, even though we feel that this is rather the same thing.

P5, L38: “The results are presented ...”→consider rephrasing the whole sentence, as it is very difficult to understand. It should also be mentioned at least once that whenever you mention winter, spring or fall, you are always pointing out to “boreal” seasons. It is not necessary to repeat it all over the text, but I only found it mentioned properly once in the conclusions (P13, L39).

We put the seasons for which the measurements are representative in parentheses to improve the readability of the sentence. We also added the reference to the Northern Hemisphere in the parentheses. It now reads:
"The results are presented for the two main VSLS bromine source gases CH_2Br_2 and $CHBr_3$, averaged over equivalent latitude of 40-60°N in Figure 4 for PGS (Northern Hemispheric winter) and the WISE_TACTS combined data set (Late summer to fall, Northern Hemisphere)."*

P6,L15: "again in line with their atmospheric lifetimes, which generally decrease with an increase in the bromine atomicity of the molecule". Atomicity should also be used in
P7,L25.

The term atomicity is not very widely used and may not be familiar to many readers of ACP. We therefore prefer to stay with the term "number of bromine atoms in the molecule".

P7,L10: "The shorter-lived CHBr3 is strongly depleted already about 20 K above the tropopause"→Based on Figure 5, this is only the case during PGS, but not for WISE_TACTS during the summer. Could this be related to stronger convective transport during the summer? Please explain.

This is more likely an effect due to the strong diabatic descent in the vortex during winter. We quantified the depletion (see comment from reviewer #1) and added a statement about the effect mainly occurring during winter. The explanation that this is probably related to the descent in the vortex during winter was already presented in the following. We have not added more explanation, as the restriction of the statement to the winter campaign relates the low values to the following explanation.

P7,L20-22: "In order to ..."→there are many sentences that begins with this wording. Although I found it correct, please avoid it using more than once within a paragraph(i.e., here it is used in two consecutive sentences).

Second sentence has been changed to:
"All data in a range of 10 K below the local dynamical tropopause have been averaged to characterize the upper tropospheric input region."

P7,L23: "Again, for the tropospheric data, standard latitude has been chosen, while equivalent latitude was used for all data with$\triangle\theta$above zero"→This got me confused:
Figure 6 focus on extra-tropical tropopause values (averaged considering bins 10 K below the local tropopause).
Wouldn't this correspond to negative$\triangle\theta$?

That is correct and indeed for the upper tropospheric data we have used latitude and not equivalent latitude. The axis description of Figure 6 is therefore lat. and not eq. lat. We have rephrased to make this clearer:
"For these upper tropospheric data, standard latitude has been chosen and not equivalent latitude as for the stratospheric data."

P7,L29: explicitly point at Tables 3 and 4.

done

P7,L30 and Figure 6: Could the "negative latitudinal gradient" observed for WISE_TACTS be somehow unrealistic/largely-biased because of using a small amount of measurements below the tropopause at larger latitudes? Or because of any type of cos(lat) averaging factor?

The reviewer is correct that the amount of data north of 60° lat is much smaller than south of 60° N for the TACTS and WISE campaigns. However, it is also well understandable that the mixing ratios to not show a further decrease to the north, as due to longer insolation during NH summer the lifetimes are expected to decrease again. This discussion is taken up a few lines further down, where we note that: "Nevertheless, there is a clear tendency for an increase in tropopause values with latitude, particularly during Northern Hemisphere winter. This is most probably related to the increase in lifetime with latitude, as especially during the wintertime PGS campaign the photolytical breakdown in higher latitudes is slower than in lower latitudes."

P7,L34: "derived around the tropopause"→wouldn't it be "below" (-10 K) the tropopause.

Changed to "in the upper troposphere".

P8,L1-5: Sentence is too long. Please rephrase.

The sentence has been broken down into two sentences:

"As bromocarbons are an important source of stratospheric bromine, it is worthwhile to investigate if current models can reproduce the observed distributions shown in Section 3. This is a prerequisite to realistically simulate the input of bromine from VSLS source gases to the stratosphere, but also the further chemical breakdown and the transport processes related to the propagation of these gases in the stratosphere."

P8,L13: "Here we compare vertical profiles, geographical distributions and latitudinal gradients between our observations and the model results".→What do you mean by"geographical distributions"? 20◦-40◦bin?? If not appropriate, please remove.

Geographical distributions has been replaced by latitude-altitude cross section, which is clearer.

P8,L23: "about 40 K"→"~40 K"

In this case, we would prefer to stay with the written "about", unchanged.

P9,L4: "Using the Ziska et al. (2013) emission scenario, the overestimation of CH2Br2 and the underestimation of CHBr3 tend to cancel out, resulting in a reasonable agreement in total VSLS bromine. Because of the different chemical lifetimes of the two species, this results in a wrong vertical distribution of Bry with too high mixing ratios above 20 K above the tropopause in winter and a much steeper vertical gradient in late summer."→First, in the initial sentence it should also been explicitly mentioned that, in addition to the CH2Br2 overestimation and the CHBr3 underestimation, the contribution form "minor VSLS" which is also considered for the total "organic" bromine results is based on the Ordoñez inventory...adding an additional uncertainty to the different contributions that "cancel out" each other. Second, What do you mean by "vertical distribution of Bry" in this context?. Please be careful when pointing out to the inorganic or organic bromine in this section.

First: changed to: "When adding the contribution from minor VSLS based on the scenario by Ordóñez et al. (2012) this results in a reasonable agreement in total VSLS organic bromine.

Second: this sentence has been deleted.

P9,L23: Fig. 9 to 12 instead of 9 and 10? *Yes, changed*

P10,L6: "much lower"→please be more specific

Added difference: "Our low latitude observations from HALO during late summer and fall (WISE and TACTS) and the values compiled in the WMO 2018 report for the tropics (Engel and Rigby, 2018) are lower by about 0.3-0.5 ppt than the values of CH2Br2 in the tropics using the Warwick et al. (2006) and Ziska et al. (2013) emissions."

P10,L15: "Therefore, we compare the observed mole fractions of the brominated VSLS in the upper troposphere with those determined from the different model setups, in order to investigate if the models are able to represent the latitudinal gradient in uppertropospheric mole fractions."→please rephrase.

Rephrased: "In order to investigate if the models are able to represent the latitudinal gradient in upper tropospheric mole fractions, we compare the observed mole fractions of the brominated VSLS in the upper troposphere with those determined from the different model setups."

P10:L17: "or respectively modelled (EMAC)"→please rephrase (see comment on respectively below)

We have had this checked by a native speaker, who had no objections to the way that respectively is used here. In any case, we expect that this will also be checked once more during the typesetting process. Unchanged

P10,L32-37: The text goes back and forth a couple of times between wintertime results and summertime results. It would be simpler to describe all results for one season before moving to the other.

We considered this. However, the logic is to start with the observations and then to compare with the models. Unchanged.

P10,L36: Here and elsewhere..."extremely high"→what do you mean by extremely? Wouldn't just "larger" be enough?

Changed to larger

P11,L12: "is expected to add more bromine on top of SGI"

The reference to SGI has been added and we have made two sentences out of this one sentence: "The input of bromine into the stratosphere in the inorganic form (product gas injection) is expected to add more bromine in

addition to the SGI discussed here. However, PGI cannot be investigated with the source gas measurements presented here."

P11,L14: "imply for the total bromine and inorganic bromine"→you mean total organic bromine or total (organic + inorganic) bromine? Or both? Please see the general comment above.

We have checked the usage and made it more consistent: throughout the manuscript we have made sure that the term total is always used together with organic if it only refers to total organic bromine from VSLS. Especially here, we have specified in parentheses behind total bromine that it refers to the organic and inorganic bromine

P11,L18: Too many "and" within a single sentence. Please rephrase

Rephrased to two sentences: We have shown in Sections 3 and 4 that the organic bromine around the tropopause shows significant variability and also latitudinal gradients. We have also shown that large differences between the different model setups and observations are found.

P11,L23: "No studies on mass fractions are available for the campaigns discussedhere, so we will rely on previous studies for these fractions."→I do not understand the rationale for including this sentence. Please make it clear or remove.

In order to make the meaning clearer we have extended the sentence: "No studies on mass fractions are available for the campaigns discussed here, so we will rely on previous studies for these fractions as discussed in the introduction to estimate the fractions of tropical and extratropical air in the lowermost stratosphere."

P11,L24: "order of magnitude difference" is normally used to point at scaling factors like 10, 100, 1000. Please rephrase.

Changed to "how much"

P11,L41: Here and elsewhere. "at the tropical, respectively extratropical (40-60◦N) tropopause,"→It is very unfamiliar for me the way the "respectively" sentences have been written throughout the text. I suggest replacing them by "at the tropical and extratropical (40-60◦N) tropopause, respectively". See also P12,L19-L23.

We have had this checked by a native speaker, who had no objections to the way that respectively is used here. In any case, we expect that this will also be checked once more during the typesetting process. Unchanged

P12,L6: "by averaging the model respective observations"→This sentence is sense-less, in any case "the model results"

We have changed to model results and specified that extratropical input values are meant.

P12,L14: fext-trop decreases with altitude, not increases.

Thank you, you are right. Changed.

P14,L6: "with a downward revision"→do you mean shifted to the lower edge of the range of emissions?

We refer to the range being reduced and some older very high emission estimates being judged unrealistic in the last WMO assessment. The sentence has been changed to :

a recently proposed revision of the best estimate of global CH2Br2 emissions towards the lower edge of previous estimates

P14,L26: "The bromine budget in the lower stratosphere will depend on the relative fraction of air from the tropical and extratropical tropopause. The relative contribution of extratropical air will decrease with altitude and should reach zero at about 400 K potential temperature.."→is it the future (will) tense appropriate here??. In any case, I believe the authors are pointing at a decrease with altitude and not latitude here (if not, please explain the idea and make it clear).

Changed to present tense to emphasize that this is a general feature and, yes, we refer to altitude.

Tables and Figures:

Most of Figures and Table Captions include the "long-name" of each of the Cam-paigns instead of just providing their "short-name"/acronym (PSG=POLSTRACC+GW-CYCLE+SALSA, TACTS_WISE, HALO, ECMWF, etc.), which is not only simpler, but also more familiar to everyone. Using the short-name version will certainly improve the captions readability. Also, there is no need to define ppt each time you use it (only once at the beginning within the text is enough).

Done in all tables and Figures.

All Tables: Consider using a “one line title” at the top of each table, and then provide all specific information regarding the season, specific campaign, altitude/latitude range,etc. as footnotes on the table.

Due to using acronyms in the table headers these have become much shorter. We would thus prefer to stay with the original presentation.

All multiple-panel Figures should indicate, in addition to the (letf, PSG) and(right,WISE_TACTS) information, that results are provided for (top, CH2Br2), (middle, CHBr3) and (bottom, total organic bromine). (This example was based on Fig. 13, and should be adapted to the specific figure).

Done by including top/middle/bottom in parentheses behind the substance name.

Table 3 and 4: What does “TP” stands for (tropopause)?. Why Table 3 provides values for TP + 30-40 K, while Table 4 only for TP + 40 K? Define what does the stdev. Stands for and how is computed? Wouldn’t it better to provide the stdev. value with a +/- sign (0,55 +/- 0,09) ppt within the mole fraction column?

The heading in Table 4 has been updated to read TP + 30-40 K (which it is, similar to the column in Table 3). The stdev. column has not been included in the mixing ratio column, as this column shows the average standard deviation in the 4 lowest stratospheric bins, with the purpose of showing that this is significantly reduced when using △θ. In order to explain better what this column means we have included the following explanation in the table headers for Table 3 and 4:

The 10K bin standard deviations in the table represent the variability averaged over the four lowest stratospheric bins.

The abbreviation TP has been introduced in the heading of both tables. Also we have changed the column heads to θ and △θ.

Table 5: Have you used the annual mean or the seasonal mean for computing the tropical tropopause values?? (P12,L6). In case a seasonal mean has been used, please specify which months have been used for the model output. Replace bromide by bromine. Rephrase respectively. Explicitly indicate that the Br_ext-trop and Br_trop are for (△θ= 0). Indicate that ML stands for Mid-latitudes, which you called extra-tropics throughout the text. Define explicitly in a table footnote the△θ, latitude range and any other relevant information that has been used for computing the values presented in Table 5.

Bromide has been changed to bromine.

The explanation of the tropical values is detailed in the table heading: For the Tropics, annual average for the years 2012 to 2016 have been calculated between 10°N and 10°S in a potential temperature range from 365 to 375 K. The tropical values for the observations are from the observations compiled in the 2018 WMO report (Engel and Rigby, 2018) in the tropics between 365 and 375 K potential temperature.

The latitude ranges for the extratropics are also stated as 40-60°N.

ML has been replaced by extratropics.

Figure 4: What are the horizontal and vertical bars? 1-2 sigma? Also, in the text it would be good to explain within the main text why for WISE_TACTS there are some points for which the mixing ratio as a function of△θ can be computed (△θ= 100), but not for the θ coordinate (θ= 420 K).

The following has been added to explain the error bars in the caption:

Both vertical and horizontal error bars denote 1 sigma variability.

The reason why sometimes sampling in △θ reaches higher values is that somtimes the tropopause is lower than the climatological tropopause. A sentence explaining this has been added in the main text:

Due to this different sampling a higher range in Δθ is achieved than in θ, as the actual tropopause altitude varies.

Figure 5: Consider introducing a dashed/dotted vertical line indicating the 40-60◦boundaries (and any other important latitude) used for the extra-tropics vertical pro-file computation.

We have considered this, but have decided against it, as we believe that this would highlight an area which is actually arbitrary and is only motivated by the comparison plots for the vertical profiles. No changes.

Figure 7: Consider reducing the length of the caption, and moving some of information at the end of the caption to the main text.

The caption length has been reduced by only using the acronyms of campaigns and models.

Figure 8: Specify output for this simulations is not in SD mode as for the other simulations (here and in the main text).

This was actually a mistake in the original manuscript. These EMAC simulations are in SD mode, but not for the correct time period. We modified the Figure caption:

"Model results are for nudged simulations of EMAC but do not cover the time period of our observations."

And in the text we have extended the following sentence:

Note that these simulations are only available for the time period up to 2011.

Figure 9-12: Consider including vertical dashed/dotted lines as suggested for Fig. 5.

We have considered this, but have decided against it, as we believe that this would highlight an area which is actually arbitrary and is only motivated by the comparison plots for the vertical profiles. No changes.

Also...for the model (right) panels: Why there are some "empty/blank" boxes within tropical lower stratosphere above 400K? Is that because of the vertical model resolution and/or upper limit of the models?

The reason for the blanc boxes is the vertical resolution of the model, as values are not interpolated, but rather shown as blanc where no values are available. A sentence has been added to explain this in the Figure captions:

Boxes in which due to the vertical resolution of the model no values are available are left blanc.

Figure 13: Have you considered the idea of expanding the lower latitudinal edge of the figure to 0◦Lat, and include the model/WMO results for the Tropical mean (as shown in Table 5)? Also, for the most poleward latitudinal bin, it looks like the "modelled" values are plotted at a higher latitude than the "observations". This must be due to the total number of data-points used to compute the VSLS value. This should be explained either in the caption or in the text.

We thank the reviewer for this valuable suggestion. The Figures 13 and also 6 have been extended in this way to include the tropical WMO values and also model values (Fig. 13) including a 0-20°N bin. We have also added a sentence explaining the different latitude centres:

Due to the different sampling of the observations and the models the centers of the different latitude bins are not the same for observations and models.

Figure 15: Why not including panel for WISE_TACTS in this figure?

This would add too many plots to the paper and we would also like to make clear that this is basically a sensitivity study, why it can be shown with one campaign only. The respective Figure has however been produced and is now shown in the appendix.

Reviewer # 3

The manuscript by Keber et al. describes measurements of short-lived organic bromine gases from several airborne campaigns in the UTLS mostly north of 40◦latitude in different seasons. The authors then evaluate how different combinations of models and emission scenarios compare to observations. The study is relevant to better quantifying the role of organic bromine in catalytic cycles that deplete stratospheric ozone. The main points of the paper are the demonstration of a latitudinal gradient in UTLS organic bromine, a winter maximum in VSL Br gases in the UTLS, recognition that VSL Br concentration near the extratropical tropopause is greater than that at the tropical tropopause, and that current emission scenarios show a range of imperfections that limit their accuracy. I might argue that all of these conclusions are not new, but the measurements, importantly, quantify the levels of UTLS organic Br that provide a solid basis for more detailed and quantitative analysis. Thus, the manuscript will be a valuable contribution to the further understanding of halogen chemistry in the lower stratosphere.

I think the strength of the manuscript is in the presentation of the data and identification of the seasonal and latitudinal variability in the measured Br gases. However, much of the paper focused on the model and emission scenario comparisons to the data. The authors state in their summary, "While it is not the main purpose of this paper to evaluate emission scenarios . . . " they nonetheless spend a large amount of effort to do just that, and they do so in more detail than is needed to demonstrate their point that models have problems. If model comparison to data is a significant part of the message, then I would like to see (perhaps in the Supplement) how the models compare to measurements for CFCs, halons, CH4 or other gases with better understood tropospheric distributions. Does model SF6 compare well to the binned measurements from these missions? This would help provide some

context for looking at the Br distributions and their deviations from model predictions. My suggestion, though, is not to add more model discussion in this paper, but to reduce the level of different comparisons to models that is done in the text and just highlight major issues associated with emission scenarios.

This suggestion (less model comparisons) is contradictory especially to reviewer #2, who actually suggested more model comparisons. We have chosen to include more model comparison in the appendix, but not in the main part of the paper. We also considered reducing the number of comparisons. This number is rather large, as 4 different combinations of emission scenarios and model are used. The extension to better constrained species (e.g. halons, CFCs etc) would indeed be an interesting aspect, but we feel that it is beyond the scope of this paper, as this would go into a model evaluation direction. Therefore, we have left the level of model comparison in the main text as it is. However, we agree with the reviewer that as a large part of the paper is devoted to comparing the observations with models and different scenarios, the statement "While it is not the main purpose of this paper to evaluate emission scenarios…" is odd. We have removed this statement.

I also had some trouble sorting through the different manipulations that the authors used to help with the comparisons between measurements and models. The authors go into great detail in how they adjusted and binned the data to presumably reduce variability from variations in dynamics and transport, and to provide a more robust comparisons to model outputs. While I would agree that these might be reasonable adjustments, I found the multiple presentations confusing and left me wondering about what I was viewing in the plots and how the data might look with no adjustments. Perhaps the authors can think about possibly simplifying (or better explaining) the discussion of the adjustments. Even though the goal of the adjustments was to reduce variability due to dynamical factors, the resulting distributions retained significant spread in the data, particularly within -+40K of the tropopause. The authors chose to focus on the average profiles, but it would seem that a more detailed evaluation of the variation (and its comparison to variance in a model) could produce interesting results on sources, transport and variability of Br in the critical region near the tropopause. Maybe a subsequent paper can do this.

The use of tropopause centred coordinates is something rather common in UTLS studies. It has also been shown by previous studies that variability is considerably reduced using these coordinates. Also, we have shown that the variability in our data is reduced when using tropopause centred coordinates, while the general shape and overall vertical profiles remain quite similar (see Figure 4 and tables 3 and 4, which uses tropopause centred coordinates in comparison to potential temperature). In order to make this point clearer, we have added some explanation of this in the section 3.1. on mean vertical profiles. The description has been updated for more clarity (see also comment by reviewer #1):

"For all campaigns, the variability averaged over the four lowest stratospheric bins when using $\Delta\theta$, was always lower than in the 4 lowest bins above the climatological tropopause using θ as a coordinate(see Tables 3 and 4). This shows that using the tropopause centered coordinate system $\Delta\theta$ reduces the variability in the stratosphere and that this coordinate system is thus best suited to derive typical distributions. In the troposphere, the variability is larger when using $\Delta\theta$ coordinates than for θ, indicating that the variability in the free troposphere is not influenced by the potential temperature of the tropopause."

We agree with the reviewer that a point-by-point discussion, which mal also include comparison of other species with better constrained lower boundary values may be the focus of a subsequent paper.

In section 5, I did not understand the need to go through the linear mixing model to show how the emission scenarios that placed high (or low) CH2Br2 (or CHBr3) in the tropical (or extratropical) tropopause were different from measured values. Data summarized in Table 5 is sufficient to demonstrate the impact of "incorrect" modeled organic Br in the tropics or extra tropics. Why go through assumptions that aren't necessarily realistic? Or you might be able to improve the mixing model with data from other gases, such as SF6, which can be used to perhaps better estimate tropical vs extratropical fractions of air.

The reason why we want to extend the study to the inorganic bromine is that inorganic bromine is the form which can participate in ozone chemistry and is thus what really needs to be known. Unfortunately, SF_6 from input of air from the tropics, respectively the extra-tropics cannot be distinguished and there is no straight forward way of determining these fractions. What would be needed would be tracers with linearly independent time series in the tropics and extra-tropics. This in parts possible with the combination of CO_2 and SF_6. However, this is a study on its own and high quality CO_2 data are needed which are not available for all missions of HALO. This is why we use estimates from previous studies and explicitly state that this is a sensitivity study and not meant to provide a robust value of how large model over- or underestimation of bromine from VSLS source gas injection is.

In order to explain better the interest in discussing possible effects on inorganic bromine, we have added a sentence in the introduction and also in the beginning of section 5:

Introduction:

"Source gases have to undergo a photochemical transformation first before the bromine is in the inorganic form which it can interact with ozone."

In section 5 the following sentence has been moved further upward to explain the importance of inorganic bromine earlier:

"Inorganic bromine is of key importance, as this is the form of bromine which can influence ozone through e.g. catalytic ozone depletion cycles."

To make the need for a mixing model clearer we have added two sentences in the introduction to section 5:

"The inorganic bromine from SGI can be derived as the difference between the organic bromine in the source region (tropopause) and the organic bromine still observed or modelled at a certain stratospheric location."

And a little further down the same paragraph:

"As both regions show different levels or organic bromine source gases, the relative contribution of these source regions needs to be known to derive total bromine which entered the stratosphere and thus also inorganic bromine from SGI."

Given the goal to provide a more robust assessment of the role of Br in the lowermost stratosphere at N latitudes, and given the availability of multiple models, I would have found valuable some discussion of the actual impact of different Br levels on the ozone budget of the impacted region. How does an uncertainty of -+ 1 ppt VSL Br propagate to modify ozone destruction rates?

While an uncertainty of 1 ppt of Bry will lead to different responses iin different regions. We have added a statement to give a rough context:

"For example, it has been shown that inclusion of about 5 ppt of Bry from VSLS leads to an expansion of the ozone hole area of ~5 million km^2 and an increase in maximum Antarctic ozone hole depletion by up to 14 % (Fernandez et al., 2017). The impact of bromine on ozone is most pronounced in the lowest part of the stratosphere (Hossaini et al., 2015)."

Other comments:

Minor VSL Br.

A) I would suggest adding profiles of the minor VSL Br in a Supplement.

Yes, they have been added to an appendix.

B) The authors state that "the observed decrease with altitude in the stratosphere is consistent with the relative lifetimes of the different compounds". While generally true, this does not seem to be the case for CHBrCl2 compared to CH2Br2 (page 7 line 15). Lifetimes of these compounds differ by a factor of about 3.5, but the gradients appear close to the same. Perhaps something is wrong with the lifetime estimate?

We have checked the lifetime estimates from Table 1, and they are in line with the WMO 2014 report. However, we observed that the values in Table 3 for the TACTS_WISE dataset where still from an older version. We therefore updated the values in Table 3. The values in Table 4 (PGS were correct).

CH_2BrCl_2 and CH_2Br_2 are not separated chromatographically during normal measurements of GhOST-MS, as this would require too much time (their physicochemical properties are very similar). Therefore, as shown in Sala et al. (2014), a procedure using an observed correlation between the two and of-line measurements of the relative sensitivities and the standard mixing ratios are used to determine CH2Br2 and CHBrCl2 from one single peak. During PGS and WISE the chromatography was tuned in order to separate the two peaks during individual flights (which results in a much poorer temporal resolution) to determine this correlation. We have explained this in brief and referenced to Sala et al. (2014) for a detailed explanation. It could be that the vertical gradient is more determined by lifetime for shorter lived compounds, whereas it is more determined by large scale transport for longer lived compounds. This would explain a decreasing dependency of the vertical gradient with increasing lifetime. We have i) briefly explained the procedure to derive CH2Br2 and CHBrCl2 mixing ratios and ii) added a short discussion on the lifetime dependency.

Explanation of separation of the two species in section 2.1.:
"As explained in Sala et al. (2014), CH_2BrCl_2 and CH_2Br_2 are not separated chromatographically during normal measurements of GhOST-MS, as this would require too much time. Instead, a correlation between the two species from either independent measurements or measurements of the two species from dedicated flights are used. Such dedicated flights have been performed during the WISE and the PGS campaign. The procedure how CH_2BrCl_2 and

CH_2Br_2 are derived from the single chromatographic peak with this additional information is explained in (Sala et al., 2014)."

Discussion of vertical gradients in section 3.1. has been rephrased and focussed on the shorter lived gases, where the relationship is clearer:

"Of all species discussed here, $CHBr_3$ showed the largest vertical gradients, followed by $CHBr_2Cl$. This is well in line with their atmospheric lifetimes (see Table 1), which will generally decreases with an increase in bromine atoms in the molecule and is shortest for $CHBr_3$, followed by $CHBr_2Cl$.The relationship between lifetime and vertical gradient is less clear for the longer lived species, where vertical profiles are expected to be more influenced by transport."

C) Tables1 and 3 show the mixing ratio of CH2BrCl as 0.1 – 0.2 ppt (100 – 200 ppq), but the GhOST-MS is reported in Table 1 to have a detection limit of 130 ppq (0.13 ppt). Not sure how this is possible. I note also that the GhOST-MS characteristics are quite different here compared to that reported in Sala et al. (2014). Was there a significant modification to the instrument? Uncertainties.

Yes, there was indeed a significant modification to the instrument: this is a change in the chemical ionisation (CI) gas. While we used pure Methane during SHIVA (Sala et al., 2014) and during TACTS, we had to change this to pure Argon (PGS) for safety reasons and then later to an Argon/Methane mixture (5% Methane, non burnable). Also, we checked the detection limits again. They were indeed much poorer during WISE than during other campaigns, mainly due to the change in CI gas. We have now also added the detection limits and LOD during TACTS and PGS to Table 1 and added a comment to that in the text:

"While CH_4 has been used as chemical ionization gas for the TACTS campaign and for the tropical measurements discussed in Sala et al. (2014), a change in chemical ionization gas was necessary for later measurements due to safety reasons. During the PGS campaign, we used pure Argon, which resulted in very good sensitivities but an interference with water vapour. In order to avoid this interference for the mid-latitude (more humid measurements) during WISE, a mixture of Argon and methane (non –burnable, below 5% Methane) was used as ionization gas. These (and some other) changes resulted in different performances of the instrument during different campaigns. Typical performance of the instrument is given for the WISE and PGS campaign in Table 1 for the brominated hydrocarbons."

The sentence referring to Table 1 two lines further down has been deleted. Table 1 has been modified to include both PGS and WISE characteristics. Also the Table header to Table 1 has been modified accordingly.

Page 6, top. Please report uncertainties associated with the total organic bromine levels reported here and elsewhere. Organic/Total Br . . . I second the recommendation of one of the other reviewers to be more careful in terminology of total bromine/total organic bromine, etc.

As explained above, we have revisited the manuscript to ensure that the use is now consistent. If total does not refer to the sum of organic and inorganic, it has been specified as total organic or total inorganic bromine.

With respect to the uncertainties we have added values for uncertainties in Tables 3 and 4. Note that these uncertainties are only observed variabilities (which are a combination of atmospheric variability and measurements uncertainties), but do not include uncertainties in calibration. As noted above, Table 3 has been updated to new values, as those given where based on a previous version of the evaluation software.

Data availability. I did not see that these data are available in any public archive. Please list how the data from these flights can be accessed.

Data availability information has been added.

Data availability

The observational data are available via the HALO Database (halo-db.pa.op.dlr.de/). The data of the ESCiMo simulations using the EMAC model will be made available in the Climate and Environmental Retrieval and Archive (CERA) database at the German Climate Computing Centre (DKRZ; http://cera-www.dkrz.de/WDCC/ui/Index.jsp); the simulations results of Graf (2017 are available upon request. TOMCAT model data will be uploaded to the Lancaster University data repository upon article acceptance. Access to data may be dependent on the signature of a data protocol.

Typo: Table 1 "Reproducibility: *changed*

Bromine from short–lived source gases in the extratropical Northern Hemisphere UTLS

Timo Keber[1], Harald Bönisch[1,2], Carl Hartick[1,3], Marius Hauck[1], Fides Lefrancois[1], Florian Obersteiner[1,2], Akima Ringsdorf[1,4], Nils Schohl[1], Tanja Schuck[1], Ryan Hossaini[5], Phoebe Graf[6], Patrick Jöckel[6] and Andreas Engel[1].

[1]University of Frankfurt, Institute for Atmospheric and Environmental Sciences, Altenhöferallee 1, 60438 Frankfurt, Germany
[2]now at Karlsruhe Institute of Technology, Institute of Meteorology and Climate Research, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.
[3]now at Research Centre Jülich, Institute for Agrosphere (IBG-3), Wilhelm-Johnen-Straße, 52428 Jülich, Germany
[4] now at Max Planck Institute for Chemistry, Hahn-Meitner-Weg 1, 55128 Mainz, Germany
[5]Lancaster Environment Centre, Lancaster University, Lancaster, UK.
[6] Institut für Physik der Atmosphäre, Deutsches Zentrum für Luft- und Raumfahrt (DLR), Oberpfaffenhofen, Germany

Correspondence to: Timo Keber and Andreas Engel (keber and an.engel@iau.uni-frankfurt.de)

Abstract.

We present novel measurements of five short-lived brominated source gases (CH_2Br_2, $CHBr_3$, CH_2ClBr, $CHCl_2Br$ and $CHClBr_2$). These rather short lived gases are an important source of bromine to the stratosphere, where they can lead to depletion of ozone. The measurements have been obtained using an in-situ gas chromatograph-mass spectrometer (GC-MS) system on board the High Altitude and Long Range Research Aircraft (HALO). The instrument is extremely sensitive due to the use of chemical ionisation, allowing detection limits in the lower parts per quadrillion (10^{-15}) range. Data from three campaigns using the HALO aircraft are presented, where the Upper Troposphere/Lower Stratosphere (UTLS) of the Northern Hemisphere mid to high latitudes were sampled during winter and during late summer to early fall. We show that an observed decrease with altitude in the stratosphere is consistent with the relative lifetimes of the different compounds. Distributions of the five source gases and total organic bromine just below the tropopause shows an increase in mixing ratio with latitude, in particular during polar winter. This increase in mixing ratio is explained by increasing lifetimes at higher latitudes during winter. As the mixing ratio at the extratropical tropopause are generally higher than those derived for the tropical tropopause, extratropical troposphere-to-stratosphere transport will result in elevated levels of organic bromine in comparison to air transported over the tropical tropopause. The observations are compared to model estimates using different emission scenarios. A scenario with emissions mainly confined to low latitudes cannot reproduce the observed latitudinal distributions and will tend to overestimate organic bromine input through the tropical tropopause from CH_2Br_2 and $CHBr_3$. Consequently, the scenario also overestimates the amount of brominated organic gases in the stratosphere. The two scenarios with the highest overall emissions of CH_2Br_2 tend to overestimate mixing ratios at the tropical tropopause but are in much better agreement with extratropical tropopause values, showing that not only total emissions but also latitudinal distributions in the emissions are of importance. While an increase in tropopause values with latitude is reproduced with all emission scenarios during winter, the simulated extratropical tropopause values are on average lower than the observations during late summer to fall. We show that a good knowledge of the latitudinal distribution of tropopause mixing ratios and of the fractional contributions of tropical and extratropical air is needed to derive stratospheric inorganic bromine in the lowermost stratosphere from observations. In a sensitivity study we find maximum differences of a factor 2 in reactive inorganic bromine in the lowermost stratosphere from source gas injection derived from observations and model outputs. The discrepancies depend on the emission scenarios and the assumed contributions from different source regions. Using better emission scenarios and reasonable assumptions on fractional contribution from the different source

regions, the differences in inorganic bromine from ~~S~~source gas injection between model and observations is usually on the order of 1 ppt or less. We conclude that a good representation of the contributions of different source regions is required in models for a robust assessment of the role of short-lived halogen source gases on ozone depletion in the UTLS.

1. Introduction

Following the detection of the ozone hole during springtime over Antarctica (Farman et al., 1985) and the attribution of the decline in both polar and global ozone to the emissions of man-made halogenated compounds (see e.g. Molina and Rowland, 1974;Solomon, 1999;Engel and Rigby, 2018), production and use of long-lived halogenated species, in particular chlorofluorocarbons (CFCs), have been regulated by the Montreal Protocol (WMO, 2018). This has led to decreasing levels of chlorine in the atmosphere (Engel and Rigby, 2018), despite recent concerns over ongoing emissions of CFC-11, which have been attributed to unreported and thus illegal production (Montzka et al., 2018;Engel and Rigby, 2018;Rigby et al., 2019). Bromine reaching the stratosphere has been identified as an even stronger catalyst for the depletion of stratospheric ozone than chlorine (Wofsy et al., 1975;Sinnhuber et al., 2009). Its relative efficiency on a per molecule basis is currently estimated to be 60-65 times larger than that of chlorine (see discussion in Daniel and Velders, 2006). Long-lived bromine gases include CH_3Br with partly natural and partly anthropogenic sources and halons, which are of purely anthropogenic origin. Next to long-lived gases, some chlorine and bromine from so-called "very short-lived substances" (VSLS), i.e. substances with atmospheric lifetimes less than 6 months, can reach the stratosphere. It has been estimated that for the year 2016, about 25% of the bromine entering the stratosphere is from VSLS (Engel and Rigby, 2018). Due to the decline in chlorine and bromine from long-lived species, the relative contribution of short-lived species to stratospheric halogen loading is expected to increase, also driven by increasing anthropogenic emissions of some short-lived chlorinated halocarbons (Hossaini et al., 2017;Oram et al., 2017;Leedham Elvidge et al., 2015;Engel and Rigby, 2018;Hossaini et al., 2019).

A number of factors control the abundance of ozone at mid-latitudes, including known important influences from dynamics, chemical destruction, aerosol loading and the solar cycle (e.g. Feng et al., 2007;Harris et al., 2008;Dhomse et al., 2015). In the lowermost stratosphere, the breakdown of VSLS provides a significant bromine source, in a region where (a) ozone loss cycles involving bromine chemistry are known to be important (e.g. Salawitch et al., 2005) and (b) on a per-molecule basis, ozone perturbations have a relatively large radiative effect (Hossaini et al., 2015). At present, VSLS are estimated to supply a total of ~5 (3-7) parts per trillion (ppt, 10^{-12}) Br to the stratosphere, with source gas injection estimated to provide 2.2 (0.8-4.2) ppt Br and product gas injection 2.7 (1.7-4.2) ppt Br (Engel and Rigby, 2018). Attribution of lower stratospheric ozone trends is complex and trends in this region are highly uncertain (Steinbrecht et al., 2017;Ball et al., 2018;Chipperfield et al., 2018). It has been suggested that continuing negative ozone trends observed in the lower stratosphere (defined as about 13 to 24 km in the mid latitudes) may partly be related to increasing anthropogenic and natural VSLS (Ball et al., 2018). While Chipperfield et al. (2018) suggested that the main driver for variability and trends in lower stratospheric ozone is dynamics rather than chemistry, the bromine budget of the upper troposphere and lower stratosphere (UTLS) needs to be well understood.

In the past, the main focus of upper tropospheric bromine studies for VSLS has been on the tropics, as this is the main entry region for air masses to reach above 380 K potential temperatures (see e.g. discussion in Engel and Rigby, 2018) and thus for the main part of the stratosphere. However, as many authors have shown, the lowermost stratosphere, i.e. the part of the stratosphere situated below 380 K but above the extratropical stratosphere, is influenced by transport from the tropics and from the extratropics (e.g. Holton et al., 1995;Gettelman et al., 2011;Fischer et al., 2000;Hoor et al., 2005). Some authors have quantified the fraction of air in the lowermost stratosphere, which did not pass the tropical tropopause from tracer measurements (Hoor et al., 2005;Boenisch et al., 2009;Ray et al., 1999;Werner et al., 2010) and others have used trajectory

analyses to study mass fluxes and stratosphere-troposphere exchange (e.g. Stohl et al., 2003;Wernli and Bourqui, 2002;Škerlak et al., 2014;Appenzeller et al., 1996). Based on tracer measurements of mainly CO, Hoor et al. (2005) estimated that the fraction of air with extratropical origin in the mid latitude lowermost stratosphere of the Northern Hemisphere ranged between about 35% during winter and spring to about 55% during summer and fall. Using a different approach based on CO_2 and SF_6 observations, Boenisch et al. (2009) found a similar seasonality but higher extratropical fractions, which were consistently higher than 70% during summer and fall and values above 90% in the entire lowermost stratosphere during October. Similarly, Boenisch et al. (2009) also derived much lower fractions of air with recent extratropical origin during winter and spring, which was sometimes as low as 20% during April. It has also been argued that the relative role of different source regions for the UTLS could alter with a changing circulation (Boothe and Homeyer, 2017).

Both extratropical and tropical source regions are important for the lowermost stratosphere. A recent compilation of entry mixing ratios of brominated VSLS to the stratosphere (Engel and Rigby, 2018) has focused on values representative of the tropical tropopause. Two pathways for input of halogens from short-lived gases are discussed. Halogen atoms can be transported to the stratosphere in the form of the organic source gas (~~:~~ Source Gas Injection (SGI)) or ~~, where the halogen is transported to the stratosphere in the form of the source gases;~~ in the inorganic form as photochemical breakdown products of source gases ~~and (~~Product Gas Injection (PGI))~~, where photochemical breakdown products of source gases are transported into the stratosphere, usually in inorganic form (i.e. Br_y).~~ Halogenes from product gases are readily available for catalytic ozone depletion reactions. Source gases have to undergo a photochemical transformation first before the bromine is in the inorganic form which it can interact with ozone.~~While halogens transported into the stratosphere due to PGI are usually directly in a form available for catalytic ozone depletion reactions, halogens from source gases must first be released in the stratosphere photochemically.~~ Due to the short lifetimes of VSLS, this release is expected to occur in the lowest part of the stratosphere. Therefore, brominated VSLS are particularly effective with respect to ozone chemistry in the lower and lowermost stratosphere, below about 20 km, with the associated- ozone decreases exerting a significant radiative effect (Hossaini et al., 2015). It has been shown that observed and modelled ozone show a better agreement if bromine from short-lived species is included in models (Sinnhuber and Meul, 2015;Fernandez et al., 2017;Oman et al., 2016). In particular for the Antarctic ozone hole, an enhancement in size by 40% and an enhancement in mass deficit by 75% was simulated due to VSLS (Fernandez et al., 2017) in comparison with a model run without VSLS. A delay in polar ozone recovery by about a decade has also been reported due to the inclusion of brominated VSLS (Oman et al., 2016). In order to have solid projections on the effect of VSLS on ozone and climate, a good knowledge of their atmospheric distribution is thus needed for models.

Observations indicate that the main source of brominated VSLS is ~~believed to be~~ from oceans and in particular from coastal regions. Four global emission scenarios of short-lived brominated gases have been proposed (Warwick et al., 2006;Ordóñez et al., 2012;Ziska et al., 2013;Liang et al., 2010)~~-~~, with variations in VSLS source strengths of more than a factor of two between them (Engel and Rigby, 2018). In the past, these scenarios have been compared to each other and to observations; large differences have been identified in modelled tropospheric mixing ratios of $CHBr_3$ and CH_2Br_2, along with estimates of stratospheric bromine input (Hossaini et al., 2013;Hossaini et al., 2016;Sinnhuber and Meul, 2015). Hossaini et al. (2013) concluded that the lowest suggested emissions of $CHBr_3$ (Ziska et al., 2013)) and the lowest suggested emissions of CH_2Br_2 (Liang et al., 2014) yielded the overall best agreement in the tropics and thus the most realistic input of stratospheric bromine from VSLS. They also concluded that "Averaged globally, the best agreement between modelled $CHBr_3$ and CH_2Br_2 with long-term surface observations made by NOAA/ESRL is obtained using the top-down emissions proposed by Liang et al. (2010)". It has also been proposed that VSLS emissions may have increased by 6-8 % between 1979-2013 (Ziska et al., 2017), although no observational evidence for this has been found (Engel and Rigby, 2018). A further future increase has been ~~projected~~ suggested (Ziska et al., 2017;Falk et al., 2017), although this projection is very uncertain and the processes associated

with the oceanic production of brominated VSLS are still poorly understood. It has also been proposed that certain source regions could be more effective with respect to transport to the stratosphere, in particular the Indian Ocean, the Maritime Continent and the tropical Western Pacific (Liang et al., 2014;Fernandez et al., 2014;Tegtmeier et al., 2012). The Asian monsoon has also been named as a ~~significant~~ possible pathway for transport of bromine from VSLS to the stratosphere (Liang et al., 2014;Fiehn et al., 2017;Hossaini et al., 2016).

While most investigations of natural VSLS focused on tropical injection of bromine to the stratosphere, in this study we focus on the extratropical bromine VSLS budget. In order to investigate the regional variability of bromine input into the lowermost stratosphere ~~and the inorganic bromine loading of the extratropical lowermost stratosphere~~, we have performed a range of airborne measurement campaigns using an in-situ gas chromatograph (GC) coupled to a mass spectrometer (MS) on board the High Altitude and Long Range Research Aircraft (HALO). ~~These observations are compared with results from state-of-the-art atmospheric models run with the different emission scenarios mentioned above.~~ The ~~implications~~ differences in~~for~~ stratospheric ~~reactive~~ inorganic bromine from observations and from models are discussed. In Section 2 we give a brief introduction into the instrument, the available observations and the models used for this study. Typical distributions of brominated VSLS derived from these observations are then presented in Section 3 and compared to model output from two different atmospheric models run with the different emission scenarios mentioned above in Section 4. Finally, in Section 5 the implications of the observations for inorganic bromine in the stratosphere are discussed.

2. Observations and models.

2.1. Instrumentation and ~~O~~observations

The data presented here have been measured with the in-situ **G**as C**h**romatograph for **O**bservational **S**tudies using **T**racers (GhOST-MS) deployed on board the HALO aircraft. GhOST-MS is a two channel GC instrument. ~~An isothermal channel uses an~~ An Electron Capture Detector (ECD) is used in an isothermal channel, in a similar set-up as used during the SPURT campaign (Boenisch et al., 2009;Boenisch et al., 2008;Engel et al., 2006) to measure SF_6 and CFC-12 with a time resolution of one minute. The second channel is temperature-programmed and uses a cryogenic pre-concentration system (Obersteiner et al., 2016;Sala et al., 2014) and a mass spectrometer (MS) for detection. It is similar to the set-up described by Sala et al. (2014) and measures halocarbons in the chemical ionization mode (e.g. Worton et al., 2008) with a time resolution of 4 minutes. As explained in Sala et al. (2014), CH_2BrCl_2 and CH_2Br_2 are not separated chromatographically during normal measurements of GhOST-MS, as this would require too much time. Instead, a correlation between the two species from either independeant measurements or measurements of the two species from dedicated flights are used. Such dedicated flights have been performed during the WISE and the PGS campaign. The procedure how CH_2BrCl_2 and CH_2Br_2 are derived from the single chromatographic peak with this additional information is explained in Sala et al. (2014). While CH_4 has been used as chemical ionization gas for the TACTS campaign and for the tropical measurements discussed in Sala et al. (2014), a change in chemical ionization gas was necessary for later measurements due to safety reasons. During the PGS campaign, we used pure Argon, which resulted in very good sensitivities but an interference with water vapour. In order to avoid this interference for the mid-latitude (more humid measurements) during WISE, a mixture of Argon and methane (non –burnable, below 5% Methane) was used as ionization gas. These (and some other) changes resulted in different performances of the instrument during different campaigns. Typical performance of the instrument is given for the WISE and PGS campaign in Table 1 for the brominated hydrocarbons.

The instrument is tested for non-linearities, memory and blank signals, which are corrected where necessary (see the description in Sala (2014) and Sala et al. (2014) for details). ~~Here we focus on the brominated hydrocarbons measured with GhOST-MS (see Table 1).~~ Table 1 also includes typical local lifetimes of the different VSLS species and the global lifetimes

of the long-lived species. The instrument was deployed during several campaigns of the German research aircraft HALO, providing observations in the UTLS over a wide range of latitudes and different seasons mainly in the Northern Hemisphere. Some observations from the Southern Hemisphere are also available, but due to their sparsity will not be part of this work.

GhOST-MS measurements from three HALO Missions will be presented and discussed here. The first atmospheric science mission of HALO was TACTS (Transport and Composition in the Upper Troposphere/Lowermost Stratosphere), conducted between August and September 201~~1~~2, with a focus on the Atlantic sector of the mid latitudes of the Northern Hemisphere. The second campaign was PGS, a mission consisting of three sub-missions: **P**OLSTRACC (The Polar Stratosphere in a Changing Climate), GW-LCYCLE (Investigation of the Life cycle of gravity waves) and **S**ALSA (Seasonality of Air mass transport and origin in the Lowermost Stratosphere). PGS took place mainly in the Arctic between December 2015 and March 2016. Finally, the GhOST-MS was deployed during the WISE (Wave driven isentropic exchange) mission between September and October 2017. The dates of the missions and some parameters on the available observations are summarized in Table 2 and the flight tracks are shown in Figures 1 and 2. As the WISE and TACTS campaigns covered a similar time ~~period~~ of the year and latitude range, we have chosen to present the results from both campaign in a merged format, i.e. the data from the two campaigns have been combined to single data set which we will refer to as "WISE_TACTS". For this combined data set, some observations from the TACTS campaign have been omitted, where some extremely high values of VSLS (up to a factor of 10 above typical tropospheric values) were observed in the UTLS which are suspected of being contaminated. The source of the contamination is, however, unknown. Figure 3 shows an example time series of Halon-1301 (CF_3Br), CH_2Br_2 and $CHBr_3$, ozone and mean age of air calculated from the SF_6 measurements obtained during a typical flight in the Arctic in January 2016. It is clearly visible that the halocarbons are correlated amongst each other, whereas they are anticorrelated with ozone and mean age. It is further evident from Figure 3 that the shortest-lived halocarbon measured by GhOST-MS, i.e. $CHBr_3$, decreases much faster with increasing ozone than the longer-lived CH_2Br_2 or the long- lived source gas Halon 1301. Note that the local lifetimes of the halocarbons may differ significantly from their typical mid latitude lifetimes shown in Table 1. Lifetimes generally increase with a) decreasing temperature for species with a sink through the reaction with the OH radical and b) with decreasing solar irradiation for species with direct photolytic sink. Therefore, in particular during winter, lifetimes are estimated to increase considerably with increasing latitude due to the decreased solar illumination and low temperatures.

~~2.~~2.2 Models and m~~M~~eteorological ~~D~~data

Data from two different models were used in this study: ESCiMo (Earth System Chemistry Integrated Modelling) data from the EMAC (ECHAM/MESSy Atmospheric Chemistry) chemistry climate model (CCM) and the TOMCAT (Toulouse Off-line Model of Chemistry And Transport) chemistry transport model (CTM).

For EMAC data, we used results from the simulations in the so-called specified dynamics mode, for which the model was nudged (by Newtonian relaxation) towards ERA-Interim meteorological reanalysis data from European Centre for Medium-Range Weather Forecasts (ECMWF; (Dee et al., 2011). T42 spectral model resolution was used, corresponding to a quadratic Gaussian grid of approximately 2.8° by 2.8° horizontal resolution, and the vertical resolution comprised 90 sigma-hybrid pressure levels up to 0.01 hPa. The model output has been subsequently interpolated to pressure levels between 1000 and 0.01 hPa. The emissions of VSLS were taken from the emission scenario 5 in Warwick et al. (2006). The model setup for the ESCiMo simulation is described in detail by Jöckel et al. (2016). For the results presented in this paper, EMAC was operated in the so-called specific dynamics mode, in which the synoptic scale meteorology is relaxed towards meteorological reanalysis data. The EMAC SD-simulations with 90 vertical levels, as described in detail by Jöckel et al. (2016), were integrated with an internal model time step length of 12 minutes and the data has been output every 10 hours from which the monthly averages

on pressure levels have been derived. The SC1SD-base-01 simulation which has been used here has been branched off from RC1SD-base-10 (see Jöckel et al., 2016) at January 1, 2000 using the RCP8.5 emissions and greenhouse gas scenario.

The TOMCAT ~~(Toulouse Off-line Model of Chemistry And Transport)~~ model (Chipperfield, 2006;Monks et al., 2017) is driven by analyzed wind and temperature fields taken 6-hourly from the ECMWF ERA-Interim product. Here, the model was run with T42 horizontal resolution (2.8° by 2.8°) and with 60 vertical levels, extending from the surface to ~60 km. The internal model time step was 30 minutes and tracers were output as monthly means. This configuration of the model has been used in a number of VSLS-related studies and is described by Hossaini et al. (2019).~~—~~ In this study, three different VSLS emission scenarios are used with TOMCAT (Liang et al., 2010;Ordóñez et al., 2012;Ziska et al., 2013). In the case of the Liang et al. scenario, their scenario A has been used. ~~-~~Chemical breakdown by reaction with OH and photolysis in the model for all VSLS ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$ and $CHBrCl_2$) are calculated using the relevant kinetic data from Burkholder et al. (2015). ~~Emitted VSLS ($CHBr_3$, CH_2Br_2, CH_2BrCl, $CHBr_2Cl$ and $CHBrCl_2$) are destroyed by reaction with OH and photolysis in the model, calculated using the relevant kinetic data from Burkholder et al. (2015).~~

Local tropopause information for the flights with HALO have been derived from ERA-interim data (J.U.Grooß, FZ Jülich, private communication). The climatological tropopause has been calculated based on potential vorticity (PV) according to the method described in Škerlak et al. (2015) and Sprenger et al. (2017) based on the ERA-Interim reanalysis. ~~(M. Sprenger, ETH Zürich, private communication).~~ As the PV tropopause is not physically meaningful in the tropics, the level with a potential temperature of 380 K has been adapted for the tropopause where the 2-PVU (Potential Vorticity Unit) level is located above the 380-K level.

3. Observed distribution and atmospheric gradients of different brominated VSLS

Spatial distributions are shown in tropopause-relative coordinates and as functions of equivalent latitude. As equivalent latitude is mainly a useful horizontal coordinate for the stratosphere, we chose to use standard latitude for all measurements below the tropopause and equivalent latitude for all measurements above the tropopause. We refer to this coordinate as equivalent latitude*. As the observations typically cover a range of latitudes, vertical profiles are shown for 20° bins. In the vertical direction, three different coordinates are used in this paper. These are potential temperature θ, potential temperature above the local tropopause $\Delta\theta$, and finally a coordinate we refer to as θ^*, which is calculated by adding the potential temperature of the mean tropopause to $\Delta\theta$. We used the dynamical tropopause, defined by a potential vorticity value of 2 PVU or by a potential temperature value of 380 K in the tropics (see Section 2), as a reference surface.

3.1 Mean vertical profiles.

All measurements from the individual campaigns have been binned into 10 K potential temperature bins between -40 and 100 K of $\Delta\theta$. ~~In addition, we have also binned the data in~~For ~~-~~potential temperature binning, the 10 K bins have been chosen ~~in 10 K potential temperature intervals~~ ranging from 40 K below the mean tropopause to 100 K above the mean tropopause. In this way, the centers of the $\Delta\theta$ and θ bins are the same relative to the mean tropopause observed during the ~~campaign~~measurements. The results are presented for the two main VSLS bromine ~~species~~ source gases CH_2Br_2 and $CHBr_3$, averaged over equivalent latitude* of 40-60°N in Figure 4 for ~~the~~ PGS (Northern Hemispheric winter) ~~campaign~~ and the WISE_TACTS combined data set ~~representing (L~~late summer to fall, Northern Hemisphere) ~~conditions~~. Only bins which contain at least five data points have been included in the analysis. The results are also summarized in Tables 3 and 4 for the same latitude intervals for all species and for total organic bromine derived from the five brominated VSLS. The tropopause mole fractions shown in Tables 3 and 4 have been derived as the average of all values in that latitude interval and within 10 K below the tropopause. The potential temperature of the average tropopause has been used for θ averaging, while the potential

temperature difference to the local tropopause has been used as reference when averaging in $\Delta\theta$ coordinates. Due to this different sampling a higher range in $\Delta\theta$ is~~a~~ achieved than in θ, as the actual tropopause altitude varies. We have checked the validity of using means to represent the data, by comparing means and medians. Differences were always below 5% of the mean tropopause values. We have thus chosen to use means throughout this paper. The uncertainties given in all Figures are 1 sigma standard deviations of these means, both for the vertical and horizontal error bars. In the WISE_TACTS data set, total organic bromine at the dynamical tropopause between 40 and 60 °N was ~~3.4~~4.0~~-~~5 and ~~3.6~~3.5 ppt, using $\Delta\theta$ and θ as vertical coordinates, respectively. Higher values of total organic bromine were found during the winter campaign PGS, when average tropopause values were 5.2 and 4.9 ppt both using $\Delta\theta$ and θ as vertical coordinates. These values are considerably higher than the tropical tropopause values of organic bromine derived in the vicinity of the tropical tropopause (Engel and Rigby, 2018) as will be discussed in detail below. When using the WMO definition of the tropopause, the total organic bromine at mid-latitudes was ~~about 0.3 to~~lower by up to 0.5 ppt lower than using the PV tropopause, reflecting the fact that the WMO tropopause is usually slightly higher than the dynamical tropopause using the 2 PVU definition (e.g. Gettelman et al., 2011).

Of all species discussed here, $CHBr_3$ ~~CH_2BrCl~~ showed the ~~smallest~~ largest vertical gradients, followed by $CHBr_2Cl$. ~~and $CHBr_3$ the largest.~~ This is well in line with their atmospheric lifetimes (see Table 1), which will generally decreases with an increase in bromine atoms in the molecule ~~which~~ and is shortest for $CHBr_3$~~–~~, followed by~~and longest for CH_2BrCl.~~ $CHBr_2Cl$.~~–~~The relationship between lifetime and vertical gradient is less clear for the longer lived species, where vertical profiles are expected to be more influenced by transport. ~~showed the second strongest vertical gradients, while CH_2Br_2 and $CHBrCl_2$ usually showed comparable relative decreases with altitude, again in line with the atmospheric lifetime, which will generally decrease with an increase in bromine atoms in the molecule.~~ The strongest vertical gradients with respect to both θ and $\Delta\theta$ were observed during the winter campaign PGS, with the exception of $CHBr_3$, which was nearly completely depleted for all campaigns at 40 K above the tropopause and thus shows very similar averaged gradients over this potential temperature region. When evaluated only for the first 20 K above the tropopause, the gradient of $CHBr_3$ was also highest during PGS. The short lifetime and strong vertical gradient of $CHBr_3$ is also reflected in the largest relative variability (see Tables 3 and 4).

We further determined the variability of the different species in 10 K intervals of θ and $\Delta\theta$. For all campaigns, the variability averaged over the four lowest stratospheric bins ~~was always lower~~ when using $\Delta\theta$, was always lower than in the 4 lowest bins above the climatological tropopause using θ as a coordinate(see Tables 3 and 4). This shows that using the tropopause centered coordinate system $\Delta\theta$ reduces the variability in the stratosphere and that this coordinate system is thus best suited to derive typical distributions. In the troposphere, the variability is ~~very similar~~larger when using $\Delta\theta$ coordinates than for ~~for~~ θ ~~and $\Delta\theta$ coordinates~~, indicating that the variability in the free troposphere is not ~~strongly~~ influenced by the potential temperature of the tropopause. The observed variabilities were found to be very similar for the WMO and PV tropopause definitions (not shown). As the dynamical PV tropopause is generally expected to be better suited for tracer studies, we decided to reference all data to the dynamical tropopause.

3.2. Latitude altitude cross sections

We slightly diverge from the coordinate system used to present zonal mean latitude-altitude distributions used in previous work (e.g. Boenisch et al., 2011;Engel et al., 2006), where ~~present the latitudinal distribution as a zonal mean and using~~ equivalent latitude and potential temperature were used as horizontal and vertical coordinates. ~~However, we propose a somewhat different approach here, in which~~ We use equivalent latitude* ~~is used~~ as a horizontal coordinate, i.e. latitude for all tropospheric observations and equivalent latitude for observations at or above the tropopause. As a vertical coordinate we have chosen to use a modified potential temperature coordinate~~, which we refer to as~~ θ^* (see explanation above, section 3.)~~and which is calculated by adding the potential temperature of the climatological tropopause to $\Delta\theta$.~~ In this way, all measurements are presented relative to a climatological tropopause, which has been derived from ERA-Interim reanalysis as zonal mean for the latitude of interest and the specific months of the campaign (see Section 2 for campaign details). This is expected to reduce

variability by applying the information from $\Delta\theta$, yet the absolute vertical information is also maintained. In order to ensure that this tropopause value is representative also for the period of our observations, we compare the potential temperature of the campaign-based tropopause~~, averaged for all the location and times when we have observations,~~ with th~~e~~is climatological tropopause. The campaign based tropopause has been calculated by averaging the tropopause at all locations for which observations are available during the campaign. For the latitude band between 40 and 60°N, the climatological PV tropopause for the TACTS_WISE time period was derived to be at 329 K, in excellent agreement with the campaign-based tropopause, which was also at 329 K. For the PGS campaign, both the climatological tropopause and the campaign-based tropopause were found to be at 312 K. In contrast to the campaign-based tropopause, the climatological tropopause is also available for latitude bands and longitudes not covered by our observations and will be more representative for typical conditions during the respective season and latitude.

Figure 5 shows the distributions of the two main VSLS bromine source gases CH_2Br_2 and $CHBr_3$ in the coordinate system discussed above for the two campaign seasons (PGS: winter; WISE_TACTS: late summer to early fall). The data have been binned in 5° latitude and 5 K intervals of the modified potential temperature coordinate θ^*. As expected, the distributions closely follow the tropopause (indicated by the dashed line), with values decreasing with distance to the tropopause and also with increasing equivalent latitude. The distributions observed during the WISE and the TACTS campaigns show ~~significant amounts~~rather high levels of CH_2Br_2~~,~~ in the lower stratosphere, with a depletion of only about 35% at 40-50 K above the tropopause. This is consistent with~~which has a~~ the rather long lifetime of CH_2Br_2 in the cold upper troposphere and lower stratosphere (Hossaini et al., 2010)~~ even quite deep into the stratosphere~~. The shorter-lived $CHBr_3$ is ~~strongly~~ depleted by about 85% already a~~tbout~~ 20-30 K above the tropopause during the winter campaign PGS. In the case of the winter campaign PGS, values close to zero at the highest flight altitudes~~levels~~ are also observed for the longer-lived CH_2Br_2, indicating that in the most stratospheric air masses observed during PGS nearly all bromine from VSLS has been converted to inorganic bromine. This ~~is~~ stratospheric character is in agreement with the observation of air masses with very high mean age of air derived from SF_6 observations of GhOST-MS (see e.g. Figure 3), reaching up to 5 years for the oldest air (not shown). This is air which has descended inside the polar vortex and has not been in contact with tropospheric sources for a long time, allowing even the longer-lived CH_2Br_2 to be nearly completely depleted.

3.3. Upper tropospheric latitudinal gradients

If air is transported into the lowermost stratosphere via exchange with the extratropical upper troposphere, the levels of organic bromine compounds are likely to be different than for air being transported into the stratosphere via the tropical tropopause. In order to investigate the variability and the gradient in the upper tropospheric input region, we binned our data according to latitude and to potential temperature difference to the tropopause. All data in a range of 10 K below the local dynamical tropopause have been averaged ~~In order~~ to characterize the upper tropospheric input region.~~, we have chosen to average all data in a range of 10 K below the local dynamical tropopause~~. ~~Again, F~~f~~or these upper tropospheric data, standard latitude has been chosen and not~~, while~~ equivalent latitude as for the stratospheric data~~was used for all data with $\Delta\theta$ above zero~~. The latitudinal gradients are shown in Figure 6 for CH_2Br_2, $CHBr_3$ and total organic bromine derived from the sum of all VSLS (including the mixed bromochlorocarbons CH_2BrCl, $CHBrCl_2$ and $CHBr_2Cl$), each weighted by the amount of bromine atoms. For the tropical tropopause, input values from different measurement campaigns have recently been reviewed by Engel and Rigby (2018). They found that total organic bromine from these five compounds averaged between 375 and 385 K, i.e. around the tropical tropopause was 2.2 (0.8-4.2) ppt, and in the upper TTL (365-375K potential temperature) was around 2.8 (1.2-4.6) ppt. These upper TTL values have also been included as reference Figure 6 (see also Table 5). The average values derived here for the 10 K interval below the extratropical tropopause are ~~significantly~~ larger. For the late summer to early fall data from TACTS and WISE (Table 3), they increase from 2.6 ppt around 30°N (20-40° N equivalent latitude*) to 3.8 ppt around 50°N

(40-60°N equivalent latitude*), while no further increase is found for higher latitudes with a value of 3.4 ppt. For the winter measurements during PGS (Table 4) a clear increase with latitude is observed from 3.3 ppt around 30°N (20-40°N equivalent latitude*) to 3.8 ppt around 50°N (40-60°N equivalent latitude*) to 5.5 ppt in the high latitudes (60-80°N equivalent latitude*). There is considerable variability in these values derived ~~around the tropopause~~in the upper troposphere, due to the short lifetime of these compounds and the high variability in emissions depending on the source region. Nevertheless, there is a clear tendency for an increase in tropopause values with latitude, particularly during Northern Hemisphere winter. This is most probably related to the increase in lifetime with latitude, as especially during the wintertime PGS campaign the photolytical breakdown in higher latitudes is ~~significantly~~ slower than in lower latitudes. Additional effects due to the sources and their latitudinal, seasonal and regional variability cannot be excluded. However, we note that emissions are most likely to be largest during summer, as shown e.g. in Hossaini et al. (2013), which would not explain the large values of brominated VSLS in the upper troposphere in high latitudes during winter.

4. Comparison with model derived distributions.

As bromocarbons are an important source of stratospheric bromine, it is worthwhile to investigate if current models can reproduce the observed distributions shown in Section 3. This is a prerequisite~~, and are thus able~~ to realistically simulate the input of bromine from VSLS source gases to the stratosphere, but also the further chemical breakdown and the transport processes related to the propagation of these gases in the stratosphere. As explained in Section 2, we used two different models, with different emissions scenarios for the brominated very short-lived source gases. The ESCiMo simulation results from the chemistry climate model EMAC (Jöckel et al., 2016) are based on the emission scenario by Warwick et al. (2006), while the TOMCAT model (Hossaini et al., 2013) was run with three different emission scenarios (Ordóñez et al., 2012;Ziska et al., 2013;Liang et al., 2010). Both models have been used in the past to investigate the effect of brominated VSLS on the stratosphere (e.g. Sinnhuber and Meul, 2015;Hossaini et al., 2012;Wales et al., 2018;Hossaini et al., 2015;Graf, 2017). For the EMAC model, we have chosen to use results from a so called "specified dynamics" simulation, which has been extended from the ESCiMo simulations to cover our campaign time period (see Section 2). The model data have been extracted for the time period and latitude ranges of the observations and have been zonally averaged. Here we compare vertical profiles, ~~geographical distributions~~latitude-altitude cross sections and latitudinal gradients between our observations and the model results, in a similar way as the observations have been presented in Section 3. We also compare results for total organic bromine. Only the scenarios of Warwick et al. (2006) and Ordóñez et al. (2012) contain emissions of the mixed bromochlorocarbons CH_2BrCl, $CHBrCl_2$ and $CHBr_2Cl$. For the calculation of total VSLS organic bromine based on the emission scenarios by Liang et al. (2010) and Ziska et al. (2013) we have therefore adopted the results from the TOMCAT model using the emissions by Ordóñez et al. (2012). The contribution from these mixed bromochlorocarbons to total VSLS organic bromine are typically on the order of 20%, while about 80% of total VSLS organic bromine in the upper troposphere and lower stratosphere is due to CH_2Br_2 and $CHBr_3$. This relative contribution of 20% from minor VSLS is found in our observations (Tables 3 and 4) as well as in the values compiled in Engel and Rigby (2018) (see Table 5) and is slightly larger than that derived e.g. in Fernandez et al. (2014).

4.1. Mean vertical profiles.

Observed vertical profiles are available up to the maximum flight altitude of the HALO aircraft, which is about 15 km, corresponding to about 400 K in potential temperature. Due to the variability of the tropopause potential temperature, this translates into maximum values of $\Delta\theta$ of about 100 K. The emphasis of this Section is on the mid latitudes of the northern hemisphere, i.e. values averaged between 40 and 60° equivalent latitude*. All comparison are shown as function of $\Delta\theta$. As no direct tropopause information was available for the TOMCAT output, we have chosen to derive $\Delta\theta$ for this comparison from the difference between model potential temperature and the potential temperature of the climatological zonal mean tropopause,

which has been derived as explained in Section 2. As we are comparing our observations to the models in tropopause relative coordinates, ~~W~~we have also compared this climatological tropopause with the tropopause derived from the EMAC model results for the time of our campaigns. The potential temperature of the EMAC tropopause and the climatological tropopause differed by less than 3 K for all campaigns at mid latitudes.

Figure 7 presents the model-measurement comparisons for the two main VSLS bromine ~~species~~ source gases for the winter PGS campaign and for the combined dataset from WISE and TACTS. Overall the Liang et al. (2010) and the Ordoñez et al. (2012) emission scenarios give the best agreement with our observations of CH_2Br_2, with an averaged deviation of 0.1 ppt or less, averaged over all campaigns and all stratospheric measurements in the 40-60°N equivalent latitude band, corresponding to a mean absolute percentage difference (MAPD) on the order of 10-25%. Using the Ziska et al. (2013) emissions, CH_2Br_2 is overestimated in the mid latitude lowest stratosphere during both campaigns by about 0.2 ppt, corresponding to about 40-60% ~~overestaimtion~~overestimation. Using the Warwick et al. (2006) emissions in the EMAC model, the overestimation is even larger with 0.25-0.3 ppt, corresponding to 50-70%. As $CHBr_3$ is nearly completely depleted in the upper part of the profiles, differences will become negligible there. Therefore, we only compared values in the lowest 50 K potential temperature above the tropopause. In this region, the best agreement is again found with the Liang et al. (2010) and Ordoñez et al. (2012) emission scenarios, with mean differences always below 0.1 ppt, corresponding to about a MAPD of 20-30%. Using the Ziska et al. (2013) emission scenario we find an underestimation on the order of 0.05-0.1 ppt (40-70%), while $CHBr_3$ is overestimated by about 0.15 ppt (120-180%) in the EMAC model based on the Warwick et al. (2006) emission scenario.

Using the Ziska et al. (2013) emission scenario, the overestimation of CH_2Br_2 and the underestimation of $CHBr_3$ tend to cancel out. When adding the contribution from minor VSLS based on the scenario by Ordóñez et al. (2012)~~,~~ this results ~~resulting~~ in a reasonable agreement in total VSLS organic bromine. ~~Because of the different chemical lifetimes of the two species, this results in a wrong vertical distribution of Br_y with too high mixing ratios above 20 K above the tropopause in winter and a much steeper vertical gradient in late summer.~~ The EMAC model with the Warwick et al. (2006) emissions ~~significantly~~ substantially overestimates both CH_2Br_2 and $CHBr_3$ in the lowermost stratosphere of the mid latitudes. The vertical profiles of CH_2Br_2 and $CHBr_3$ from the EMAC model with the Warwick et al. (2006) emission scenario is therefore completely different from the observations, showing a maximum around the tropopause or even above.

We additionally compare model data from EMAC simulations using all four emission scenarios (Graf, 2017) ~~I~~in order to investigate if th~~e~~is large deviation ~~when using the EMAC model with~~of the Warwick et al. (2006) emission scenario is due to the EMAC model~~model~~ or due to the specific emission scenario.~~, we additionally compare model data from EMAC simulations using all four emission scenarios (Graf, 2017). Note that t~~hese simulations are only available for the time period up to 2011 ~~and not in the specified dynamics mode~~. This comparison for the January-March period (representative for the PGS campaign) is shown in Figure 8 for CH_2Br_2 and $CHBr_3$. Fig. 8 looks qualitatively very similar to the comparisons in Figure 7, i.e. both CH_2Br_2 and $CHBr_3$ using the Warwick et al. (2006) emission scenario show highest values in the lower stratosphere and $CHBr_3$ shows the least pronounced vertical gradients. Also, the pattern for the Ziska et al. (2013) emission scenario are the same, with second highest CH_2Br_2 values and lowest $CHBr_3$ values. Differences between the different models are certainly a factor in the explanation of model-observation differences. ~~It is therefore~~ However, it is ~~-~~clear that the ~~observed~~ pattern when comparing all scenarios in the EMAC model is similar to that described above and that differences ~~are not primarily caused by the model but rather by~~in the emission scenarios are the main driver of model-observation differences.

4.2. Latitude altitude cross sections

As has been shown in the comparison of the vertical profiles, ~~significant~~ differences between model results and observations are found, especially in the case of the Ziska et al. (2013) emissions in the TOMCAT model and in case of the Warwick et al. (2006) emissions in the EMAC model for the Northern Hemisphere mid latitudes (40-60°N). To visualize these differences, we present latitude-altitude cross sections of the model data sets and the differences to our observations in Fig. 9 ~~and~~ to ~~10~~12.

~~Again, we use~~While we use equivalent latitude* as the latitudinal coordinate for the observations and θ^* as vertical coordinate~~.~~ ~~For the model results~~, the zonal mean data are displayed as function of latitude and potential temperature θ for the model results. The comparison is shown here for the winter data set from PGS, for which the observational set covers a wide range of latitudes and also reaches very low tracer mole fractions. The comparison for the late summer to fall campaigns (TACTS and WISE) gives a rather similar picture (not shown). The overall best agreement in the vertical profiles has been found for the TOMCAT model using the emissions scenarios by Liang et al. (2010) and Ordóñez et al. (2012)~~Ordonez et al. (2012)~~. The latitude-altitude cross section for these two datasets ~~are~~ is ~~therefore~~ shown in Figure 9 and 10. Using these two emissions scenarios, the TOMCAT model tends to overestimate high latitude tropospheric mole fractions of $CHBr_3$ during this winter campaign. However, the stratospheric distribution is rather well reproduced with absolute deviations to the model mostly being below 0.1 ppt. In the case of CH_2Br_2, overall stratospheric mole fractions are slightly larger in the model results compared to the observations. The deviations between the TOMCAT model using the Ziska et al. (2010) emissions and the EMAC model using the Warwick et al. (2006) emissions are ~~significantly~~ substantially larger. These are shown in Figures 11 and 12 again for the PGS campaign. As noted above, the TOMCAT model with the Ziska et al. (2013) emissions overestimates stratospheric CH_2Br_2, while stratospheric $CHBr_3$ is reasonably well captured. The largest discrepancies between model and observations are observed in the case of the EMAC model with the Warwick et al. (2006) emissions. In this case, both CH_2Br_2 and $CHBr_3$ are overestimated ~~significantly~~ in the lower stratosphere.

~~The direct comparison of the distributions between the different model data sets is also interesting.~~ In the case of $CHBr_3$, the two emission scenarios which have a more even distribution of emissions with latitude, i.e, the emission scenarios by Liang et al. (2010) and Ordoñez et al. (2012) show the best agreement with the observations. The emission scenario by Warwick et al. (2006) yields much higher mole fractions in the tropics and has the poorest agreement with measurement data. The emission scenario by Ziska et al. (2013) yields overall much lower $CHBr_3$ in large parts of the atmosphere and seems to be the only setup in which mid latitude tropopause mole fractions of $CHBr_3$ are underestimated in comparison to our observations. For CH_2Br_2, again the Ordoñez et al. (2012) and Liang et al. (2010) emission scenarios in the TOMCAT model result in rather similar distributions and rather good agreement with our observations. In the case of the TOMCAT model with the Ziska emissions, very high mole fractions of CH_2Br_2 are simulated throughout the tropics. Our low latitude observations from HALO during late summer and fall (WISE and TACTS) and the values compiled in the WMO 2018 report for the tropics (Engel and Rigby, 2018) are ~~much~~ lower ~~than~~ by about 0.3-0.5 ppt than the values of CH_2Br_2 in the tropics using the Warwick et al. (2006) and Ziska et al. (2013) emissions. The latitudinal distribution in the upper troposphere in models and observations is therefore investigated in more detail in the next section.

4.3. Upper tropospheric latitudinal gradients

The input of organic bromine into the stratosphere is crucial in understanding the stratospheric bromine budget and, therefore, also in determining the amount of inorganic bromine available for catalytic reactions involved in ozone depletion. For air masses in the stratosphere above about 400 K, it is generally assumed that the input is nearly exclusively through the tropical tropopause. For the lowermost stratosphere, however, input via the extratropical tropopause is also expected to play an important role (e.g. Holton et al., 1995;Gettelman et al., 2011). In order to investigate if the models are able to represent the latitudinal gradient in upper tropospheric mole fractions~~Therefore~~, we compare the observed extratropical mole fractions of the brominated VSLS in the upper troposphere (section 3.3) and compiled tropical observations (Engel and Rigby, 2018) with those determined from the different model setups~~, in order to investigate if the models are able to represent the latitudinal gradient in upper tropospheric mole fractions~~. For this purpose, the model data have been averaged in an interval of 10 K below the climatological (TOMCAT), or respectively modelled (EMAC), tropopause. The results are shown for the two main bromine VSLS, CH_2Br_2 and $CHBr_3$, as well as for total VSLS organic bromine in Figure 13 and table 5 for the two campaign periods in comparison to observations. Note that for the scenarios by Liang et al. (2010) and Ziska et al. (2013), no estimates

of emissions for the mixed bromochlorocarbons are available; instead, we have used the model results based on the Ordóñez et al. (2012) ~~Ordonez et al. (2012)~~ emissions for the calculation of total VSLS organic bromine.

During the two campaigns in late summer to fall (TACTS and WISE), all model setups show a decrease of CH_2Br_2 mixing ratios with latitude. Although, the latitudinal gradients are much steeper when the scenarios by Warwick et al. (2006) and Ziska et al. (2013) are used, which is due to overestimated values at low latitudes. This is in good agreement with findings by Hossaini et al. (2013), who showed that TOMCAT using the Warwick et al. (2006) emission scenario ~~significantly~~ overestimated HIAPER Pole-to-Pole Observations (HIPPO) in Northern Hemisphere mid latitudes. An increase in observed mixing ratios with latitude was found, especially during the winter PGS campaign, which is presumably related to the increase in atmospheric lifetime of compounds in the cold and dark high latitude tropopause region during winter. This feature is qualitatively reproduced by the TOMCAT simulations with Liang et al. (2010) and Ordóñez et al. (2012) ~~Ordonez et al. (2012)~~ scenarios, but not for the Ziska et al. (2013) and Warwick et al. (2006) scenario based results, which show a moderate decrease and no latitudinal gradient. This feature is consistent with emissions in these two scenarios being more strongly biased towards the tropics.

For $CHBr_3$, the observations show an increase with latitude, especially during the PGS campaign. The late summer to fall data from TACTS and WISE show a less clear picture, with an increase between the subtropics and mid latitudes but a decrease towards high latitudes. This general tendency during the wintertime is reproduced by the TOMCAT model using all emission scenarios. ~~Nontheless~~Nonetheless, the gradient in the EMAC model results with the Warwick et al. (2006) emissions is reversed, which is mainly caused by the ~~extremely high~~larger tropical mixing ratios, also evident from the latitude altitude cross sections shown before. We also note that the sub-tropical values based on the Ziska et al. (2013) emissions are lower than the observations.

The results for total organic bromine, including the three mixed bromochlorocarbons, can be mainly understood as a combination of the behavior of CH_2Br_2 and $CHBr_3$. In the case of the TOMCAT model with Ziska et al. (2013) emissions, a certain compensation is observed, i.e. total organic bromine is better reproduced than each compound by itself. This is due to an overestimation of CH_2Br_2, especially at low latitudes and an underestimation of $CHBr_3$. Total organic bromine from VSLS in the EMAC model using the Warwick et al. (2006) emissions is very different from the observations. It shows nearly constant values with latitude during northern hemispheric winter (PGS) and a strong decrease during the late summer to fall period of the TACTS and WISE campaigns. Most importantly, the overall levels, especially in the low latitudes, are much higher than our observations and also much higher than the tropical observations compiled in the WMO report (Engel and Rigby, 2018). We also note that poleward of 40°N and below 320 K (see Figures 9 and 10) there is a small negative model bias for CH_2Br_2 at the extratropical tropopause when using the scenarios by (Liang et al., 2010) and (Ordóñez et al., 2012). At the same time the model simulations using these two scenarios yield a substantial positive bias for $CHBr_3$ in the same region. ~~This will result in too much VSLS bromine being simulated in the stratosphere, and therefore also in~~this will result in a misrepresentation of the input of brominated VSLS source gases to the lowermost stratosphere via the different pathways.

5. Implications for stratospheric inorganic bromine

As shown in the previous Section, ~~significant~~ discrepancies exist between the various combinations of models and emission scenarios with respect to our observations, both around the tropopause and in the lower stratosphere. In this Section, we will discuss the possible implications for inorganic bromine in the lower and lowermost stratosphere. Inorganic bromine is of key importance, as this is the form of bromine which can influence ozone through e.g. catalytic ozone depletion cycles. Note that this discussion only focuses on the input of bromine in the form of organic source gases (so called source gas injection, SGI, (see e.g. Engel and Rigby, 2018)) from VSLS. The inorganic bromine from SGI can be derived as the difference between the organic bromine in the source region (tropopause) and the organic bromine still observed or modelled at a certain stratospheric

location. The input of bromine into the stratosphere in the inorganic form (product gas injection~~, PGI~~) is expected to add more bromine in addition to the SGI discussed here. ~~: h~~However, PGI~~this~~ cannot be investigated with the source gas measurements presented here. Here, we focus on assessing what the different mixing ratios of bromine source gases at the tropical and extratropical tropopause in both observations and in model results imply for the total (organic and inorganic) bromine and inorganic bromine content of the lower and lowermost stratosphere. ~~Inorganic bromine is of key importance, as this is the form of bromine which can influence ozone through e.g. catalytic ozone depletion cycles.~~

We have shown in Sections 3 and 4 that the organic bromine around the tropopause shows significant variability and also latitudinal gradients. We have also shown that ~~and very significant~~large ~~-~~differences between the different model setups and observations are found. As mentioned in the introduction, the air in the extratropical lower and lowermost stratosphere is influenced by both transport through the tropical and extratropical tropopause. As both regions show different levels or organic bromine source gases, the relative contribution of these source regions needs to be known to derive total bromine which entered the stratosphere and thus also inorganic bromine from SGI. Several authors have attempted to quantify the relative fractions of air masses from the different source regions based on tracer measurements (e.g. Hoor et al., 2005;Boenisch et al., 2009;Ray et al., 1999;Werner et al., 2010). No studies on mass fractions are available for the campaigns discussed here, so we will rely on previous studies for these fractions as discussed in the introduction to estimate the fractions of tropical and extratropical air in the lowermost stratosphere. The differences in Br_y discussed here should thus be taken as a sensitivity study and the values derived below can only be considered to be estimates showing ~~to which order of magnitude~~how much the inorganic bromine may differ between different model setups and observations. In general, air masses close to the extratropical tropopause will be mainly of extratropical origin, while air masses near 400 K will almost be entirely of tropical origin. As a simplified approach, we have therefore chosen to assume that at the extratropical tropopause ($\Delta\theta$ = 0), the extratropical fraction is 100% and that this fraction decreases linearly to 0% at 100 K above the tropopause. The organic bromine species transported into the stratosphere are chemically or photochemically depleted and the bromine is transferred to the inorganic form. The total (organic and inorganic) bromine content from VSLS SGI in an air parcel in the lowermost stratosphere at $\Delta\theta$ above the tropopause, $Br_{tot}(\Delta\theta)$, is thus the sum of organic, $Br_{org}(\Delta\theta)$, and inorganic, $Br_{inorg}(\Delta\theta)$, bromine. Inorganic bromine is usually referred to as Br_y.

$$Br_{tot}(\Delta\theta) = \sout{Br_{inorg}(\Delta\theta) + Br_{org}(\Delta\theta) =} Br_y(\Delta\theta) + Br_{org}(\Delta\theta) \quad (1)$$

The total bromine can also be described by summing up the organic bromine transported to the stratosphere via input through the tropical and extratropical tropopause.

$$Br_{tot}(\Delta\theta) = f^{ex-trop}(\Delta\theta) \sout{*} \cdot Br_{org}^{ex-trop}(0) + f^{trop}(\Delta\theta) \sout{*} \cdot Br_{org}^{trop}(0) \quad (2)$$

where $f^{ex-trop}$ and f^{trop} are the fractions of air of extratropical and of tropical origin, respectively, and $Br_{org}^{ex-trop}(0)$ and $Br_{org}^{trop}(0)$ are the total organic VSLS bromine contents in air at the tropical, respectively extratropical (40-60°N) tropopause, i.e. at $\Delta\theta$ = 0. For observations only, the extratropical $Br_{org}^{ex-trop}(0)$ is available from our HALO aircraft campaigns. $Br_{org}^{trop}(0)$ for the observations is therefore taken from observations at the tropical tropopause compiled in the 2018 WMO Ozone assessment (Engel and Rigby, 2018). For the different model set-ups $Br_{org}^{ex-trop}(0)$ and $Br_{org}^{trop}(0)$ are derived from the global model fields. For the tropical values, the model output has been averaged between 10°S and 10°N in a potential temperature range from 365 to 375 K, in a similar way as used for the observations (Engel and Rigby, 2018). Extratropical values have been derived by averaging the model results~~s~~, respective observations, in a range of 10 K below the tropopause.

In order to be consistent between models and observations, extra-tropical reference values are taken as the values during the time of the campaign, while the tropical tropopause values are taken as seasonal mean.

Due to mass conservation, the sum of $f^{ex-trop}$ and f^{trop} must be unity, so we can rewrite equation (2) to yield

$$Br_{tot}(\Delta\theta) = f^{ex-trop}(\Delta\theta) \cdot Br_{org}^{ex-trop}(0) + \left(1 - f^{ex-trop}(\Delta\theta)\right) \cdot Br_{org}^{trop}(0) \quad (3)$$

If we assume that $f^{ex-trop}$ increases linearly from 0~~1~~ at $\Delta\theta = 0$ K to 1~~0~~ at $\Delta\theta = 100$ K, the total bromine from VSLS SGI can be derived and the inorganic bromine $Br_y(\Delta\theta)$ is then calculated by combining (1) and (3)

$$Br_y(\Delta\theta) = \left(f^{ex-trop}(\Delta\theta) \cdot Br_{org}^{ex-trop}(0) + \left(1 - f^{ex-trop}(\Delta\theta)\right) \cdot Br_{org}^{trop}(0)\right) - Br_{org}(\Delta\theta) \quad (4)$$

where $Br_{org}(\Delta\theta)$ is the organic bromine measured, respectively simulated at $\Delta\theta$ above the tropopause.

~~Figure 14 compares the~~ The vertical profiles of total and inorganic bromine derived in this way from the observations and the different model set-ups for the PGS campaign and the combined WISE-TACTS dataset are compared in Figure 14. The values of $Br_{org}^{ex-trop}(0)$ and $Br_{org}^{trop}(0)$ used for the models, respectively the observations, are shown in Table 5.

Due to the nature of the setup for the calculation of the SGI contribution to Br_y described above, both model- and observation-derived Br_y is close to zero at the extratropical tropopause. The assumed fractional contribution of tropical air increases with altitude and thus the amount of organic bromine assumed at the tropical tropopause becomes more important in the calculation of total bromine and thus also in Br_y. Overall, all model setups capture Br_y from CH_2Br_2 rather well. For all campaigns, the Br_y estimate from the observations is smaller than the model calculations above about 60 K above the tropopause and larger below this level. Under the given assumptions about fractional input, ~~T~~the larger Br_y derived in the model calculations above 60 K is caused by the higher total bromine values from CH_2Br_2, which are caused by the higher CH_2Br_2 levels at the tropical tropopause in comparison to the observations. For the late summer/early fall campaigns this difference is largest for the TOMCAT model with the Ziska et al. (2013) emissions and the EMAC model with the Warwick et al. (2006) emissions, consistent with these two model setups having the largest CH_2Br_2 values at the tropical tropopause (1.13 and 1.28 ppt, see Table 5). Under the given assumptions about fractional input, ~~In the lower part~~ the discrepancy in the lower part is more due to higher simulated CH_2Br_2 in the lowermost stratosphere than found in the observations. Using the emission scenarios by Liang et al. (2010) and Ordóñez et al. (2012) ~~Ordonez et al. (2012)~~, the differences are usually below 0.3 ppt of Br_y, corresponding to a MAPD of less than 40%.

Much larger variations are found in the amount of Br_y derived from $CHBr_3$. As can be seen from Figure 7, the remaining organic bromine in the form of $CHBr_3$ is very small for all three setups using the TOMCAT model and the observations already at about 30 to 40 K above the tropopause. The Br_y from $CHBr_3$ (solid lines in Figures 14) is thus close to the total bromine in form of $CHBr_3$ (dotted lines in Figure 14). In contrast, EMAC results using the Warwick et al. (2006) emissions still show ~~significant~~ substantial amounts of $CHBr_3$ in the organic form even at 50 K above the tropopause and above. For the EMAC setup, the Br_y derived from $CHBr_3$ is thus influenced by both the assumed input and the remaining organic $CHBr_3$ in the stratosphere. However, the tropical input of $CHBr_3$ in the EMAC model using the Warwick et al. (2006) emissions is very large (0.84 ppt, corresponding to about 2.5 ppt of bromine). Therefore, despite the fact that EMAC still shows ~~significant~~ substantial remaining $CHBr_3$ rather deep into the lowermost stratosphere, this model setup ~~significantly~~ overestimates the amount of Br_y due to $CHBr_3$ in comparison to the observations, with differences of about 1.5 ppt of Br_y at about 100 K above the tropopause, which is about factot of 3 higher than the value derived from the observations. Br_y from $CHBr_3$ in the different emission scenarios used in TOMCAT is mainly determined by the amount of $CHBr_3$ reaching the stratosphere, and especially

for regions with $\Delta\theta$ above 50 K by the tropical input. As the TOMCAT model with the Ziska et al. (2013) emissions underestimates these tropical tropopause values, it shows too little Br_y from $CHBr_3$ throughout the stratosphere. In contrast, the tropical tropopause values of $CHBr_3$ from the ~~Ordonez et al. (2012)~~ Ordóñez et al. (2012)and Liang et al. (2010) scenarios are in better agreement with the observations presented here and thus Br_y estimates at 100 K above the tropopause are in good agreement with the observation-based estimates.

The total Br_y from VSLS SGI can be understood mainly as an addition of the contributions of CH_2Br_2 and $CHBr_3$, as these are responsible for about 80% of total VSLS organic bromine. As the differences are largest for $CHBr_3$, the differences in total Br_y from VSLS SGI is dominated by the differences in $CHBr_3$. Interestingly, while the Ziska et al. (2013) emissions in TOMCAT showed some significant differences, in particular of $CHBr_3$ at the tropopause, the differences in total Br_y are not as large. The underestimation of Br_y from $CHBr_3$ is partly compensated by an overestimation of Br_y from CH_2Br_2. The EMAC model with the Warwick et al. (2006) emissions overestimates Br_y from both CH_2Br_2 and $CHBr_3$, so that in total a difference in Br_y of more than 2 ppt is derived, corresponding to an overestimation by a factor of more than 2 with respect to observation derived values. This difference is expected to have ~~e~~ a significant effect on ozone chemistry in the lower stratosphere.

The Br_y values derived in the approach described above depend on the assumed input values but also on the assumed fractional contribution of air from the tropics and the extratropics. In order to test the sensitivity of the results on the assumed fractions, we have varied the fractional input. Figure 15 shows the Br_y derived from CH_2Br_2 and $CHBr_3$ for the PGS campaign at 40K above the tropopause, as a function of the assumed fractional contribution from the extratropical source region ($f^{ex-trop}$); the tropical fraction f^{trop} is then always 1- $f^{ex-trop}$). While the differences are not very large for CH_2Br_2, which shows a much less pronounced latitudinal gradient, differences for $CHBr_3$ can be very large. In particular for the EMAC model with the Warwick et al. (2006) scenario, where the dependency of Br_y on the fractional input behaves in an opposite way to the $CHBr_3$ observations and the other model-emission scenario combinations. This shows that for the calculation of Br_y in the lowermost stratosphere from observations, it is necessary to have a good knowledge on the relative contributions and that for models it is necessary to have a realistic representation not only of chemistry but also of transport in the lowermost stratosphere.

6. Summary and outlook

We present a large dataset of around 4000 ~~of~~ in-situ ~~observations~~ measurements of five brominated VSLS with the GhOST-MS instrument in the UTLS region using the HALO aircraft. We have used data from the three HALO missions: TACTS, WISE and PGS. Data are presented in tropopause relative co-ordinates, i.e. the difference in potential temperature relative to the dynamical tropopause, defined by the value of 2 PVU. Stratospheric data are sorted by equivalent latitude, while we have used normal latitude for tropospheric data. We have shown systematic variabilities with latitude, altitude and season. The shortest-lived VSLS mixing ratios decrease fastest with altitude. During polar winter, vertical gradients are larger than during late summer to early fall, which is in line with the well-known diabatic descent of stratospheric air during polar winter. An important aspect of the observed distributions is that $CHBr_3$ mixing ratios at the extratropical tropopause are systematically higher than at the tropical tropopause. A similar feature is found for CH_2Br_2, although the latitudinal gradient is less pronounced than in the case of $CHBr_3$. The increase of VSLS mole fractions is especially clear during Northern Hemisphere winter, when lifetimes become very long at~~in~~ high latitudes.

We have further compared the observed distributions with a range of modelled distributions from TOMCAT and EMAC, run with different global emission scenarios. The features of the observed distribution are partly reproduced by the model calculations, with large differences ~~produced~~ caused by the different emissions. Overall, for CH_2Br_2, much better agreement between observations and model output~~s~~ is found for simulations using the emission scenarios by Liang et al. (2010) and Ordóñez et al. (2012), which have lower overall emissions than the scenarios by Ziska et al. (2013) and Warwick et al. (2006). This is in agreement with a recently proposed ~~downward~~ revision of the best estimate of global CH_2Br_2 emissions ~~recently~~

~~proposed~~towards the lower edge of previous estimates (Engel and Rigby, 2018) . In the case of $CHBr_3$, the use of the emission scenario by Ziska et al. (2013), which has the lowest global emissions, results in too low mixing ratios at the tropical tropopause and also at the extratropical tropopause. The use of the emission scenario by Warwick et al. (2006) results in strongly elevated mixing ratios of $CHBr_3$ at the tropical tropopause and a reversed latitudinal gradient at the tropopause in comparison to the observations. These findings are in good agreement with previous comparisons of the different emission scenarios (Hossaini et al., 2013;Hossaini et al., 2016) for CH_2Br_2. For $CHBr_3$, Hossaini et al. (2016) found that the lower emissions in the Ziska et al. (2013) scenario generally gave best agreement with ground based observations in the tropics. However, we find that the tropopause values using this scenario are too low, both in the tropics and in the extratropics. In a recent paper, Fiehn et al. (2018) discussed that a modified version of the Ziska et al. (2013) scenario with seasonally varying emissions, yielded significantly higher tropopause values. The Ordóñez et al. (2012) ~~Ordonez et al. (2012)~~ scenario, which has higher emissions than the Ziska et al. (2013) scenario, yielded too high mixing ratios of $CHBr_3$ during the winter period. ~~While it is not the main purpose of this paper to evaluate different emission scenarios, i~~It is clear that no scenario is able to capture tropical and extratropical values from our observations. However, it is clear from the comparison with the scenario by Warwick et al. (2006), which restricts emissions to latitudes below 50°, that the sources of these short-lived brominated compounds are not only in the tropics, but that significant emissions must also occur in higher latitudes. This is consistent with comparison of tropospheric data (see e.g. Fig. 6 in Hossaini et al., 2013). For future improved emission scenarios, more emphasis on the seasonality of the sources might also lead to an improvement.

Air in the lowermost stratosphere is composed of air masses originating from both the tropical and the extratropical upper troposphere. The latitudinal gradient of VSLS will therefore impact the amount of bromine transported into the stratosphere and thus also the amount of reactive, inorganic bromine (Br_y) in the lowermost stratosphere able to contribute to catalytic ozone depletion. The bromine budget in the lower stratosphere will depend on the relative fraction of air from the tropical and extratropical tropopause. The relative contribution of extratropical air ~~will~~ decreases with latitude and ~~should reach~~reaches zero at about 400 K potential temperature. Using simplified assumptions about the fractional distributions, we have shown that there will be ~~significant~~ substantial differences in stratospheric Br_y depending on the emission scenario, which can be as high as 2 ppt, corresponding to a difference of a factor 2 relative to observation-derived values, when using the scenario by Warwick et al. (2006). Typical differences in Br_y when using the other scenarios are on the order of 1 ppt. This is expected to have an impact on modelled ozone depletion in the lower stratosphere. For example, it has been shown that inclusion of about 5 ppt of Bry from VSLS leads to an expansion of the ozone hole area of ~ 5 million km^2 and an increase in maximum Antarctic ozone hole depletion by up to 14 % (Fernandez et al., 2017). The impact of bromine on ozone is most pronounced in the lowest part of the stratosphere (Hossaini et al., 2015). Further, as the efficiency of bromine to destroy ozone depends on the amount of available chlorine, it is also likely that modelled temporal trends of ozone will be influenced, even if there are no long-term changes in VSLS bromine. If relative contributions of the different pathways (tropical vs. extratropical air) change, e.g. due to changes in stratospheric circulation, this could further influence ozone due to the different amounts of bromine in these air masses. As shown in our sensitivity study (Section 5), the assumptions on the relative contribution of the different source regions has a ~~significant~~ substantial impact especially on the Br_y produced from $CHBr_3$ in the lowermost stratosphere.

While the dataset presented here gives a much better picture of the distribution of brominated VSLS in the UTLS region than previously available, there are still considerable gaps in our knowledge of the distribution of these species. Only late summer to fall and winter data have been presented here for the Northern Hemisphere. Spring and early summer are less well covered, as is the Southern Hemisphere. Southern hemispheric distributions are expected to differ ~~significantly~~ from northern hemispheric distributions, as the main sources of many brominated VSLS are believed to be from coastal ocean regions. Due to the different distribution of oceans, land and coastal areas between the hemispheres, it is not possible to extrapolate northern hemispheric observations to the Southern Hemisphere. Further, while no signs of increasing emissions of natural brominated VSLS have been observed so far, such an increase is possible in a changing climate and needs to be monitored.

Data availability

The observational data are available via the HALO Database (halo-db.pa.op.dlr.de/). The data of the ESCiMo simulations using the EMAC model will be made available in the Climate and Environmental Retrieval and Archive (CERA) database at the German Climate Computing Centre (DKRZ; http://cera-www.dkrz.de/WDCC/ui/Index.jsp); the simulations results of Graf (2017 are available upon request. TOMCAT model data will be uploaded to the Lancaster University data repository upon article acceptance. Access to data may be dependent on the signature of a data protocol.

~~7.~~ *Acknowledgements*

The work of University Frankfurt has been funded through several projects by the German Science foundation for the development and operation of GHOST-MS and for the measurement campaigns (EN367/5, EN367/8, EN367/11. EN367/13 and EN367/14). A.E. would like to thank CSIRO in Aspendale/Australia for a Frohlich Fellowship during which parts of this analysis was performed. Many thanks also to Kieran Stanley for proof reading and improving the manuscript. We would further like to thank the DLR staff, including pilots and ground staff, for the operation of HALO and the support during the campaigns. The good collaboration with the other groups involved in the HALO campaigns is also acknowledged. We would like to thank Andreas Zahn from KIT Karlruhe for provision of the ozone data in Figure 3. We further thank Jens-Uwe Grooß from FZ Jülich for the calculation of the tropopause and equivalent latitude for the HALO campaigns and Michael Sprenger from ETH Zürich for the provision of the climatological dynamical tropopause from ERA-Interim data. R.H. is supported by a NERC Independent Research Fellowship (NE/N014375/1). The EMAC simulations have been performed at the German Climate Computing Centre (DKRZ) through support from the Bundesministerium für Bildung und Forschung (BMBF). DKRZ and its scientific steering committee are gratefully acknowledged for providing the HPC and data archiving resources for this consortial project ESCiMo (Earth System Chemistry integrated Modelling).

~~8.~~ Author Contribution

T.K., F.O., H.B. and A.E. were involved in developing the GhOST instrument, operating it in the field during the missions, data evaluation and interpretation. F.L., M.H. and T.S. were also involved in the operation, evaluation and interpretation. N.S., A.R. and C.H. were involved in the evaluation and interpretation. R.H., P.G. and P.J. have provided model data and also participated in the discussion of the data and the comparisons. A.E and T.K. have mainly written the manuscript. All co-authors were involved in the discussion and iterations of the manuscript.

~~9.~~ References

Appenzeller, C., Holton, J. R., and Rosenlof, K. H.: Seasonal variation of mass transport across the tropopause, Journal of Geophysical Research-Atmospheres, 101, 15071-15078, 1996.

Ball, W. T., Alsing, J., Mortlock, D. J., Staehelin, J., Haigh, J. D., Peter, T., Tummon, F., Stübi, R., Stenke, A., Anderson, J., Bourassa, A., Davis, S. M., Degenstein, D., Frith, S., Froidevaux, L., Roth, C., Sofieva, V., Wang, R., Wild, J., Yu, P., Ziemke, J. R., and Rozanov, E. V.: Evidence for a continuous decline in lower stratospheric ozone offsetting ozone layer recovery, Atmos. Chem. Phys., 18, 1379-1394, 10.5194/acp-18-1379-2018, 2018.

Boenisch, H., Hoor, P., Gurk, C., Feng, W., Chipperfield, M., Engel, A., and Bregman, B.: Model evaluation of CO2 and SF6 in the extratropical UT/LS region, Journal of Geophysical Research-Atmospheres, 113, 10.1029/2007jd008829, 2008.

Boenisch, H., Engel, A., Curtius, J., Birner, T., and Hoor, P.: Quantifying transport into the lowermost stratosphere using simultaneous in-situ measurements of SF_6 and CO_2, Atmospheric Chemistry and Physics, 9, 5905-5919, 2009.

Boenisch, H., Engel, A., Birner, T., Hoor, P., Tarasick, D. W., and Ray, E. A.: On the structural changes in the Brewer-Dobson circulation after 2000, Atmospheric Chemistry and Physics, 11, 3937-3948, 10.5194/acp-11-3937-2011, 2011.

Boothe, A. C., and Homeyer, C. R.: Global large-scale stratosphere–troposphere exchange in modern reanalyses, Atmos. Chem. Phys., 17, 5537-5559, 10.5194/acp-17-5537-2017, 2017.

Burkholder, J. B., Sander, S. P., Abbatt, J., Barker, J. R., Huie, R. E., Kolb, C. E., Kurylo, M. J., Orkin, V. L., Wilmouth, D. M., and Wine, P. H. C. k. a. p. d. f. u. i. a. s., Evaluation number 18, JPL Publication 15-10, Jet Propulsion Laboratory, : Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation number 18, , JPL Publication 15-10, Jet Propulsion Laboratory, , 2015.

Burkholder, J. B.: (Lead Author) Hodnebrog, Ø., Orkin, V.L., Summary of Abundances, Lifetimes, Ozone Depletion Potentials (ODPs), Radiative Efficiencies (REs), Global Warming Potentials (GWPs), and Global Temperature change Potentials (GTPs) Appendix 1 to Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project-Report No. 58, World Meteorological Organization, Geneva, Switzerland 2018.

Carpenter, L. J., and Reimann, S.: (Lead Authors), J.B. Burkholder,C. Clerbaux, B.D. Hall, R. Hossaini, J.C. Laube, S.A. Yvon-Lewis,Ozone-Depleting Substances (ODSs) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in *Scientific Assessment of Ozone Depletion: 2014*, Global Ozone Research and Monitoring Project –Report No. 55, World Meteorological Organization, Geneva, Switzerland, 2014., 2014.

Chipperfield, M. P.: New version of the TOMCAT/SLIMCAT off-line chemical transport model: Intercomparison of stratospheric tracer experiments, Quarterly Journal of the Royal Meteorological Society, 132, 1179-1203, 10.1256/qj.05.51, 2006.

Chipperfield, M. P., Dhomse, S., Hossaini, R., Feng, W., Santee, M. L., Weber, M., Burrows, J. P., Wild, J. D., Loyola, D., and Coldewey-Egbers, M.: On the Cause of Recent Variations in Lower Stratospheric Ozone, Geophysical Research Letters, 45, 5718-5726, doi:10.1029/2018GL078071, 2018.

Daniel, J. S., and Velders, G. J. M.: (Lead Authors), Douglass, A. R., Forster, P. M. D.,Hauglustaine, D. A., Isaksen, I. S. A., Kuijpers, L. J. M., Mc-Culloch, A., and Wallington, T. JHalocarbon scenarios, ozonedepletion potentials, and global warming potentials, Chapter 8in World Meteorological Organization: Scientific assessment ofozone depletion: 2006, Global Ozone Research and MonitoringProject – Report No. 50, Geneva., 2006.

Dee, D. P., Uppala, S. M., Simmons, A. J., Berrisford, P., Poli, P., Kobayashi, S., Andrae, U., Balmaseda, M. A., Balsamo, G., Bauer, P., Bechtold, P., Beljaars, A. C. M., van de Berg, L., Bidlot, J., Bormann, N., Delsol, C., Dragani, R., Fuentes, M., Geer, A. J., Haimberger, L., Healy, S. B., Hersbach, H., Hólm, E. V., Isaksen, L., Kållberg, P., Köhler, M., Matricardi, M., McNally, A. P., Monge-Sanz, B. M., Morcrette, J.-J., Park, B.-K., Peubey, C., de Rosnay, P., Tavolato, C., Thépaut, J.-N., and Vitart, F.: The ERA-Interim reanalysis: configuration and performance of the data assimilation system, Quarterly Journal of the Royal Meteorological Society, 137, 553-597, 10.1002/qj.828, 2011.

Dhomse, S. S., Chipperfield, M. P., Feng, W., Hossaini, R., Mann, G. W., and Santee, M. L.: Revisiting the hemispheric asymmetry in midlatitude ozone changes following the Mount Pinatubo eruption: A 3-D model study, Geophysical Research Letters, 42, 3038-3047, 10.1002/2015gl063052, 2015.

Engel, A., Bonisch, H., Brunner, D., Fischer, H., Franke, H., Gunther, G., Gurk, C., Hegglin, M., Hoor, P., Konigstedt, R., Krebsbach, M., Maser, R., Parchatka, U., Peter, T., Schell, D., Schiller, C., Schmidt, U., Spelten, N., Szabo, T., Weers, U., Wernli, H., Wetter, T., and Wirth, V.: Highly resolved observations of trace gases in the lowermost stratosphere and upper troposphere from the Spurt project: an overview, Atmospheric Chemistry and Physics, 6, 283-301, 2006.

Engel, A., and Rigby, M.: (Lead Authors), J.B.Burkholder, R.P. Fernandez, L. Froidevaux, B.D.Hall, R. Hossaini, T. Saito, M.K.Vollmer, and B.Yao, Update on Ozone-Depleting Substances (ODS) and Other Gases of Interest to the Montreal Protocol, Chapter 1 in Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project-Report No. 58, World Meteorological Organization, Geneva, Switzerland 2018.

Falk, S., Sinnhuber, B. M., Krysztofiak, G., Jöckel, P., Graf, P., and Lennartz, S. T.: Brominated VSLS and their influence on ozone under a changing climate, Atmos. Chem. Phys., 17, 11313-11329, 10.5194/acp-17-11313-2017, 2017.

Farman, J. C., Gardiner, B. G., and Shanklin, J. D.: Large Losses of Total Ozone in Antarctica Reveal Seasonal Clox/Nox Interaction, Nature, 315, 207-210, Doi 10.1038/315207a0, 1985.

Feng, W., Chipperfield, M. P., Dorf, M., Pfeilsticker, K., and Ricaud, P.: Mid-latitude ozone changes: studies with a 3-D CTM forced by ERA-40 analyses, Atmos. Chem. Phys., 7, 2357-2369, 10.5194/acp-7-2357-2007, 2007.

Fernandez, R. P., Salawitch, R. J., Kinnison, D. E., Lamarque, J. F., and Saiz-Lopez, A.: Bromine partitioning in the tropical tropopause layer: implications for stratospheric injection, Atmos. Chem. Phys., 14, 13391-13410, 10.5194/acp-14-13391-2014, 2014.

Fernandez, R. P., Kinnison, D. E., Lamarque, J. F., Tilmes, S., and Saiz-Lopez, A.: Impact of biogenic very short-lived bromine on the Antarctic ozone hole during the 21st century, Atmos. Chem. Phys., 17, 1673-1688, 10.5194/acp-17-1673-2017, 2017.

Fiehn, A., Quack, B., Hepach, H., Fuhlbrügge, S., Tegtmeier, S., Toohey, M., Atlas, E., and Krüger, K.: Delivery of halogenated very short-lived substances from the west Indian Ocean to the stratosphere during the Asian summer monsoon, Atmos. Chem. Phys., 17, 6723-6741, 10.5194/acp-17-6723-2017, 2017.

Fiehn, A., Quack, B., Stemmler, I., Ziska, F., and Krüger, K.: Importance of seasonally resolved oceanic emissions for bromoform delivery from the tropical Indian Ocean and west Pacific to the stratosphere, Atmos. Chem. Phys., 18, 11973-11990, 10.5194/acp-18-11973-2018, 2018.

Fischer, H., Wienhold, F. G., Hoor, P., Bujok, O., Schiller, C., Siegmund, P., Ambaum, M., Scheeren, H. A., and Lelieveld, J.: Tracer correlations in the northern high latitude lowermost stratosphere: Influence of cross-tropopause mass exchange, Geophysical Research Letters, 27, 97-100, 2000.

Gettelman, A., Hoor, P., Pan, L. L., Randel, W. J., Hegglin, M. I., and Birner, T.: The extratropical upper troposphere and lower stratosphere, Reviews of Geophysics, 49, 10.1029/2011rg000355, 2011.

Graf, P.: The impact of very short-lived substances on the stratospheric chemistry and interactions with the climate, Ph.D. thesis, Ludwig-Maximilians-Universität München, URL http://nbn-resolving.de/urn:nbn:de:bvb:19-207510, 2017.

Harris, N. R. P., Kyrö, E., Staehelin, J., Brunner, D., Andersen, S. B., Godin-Beekmann, S., Dhomse, S., Hadjinicolaou, P., Hansen, G., Isaksen, I., Jrrar, A., Karpetchko, A., Kivi, R., Knudsen, B., Krizan, P., Lastovicka, J., Maeder, J., Orsolini, Y., Pyle, J. A., Rex, M., Vanicek, K., Weber, M., Wohltmann, I., Zanis, P., and Zerefos, C.: Ozone trends at northern mid- and high latitudes – a European perspective, Ann. Geophys., 26, 1207-1220, 10.5194/angeo-26-1207-2008, 2008.

Holton, J. R., Haynes, P. H., Mcintyre, M. E., Douglass, A. R., Rood, R. B., and Pfister, L.: Stratosphere-Troposphere Exchange, Reviews of Geophysics, 33, 403-439, 1995.

Hoor, P., Fischer, H., and Lelieveld, J.: Tropical and extratropical tropospheric air in the lowermost stratosphere over Europe: A CO-based budget, Geophysical Research Letters, 32, L07802, Doi 10.1029/2004gl022018, 2005.

Hossaini, R., Chipperfield, M. P., Monge-Sanz, B. M., Richards, N. A. D., Atlas, E., and Blake, D. R.: Bromoform and dibromomethane in the tropics: a 3-D model study of chemistry and transport, Atmospheric Chemistry and Physics, 10, 719-735, 10.5194/acp-10-719-2010, 2010.

Hossaini, R., Chipperfield, M. P., Feng, W., Breider, T. J., Atlas, E., Montzka, S. A., Miller, B. R., Moore, F., and Elkins, J.: The contribution of natural and anthropogenic very short-lived species to stratospheric bromine, Atmospheric Chemistry and Physics, 12, 371-380, 10.5194/acp-12-371-2012, 2012.

Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bönisch, H., Keber, T., Oram, D., Mills, G., Ordóñez, C., Saiz-Lopez, A., Warwick, N., Liang, Q., Feng, W., Moore, F., Miller, B. R., Marécal, V., Richards, N. A. D., Dorf, M., and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmos. Chem. Phys., 13, 11819-11838, 10.5194/acp-13-11819-2013, 2013.

Hossaini, R., Chipperfield, M. P., Montzka, S. A., Rap, A., Dhomse, S., and Feng, W.: Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, Nature Geosci, 8, 186-190, 10.1038/ngeo2363, 2015.

Hossaini, R., Patra, P. K., Leeson, A. A., Krysztofiak, G., Abraham, N. L., Andrews, S. J., Archibald, A. T., Aschmann, J., Atlas, E. L., Belikov, D. A., Boenisch, H., Carpenter, L. J., Dhomse, S., Dorf, M., Engel, A., Feng, W., Fuhlbruegge, S., Griffiths, P. T., Harris, N. R. P., Hommel, R., Keber, T., Krueger, K., Lennartz, S. T., Maksyutov, S., Mantle, H., Mills, G. P., Miller, B., Montzka, S. A., Moore, F., Navarro, M. A., Oram, D. E., Pfeilsticker, K., Pyle, J. A., Quack, B., Robinson, A. D., Saikawa, E., Saiz-Lopez, A., Sala, S., Sinnhuber, B.-M., Taguchi, S., Tegtmeier, S., Lidster, R. T., Wilson, C., and Ziska, F.: A multi-model intercomparison of halogenated very short-lived substances (TransCom-VSLS): linking oceanic emissions and tropospheric transport for a reconciled estimate of the stratospheric source gas injection of bromine, Atmospheric Chemistry and Physics, 16, 9163-9187, 10.5194/acp-16-9163-2016, 2016.

Hossaini, R., Chipperfield, M. P., Montzka, S. A., Leeson, A. A., Dhomse, S. S., and Pyle, J. A.: The increasing threat to stratospheric ozone from dichloromethane, Nature Communications, 8, 15962, 10.1038/ncomms15962, 2017.

Hossaini, R., Atlas, E., Dhomse, S. S., Chipperfield, M. P., Bernath, P. F., Fernando, A. M., Mühle, J., Leeson, A. A., Montzka, S. A., Feng, W., Harrison, J. J., Krummel, P., Vollmer, M. K., Reimann, S., O'Doherty, S., Young, D., Maione, M., Arduini, J., and Lunder, C. R.: Recent Trends in Stratospheric Chlorine From Very Short-Lived Substances, Journal of Geophysical Research: Atmospheres, 124, 2318-2335, 10.1029/2018jd029400, 2019.

Jöckel, P., Tost, H., Pozzer, A., Kunze, M., Kirner, O., Brenninkmeijer, C. A. M., Brinkop, S., Cai, D. S., Dyroff, C., Eckstein, J., Frank, F., Garny, H., Gottschaldt, K. D., Graf, P., Grewe, V., Kerkweg, A., Kern, B., Matthes, S., Mertens, M., Meul, S., Neumaier, M., Nützel, M., Oberländer-Hayn, S., Ruhnke, R., Runde, T., Sander, R., Scharffe, D., and Zahn, A.: Earth System Chemistry integrated Modelling (ESCiMo) with the Modular Earth Submodel System (MESSy) version 2.51, Geosci. Model Dev., 9, 1153-1200, 10.5194/gmd-9-1153-2016, 2016.

Leedham Elvidge, E. C., Oram, D. E., Laube, J. C., Baker, A. K., Montzka, S. A., Humphrey, S., O'Sullivan, D. A., and Brenninkmeijer, C. A. M.: Increasing concentrations of dichloromethane, CH2Cl2, inferred from CARIBIC air samples collected 1998–2012, Atmos. Chem. Phys., 15, 1939-1958, 10.5194/acp-15-1939-2015, 2015.

Liang, Q., Stolarski, R. S., Kawa, S. R., Nielsen, J. E., Douglass, A. R., Rodriguez, J. M., Blake, D. R., Atlas, E. L., and Ott, L. E.: Finding the missing stratospheric Br-y: a global modeling study of CHBr3 and CH2Br2, Atmospheric Chemistry and Physics, 10, 2269-2286, 2010.

Liang, Q., Atlas, E., Blake, D., Dorf, M., Pfeilsticker, K., and Schauffler, S.: Convective transport of very short lived bromocarbons to the stratosphere, Atmos. Chem. Phys., 14, 5781-5792, 10.5194/acp-14-5781-2014, 2014.

Molina, M. J., and Rowland, F. S.: Stratospheric Sink for Chlorofluoromethanes - Chlorine Atomic-Catalysed Destruction of Ozone, Nature, 249, 810-812, Doi 10.1038/249810a0, 1974.

Monks, S. A., Arnold, S. R., Hollaway, M. J., Pope, R. J., Wilson, C., Feng, W., Emmerson, K. M., Kerridge, B. J., Latter, B. L., Miles, G. M., Siddans, R., and Chipperfield, M. P.: The TOMCAT global chemical transport model v1.6: description of chemical mechanism and model evaluation, Geosci. Model Dev., 10, 3025-3057, 10.5194/gmd-10-3025-2017, 2017.

Montzka, S. A., Dutton, G. S., Yu, P., Ray, E., Portmann, R. W., Daniel, J. S., Kuijpers, L., Hall, B. D., Mondeel, D., Siso, C., Nance, J. D., Rigby, M., Manning, A. J., Hu, L., Moore, F., Miller, B. R., and Elkins, J. W.: An unexpected and persistent increase in global emissions of ozone-depleting CFC-11, Nature, 557, 413-417, 10.1038/s41586-018-0106-2, 2018.

Obersteiner, F., Bonisch, H., Keber, T., O'Doherty, S., and Engel, A.: A versatile, refrigerant- and cryogen-free cryofocusing-thermodesorption unit for preconcentration of traces gases in air, Atmospheric Measurement Techniques, 9, 5265-5279, 10.5194/amt-9-5265-2016, 2016.

Oman, L. D., Douglass, A. R., Salawitch, R. J., Canty, T. P., Ziemke, J. R., and Manyin, M.: The effect of representing bromine from VSLS on the simulation and evolution of Antarctic ozone, Geophysical Research Letters, 43, 9869-9876, 10.1002/2016gl070471, 2016.

Oram, D. E., Ashfold, M. J., Laube, J. C., Gooch, L. J., Humphrey, S., Sturges, W. T., Leedham-Elvidge, E., Forster, G. L., Harris, N. R. P., Mead, M. I., Samah, A. A., Phang, S. M., Ou-Yang, C. F., Lin, N. H., Wang, J. L., Baker, A. K., Brenninkmeijer, C. A. M., and Sherry, D.: A growing threat to the ozone layer from short-lived anthropogenic chlorocarbons, Atmos. Chem. Phys., 17, 11929-11941, 10.5194/acp-17-11929-2017, 2017.

Ordóñez, C., Lamarque, J. F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Santos, G. S., Brasseur, G., and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmos. Chem. Phys., 12, 1423-1447, 10.5194/acp-12-1423-2012, 2012.

Ray, E. A., Moore, F. L., Elkins, J. W., Dutton, G. S., Fahey, D. W., Vomel, H., Oltmans, S. J., and Rosenlof, K. H.: Transport into the Northern Hemisphere lowermost stratosphere revealed by in situ tracer measurements, Journal of Geophysical Research-Atmospheres, 104, 26565-26580, Doi 10.1029/1999jd900323, 1999.

Rigby, M., Park, S., Saito, T., Western, L. M., Redington, A. L., Fang, X., Henne, S., Manning, A. J., Prinn, R. G., Dutton, G. S., Fraser, P. J., Ganesan, A. L., Hall, B. D., Harth, C. M., Kim, J., Kim, K. R., Krummel, P. B., Lee, T., Li, S., Liang, Q., Lunt, M. F., Montzka, S. A., Mühle, J., O'Doherty, S., Park, M. K., Reimann, S., Salameh, P. K., Simmonds, P., Tunnicliffe, R. L., Weiss, R. F., Yokouchi, Y., and Young, D.: Increase in CFC-11 emissions from eastern China based on atmospheric observations, Nature, 569, 546-550, 10.1038/s41586-019-1193-4, 2019.

Sala, S.: Entwicklung und Einsatz eines flugzeuggetragenen GC/MS - Systems zum Nachweis halogenierter Kohlenwasserstoffe in der Atmosphäre, PhD Thesis, Goethe University Frankfurt, Frankfurt, Germany, 2014.

Sala, S., Boenisch, H., Keber, T., Oram, D. E., Mills, G., and Engel, A.: Deriving an atmospheric budget of total organic bromine using airborne in situ measurements from the western Pacific area during SHIVA, Atmospheric Chemistry and Physics, 14, 6903-6923, 10.5194/acp-14-6903-2014, 2014.

Salawitch, R. J., Weisenstein, D. K., Kovalenko, L. J., Sioris, C. E., Wennberg, P. O., Chance, K., Ko, M. K. W., and McLinden, C. A.: Sensitivity of ozone to bromine in the lower stratosphere, Geophys. Res. Lett., 32, L05811, 10.1029/2004gl021504, 2005.

Sinnhuber, B.-M., and Meul, S.: Simulating the impact of emissions of brominated very short lived substances on past stratospheric ozone trends, Geophysical Research Letters, 42, 2449-2456, 10.1002/2014GL062975, 2015.

Sinnhuber, B. M., Sheode, N., Sinnhuber, M., Chipperfield, M. P., and Feng, W.: The contribution of anthropogenic bromine emissions to past stratospheric ozone trends: a modelling study, Atmospheric Chemistry and Physics, 9, 2863-2871, 2009.

Škerlak, B., Sprenger, M., and Wernli, H.: A global climatology of stratosphere–troposphere exchange using the ERA-Interim data set from 1979 to 2011, Atmos. Chem. Phys., 14, 913-937, 10.5194/acp-14-913-2014, 2014.

Škerlak, B., Sprenger, M., Pfahl, S., Tyrlis, E., and Wernli, H.: Tropopause folds in ERA-Interim: Global climatology and relation to extreme weather events, Journal of Geophysical Research: Atmospheres, 120, 4860-4877, 10.1002/2014jd022787, 2015.

Solomon, S.: Stratospheric ozone depletion: A review of concepts and history, Reviews of Geophysics, 37, 275-316, 1999.

Sprenger, M., Fragkoulidis, G., Binder, H., Croci-Maspoli, M., Graf, P., Grams, C. M., Knippertz, P., Madonna, E., Schemm, S., Škerlak, B., and Wernli, H.: Global Climatologies of Eulerian and Lagrangian Flow Features based on ERA-Interim, Bulletin of the American Meteorological Society, 98, 1739-1748, 10.1175/bams-d-15-00299.1, 2017.

Steinbrecht, W., Froidevaux, L., Fuller, R., Wang, R., Anderson, J., Roth, C., Bourassa, A., Degenstein, D., Damadeo, R., Zawodny, J., Frith, S., McPeters, R., Bhartia, P., Wild, J., Long, C., Davis, S., Rosenlof, K., Sofieva, V., Walker, K., Rahpoe, N., Rozanov, A., Weber, M., Laeng, A., von Clarmann, T., Stiller, G., Kramarova, N., Godin-Beekmann, S., Leblanc, T., Querel, R., Swart, D., Boyd, I., Hocke, K., Kämpfer, N., Maillard Barras, E., Moreira, L., Nedoluha, G., Vigouroux, C., Blumenstock, T., Schneider, M., García, O., Jones, N., Mahieu, E., Smale, D., Kotkamp, M., Robinson, J., Petropavlovskikh, I., Harris, N., Hassler, B., Hubert, D., and Tummon, F.: An update on ozone profile trends for the period 2000 to 2016, Atmos. Chem. Phys., 17, 10675-10690, 10.5194/acp-17-10675-2017, 2017.

Stohl, A., Bonasoni, P., Cristofanelli, P., Collins, W., Feichter, J., Frank, A., Forster, C., Gerasopoulos, E., Gäggeler, H., James, P., Kentarchos, T., Kromp-Kolb, H., Krüger, B., Land, C., Meloen, J., Papayannis, A., Priller, A., Seibert, P., Sprenger, M., Roelofs, G. J., Scheel, H. E., Schnabel, C., Siegmund, P., Tobler, L., Trickl, T., Wernli, H., Wirth, V., Zanis, P., and Zerefos, C.: Stratosphere-troposphere exchange: A review, and what we have learned from STACCATO, Journal of Geophysical Research: Atmospheres, 108, 10.1029/2002jd002490, 2003.

Tegtmeier, S., Krüger, K., Quack, B., Atlas, E. L., Pisso, I., Stohl, A., and Yang, X.: Emission and transport of bromocarbons: from the West Pacific ocean into the stratosphere, Atmos. Chem. Phys., 12, 10633-10648, 10.5194/acp-12-10633-2012, 2012.

Wales, P. A., Salawitch, R. J., Nicely, J. M., Anderson, D. C., Canty, T. P., Baidar, S., Dix, B., Koenig, T. K., Volkamer, R., Chen, D., Huey, L. G., Tanner, D. J., Cuevas, C. A., Fernandez, R. P., Kinnison, D. E., Lamarque, J.-F., Saiz-Lopez, A., Atlas, E. L., Hall, S. R., Navarro, M. A., Pan, L. L., Schauffler, S. M., Stell, M., Tilmes, S., Ullmann, K., Weinheimer, A. J., Akiyoshi, H., Chipperfield, M. P., Deushi, M., Dhomse, S. S., Feng, W., Graf, P., Hossaini, R., Jöckel, P., Mancini, E., Michou, M., Morgenstern, O., Oman, L. D., Pitari, G., Plummer, D. A., Revell, L. E., Rozanov, E., Saint-Martin, D., Schofield, R., Stenke, A., Stone, K. A., Visioni, D., Yamashita, Y., and Zeng, G.: Stratospheric Injection of Brominated Very Short-Lived Substances: Aircraft Observations in the Western Pacific and Representation in Global Models, Journal of Geophysical Research: Atmospheres, 123, 5690-5719, doi:10.1029/2017JD027978, 2018.

Warwick, N. J., Pyle, J. A., Carver, G. D., Yang, X., Savage, N. H., O'Connor, F. M., and Cox, R. A.: Global modeling of biogenic bromocarbons, Journal of Geophysical Research-Atmospheres, 111, 10.1029/2006jd007264, 2006.

Werner, A., Volk, C. M., Ivanova, E. V., Wetter, T., Schiller, C., Schlager, H., and Konopka, P.: Quantifying transport into the Arctic lowermost stratosphere, Atmos. Chem. Phys., 10, 11623-11639, 10.5194/acp-10-11623-2010, 2010.

Wernli, H., and Bourqui, M.: A Lagrangian "1-year climatology" of (deep) cross-tropopause exchange in the extratropical Northern Hemisphere, Journal of Geophysical Research-Atmospheres, 107, -, Artn 4021

Doi 10.1029/2001jd000812, 2002.

WMO: (World Meteorological Organization), Scientific Assessment of Ozone Depletion: 2018, Global Ozone Research and Monitoring Project-Report No. 58, World Meteorological Organization, Geneva, Switzerland 2018.

Wofsy, S. C., McElroy, M. B., and Yung, Y. L.: The chemistry of atmospheric bromine, Geophysical Research Letters, 2, 215-218, 10.1029/GL002i006p00215, 1975.

Worton, D. R., Mills, G. P., Oram, D. E., and Sturges, W. T.: Gas chromatography negative ion chemical ionization mass spectrometry: Application to the detection of alkyl nitrates and halocarbons in the atmosphere, Journal of Chromatography A, 1201, 112-119, 10.1016/j.chroma.2008.06.019, 2008.

Zahn, A., Weppner, J., Widmann, H., Schlote-Holubek, K., Burger, B., Kühner, T., and Franke, H.: A fast and precise chemiluminescence ozone detector for eddy flux and airborne application, Atmos. Meas. Tech., 5, 363-375, 10.5194/amt-5-363-2012, 2012.

Ziska, F., Quack, B., Abrahamsson, K., Archer, S. D., Atlas, E., Bell, T., Butler, J. H., Carpenter, L. J., Jones, C. E., Harris, N. R. P., Hepach, H., Heumann, K. G., Hughes, C., Kuss, J., Krueger, K., Liss, P., Moore, R. M., Orlikowska, A., Raimund, S., Reeves, C. E., Reifenhaeuser, W., Robinson, A. D., Schall, C., Tanhua, T., Tegtmeier, S., Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S., and Yokouchi, Y.: Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, Atmospheric Chemistry and Physics, 13, 8915-8934, 10.5194/acp-13-8915-2013, 2013.

Ziska, F., Quack, B., Tegtmeier, S., Stemmler, I., and Krüger, K.: Future emissions of marine halogenated very-short lived substances under climate change, Journal of Atmospheric Chemistry, 74, 245-260, 10.1007/s10874-016-9355-3, 2017.

~~10.~~ Graphics and Tables

Table 1*:* Brominated species measured with Gas Chromatograph for Observational Studies using Tracers-Mass spectrometer **(**GhOST-MS) during three High Altitude and Long Range Research Aircraft campaigns, described in Table 2. Tropospheric mole fractions (parts per trillion, ppt; 10^{-12}) of the halons are taken from table 1-1 in (Engel and Rigby, 2018) and from table 1-7 for the bromocarbons (marine boundary layer values). Lifetimes of bromocarbons are local lifetimes for upper tropospheric conditions (10 km altitude, 25-60°N) from table 1-5 in (Carpenter and Reimann, 2014) and global /stratospheric lifetimes are from table A-1 in WMO 2018 (Burkholder, 2018). Reproducibilities and detection limits of GhOST have been determined during the WISE and the PGS campaigns. n.a. means not applicable. For the TACTS campaign instrument performance was similar to that reported in (Sala et al., 2014).

Name	Formula	troposph. Mole fraction [ppt]	GhOST-MS characteristics PGS/WISE		typical lifetime		
			Reproduci-bility [%]	Detection limit [ppq]	fall [days]	winter [days]	Global/ stratospheric [years /years]
Halon 1301	CF_3Br	3.36	0./1	7/50	n.a.	n.a.	72/73.5
Halon 1211	$CBrClF_2$	3.59	0.2/0.5	2/6	n.a.	n.a.	16/41
Halon 1202	CBr_2F_2	0.014	2.8/7.6	1/6	n.a.	n.a.	2.5 / 36
Halon 2402	$CBrF_2CBrF_2$	0.41	0.6/1.5	2/7	n.a.	n.a.	28/41
Dibromomethane	CH_2Br_2	0.9	0.2/0.7	3/11	405	890	n.a.
Tribromomethane	$CHBr_3$	1.2	0.6/2.2	9/85	44	88	n.a.
Bromochloromethane	CH_2BrCl	0.1	2.3/9.2	20/130	470	1050	n.a.
Dichlorobromomethane	$CHBrCl_2$	0.3	0.8/3.4	3/2	124	250	n.a.
Dibromochloromethane	$CHBr_2Cl$	0.3	0.7/2.2	4/2	85	182	n.a.

Table 2*:* Brief description of measurement campaigns with the High Altitude and Long Range Research aircraft (HALO) used for this study.

Name	Time period	Campaign base	brief description
TACTS, Transport and Composition in the Upper Troposphere/Lowermost Stratosphere	late August 2012-September 2012	Oberpfaffenhofen/ Germany and Sal/Cape Verde	Cover changes in UTLS chemical composition during the transition from summer to fall
WISE, Wave driven isentropic exchange	September - October 2017	Shannon/Ireland	Study Troposphere-Stratosphere Exchange in mid latitudes
PGS, **POLSTRACC, GW-Lcycle, SALSA***	December 2015 - March 2016	Kiruna/Sweden	Study the polar UTLS during winter, including the effect of chemical ozone depletion.

* **PGS** is a synthesis of three measurement campaigns: **POLSTRACC** (The Polar Stratosphere in a Changing Climate), **GW-LCYCLE** (Investigation of the Life cycle of gravity waves) and **SALSA** (Seasonality of Air mass transport and origin in the Lowermost Stratosphere).

Table 3: Averaged mole fractions (parts per trillion, ppt; 10^{-12}) and vertical gradients of brominated very short lived substances from the combined ~~Wave driven isentropic exchange (~~WISE~~)~~ and ~~Transport and Composition in the Upper Troposphere/Lowermost Stratosphere (~~TACTS) data set, representative for 40-60°N during late summer to early fall (data from late August to October). Data have been averaged using potential temperature $\boldsymbol{\theta}$ and potential temperature difference to the tropopause $\boldsymbol{\Delta\theta}$ as vertical profiles coordinates. ~~Data have been averaged using potential temperature and potential temperature difference to the tropopause as vertical profiles coordinates.~~ Tropopause (TP) values ~~-~~are from the 10 K bin below the dynamical tropopause (see text for details). The 10K bin standard deviations in the table represent the variability averaged over the four lowest stratospheric bins. The average potential temperature of the tropopause during the WISE and TACTS campaigns has been calculated from the European Centre for Medium Weather Forecast data at the locations of our measurements.

WISE and TACTS	~~θPotential Temperature~~				$\Delta\theta$			
	Mole fraction [ppt]		Gradient	10 K bin stdev. (TP – TP + 40K)	Mole fraction [ppt]		Gradient	10 K bin stdev. (TP – TP + 40K)
	TP	TP+(30-40 K)	[%/K]	[ppt]	TP	TP+(30-40 K)	[%/K]	[ppt]
CH_2Br_2	0.79±0.07 ~~0.80~~	0.67±0.15~~0.58~~	0.39~~0.70~~	0.12	0.83±0.08 ~~0.77~~	0.59±0.09~~0.55~~	0.74~~0.72~~	0.09
$CHBr_3$	0.45±0.18 ~~0.47~~	0.26±0.28~~0.14~~	1.08~~1.77~~	0.20	0.56±0.26 ~~0.40~~	0.11±0.05~~0.09~~	1.99~~1.92~~	0.~~10~~11
CH_2BrCl	0.18±0.1~~0.23~~	0.17±0.08~~0.13~~	0.08~~1.14~~	0.~~108~~	0.23±0.11 ~~0.19~~	0.15±0.07~~0.14~~	0.8~~0.73~~	0.~~07~~1
$CHBrCl_2$	0.16±0.03 ~~0.16~~	0.13±0.03~~0.12~~	0.48~~0.64~~	0.03	0.16±0.02 ~~0.15~~	0.12±0.02~~0.11~~	0.73~~0.71~~	0.~~02~~02
$CHBr_2Cl$	0.12±0.03 ~~0.12~~	0.09±0.04~~0.07~~	0.74~~1.13~~	0.04	0.13±0.03 ~~0.12~~	0.06±0.02~~0.06~~	1.28~~1.24~~	0.~~02~~03
total Br	3.52±0.73 ~~3.64~~	2.48±1.18~~1.89~~	0.73~~1.20~~	0.83	3.99±1.15 ~~3.40~~	1.89±0.42~~1.76~~	1.31~~1.20~~	0.~~51~~50

Table 4: Averaged mole fractions ~~(parts per trillion, ppt; 10^{-12})~~ and vertical gradients of brominated VSLS during the PGS campaign. Data have been averaged using potential temperature $\boldsymbol{\theta}$ and potential temperature difference to the tropopause $\boldsymbol{\Delta\theta}$ as vertical profiles coordinates. Tropopause (TP) values are from the 10 K bin below the dynamical tropopause (see text for details). The 10K bin standard deviations in the table represent the variability averaged over the four lowest stratospheric bins. The average potential temperature of the tropopause during the PGS campaign has been calculated from ECMWF data at the locations of our measurements.

PGS	~~Potential Temperature~~ θ				~~$\Delta\theta$Delta Theta~~			
	Mole fraction [ppt]		Gradient	10 K bin stdev	Mole fraction [ppt]		Gradient	10 K bin stdev
	TP	TP+(30-40 K)	[%/K]	[ppt]	TP	TP + 40 K	[%/K]	[ppt]
CH_2Br_2	1.08±0.08	0.50±0.09	1.34	0.18	1.09±0.13	0.53±0.09	1.28	0.11
$CHBr_3$	0.66±0.12	0.07±0.04	2.22	0.26	0.75±0.3	0.07±0.03	2.26	0.13
CH_2BrCl	0.25±0.03	0.13±0.02	1.16	0.05	0.26±0.05	0.14±0.02	1.14	0.03
$CHBrCl_2$	0.20±0.01	0.09±0.02	1.35	0.03	0.20±0.02	0.10±0.02	1.29	0.02
$CHBr_2Cl$	0.16±0.02	0.04±0.01	1.89	0.04	0.16±0.04	0.04±0.01	1.86	0.03
total Br	4.91±0.54	1.53±0.34	1.72	1.28	5.20±1.25	1.60±0.33	1.73	0.70

Table 5: Values of organic VSLS bromine in air at the tropical, respectively extratropical (40-60°N) tropopause ($Br_{org}^{ex-trop}$ and Br_{org}^{trop})used in the calculation of inorganic bromide (Br_y) for the observation (OBS), respectively the models using the emission scenarios of Liang et al. (2010), Ordóñez et al. (2012), Ziska et al. (2013) and Warwick et al. (2006). For the Warwick et al. (2006) scenario, the data have been derived from the EMAC model, while for the other scenarios the TOMCAT model has been used. For the Tropics, annual average for the years 2012 to 2016 have been calculated between 10°N and 10°S in a potential temperature range from 365 to 375 K. The tropical values for the observations are from the observations compiled in the 2018 WMO report (Engel and Rigby, 2018) in the tropics between 365 and 375 K potential temperature. All data presented are shown in parts per trillion (ppt).

	Tropics			Extratropics WISE/TATS			Extratropics PGS		
	CH_2Br_2	$CHBr_3$	TOT	CH_2Br_2	$CHBr_3$	TOT	CH_2Br_2	$CHBr_3$	TOT
OBS	0.73	0.28	2.80	0.83	0.56	3.99	1.09	0.75	5.20
LIANG	0.82	0.26	3.06	0.70	0.32	2.84	0.99	1.00	5.73
ORDONEZ	0.91	0.28	3.30	0.79	0.44	3.27	1.10	1.21	6.58
ZISKA	1.13	0.10	3.18	0.87	0.18	2.77	1.13	0.69	5.10
WARWICK	1.28	0.84	5.48	0.83	0.37	3.07	1.16	0.62	4.59

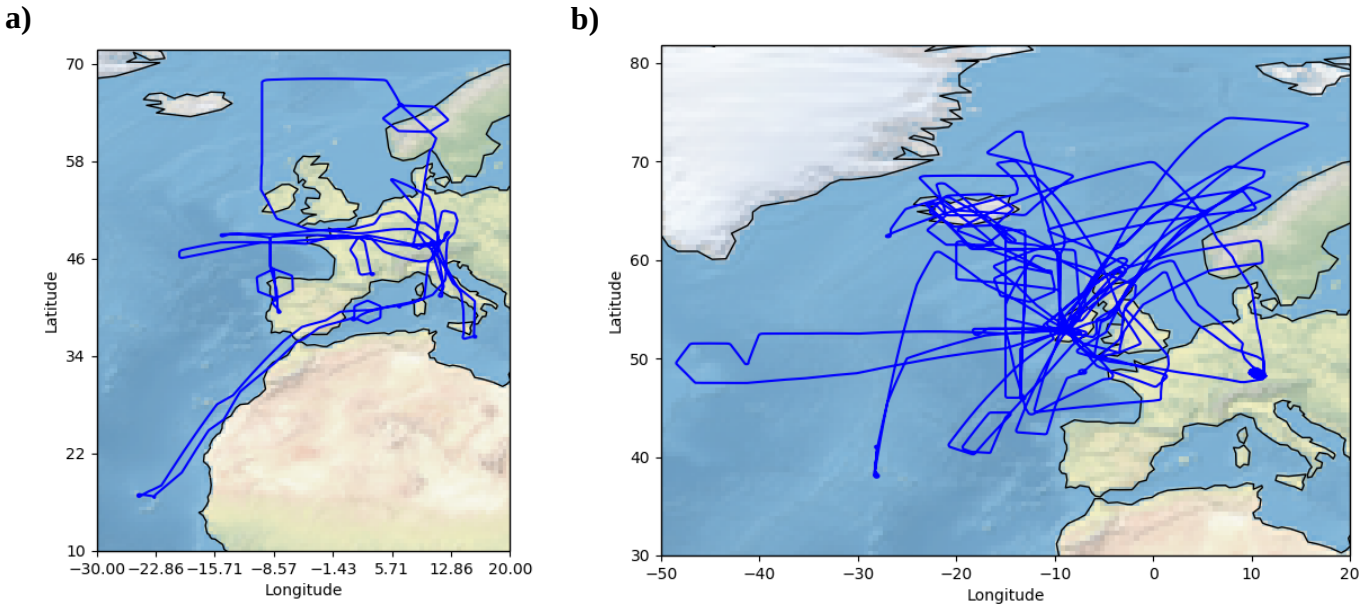

Figure 1: Flight tracks of High-Altitude and Long-Range Research AircraftHALO during the a) Transport and Composition in the Upper Troposphere/Lowermost Stratosphere (TACTS) campaign (late August and September 2012) and b) the Wave-driven isentropic exchange (WISE) campaign (September/October 2017). The basis of the TACTS campaign was mainly Oberpfaffenhofen (near Munich) in Germany, while the basis of the WISE campaign was Shannon (Ireland).

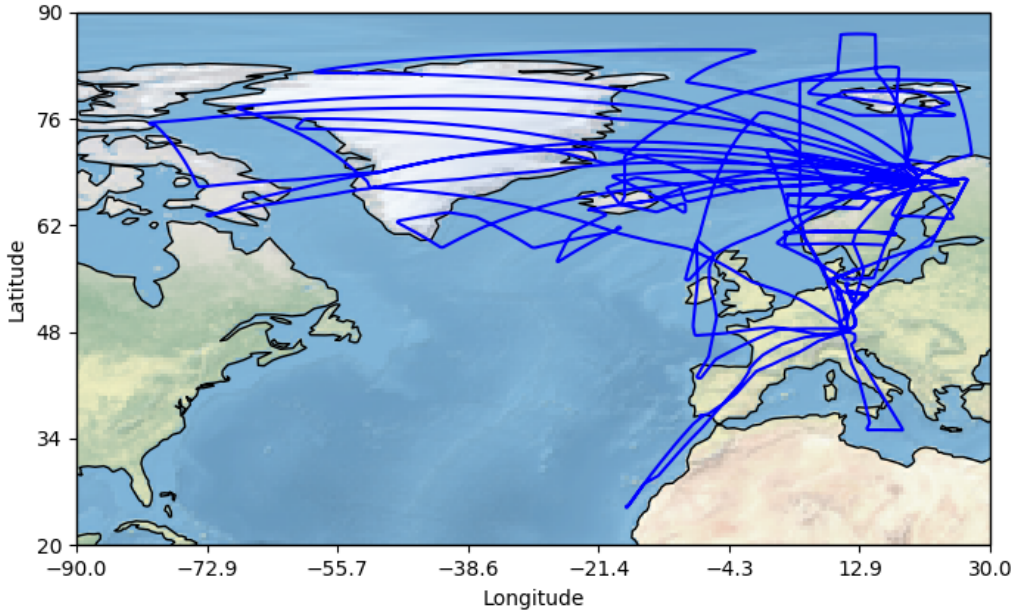

Figure 2: Flight tracks of ~~High Altitude and Long Range Research Aircraf~~HALO~~t~~ during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign (December 2015 to April 2016). The basis of the campaign was mainly Kiruna in Northern Sweden.

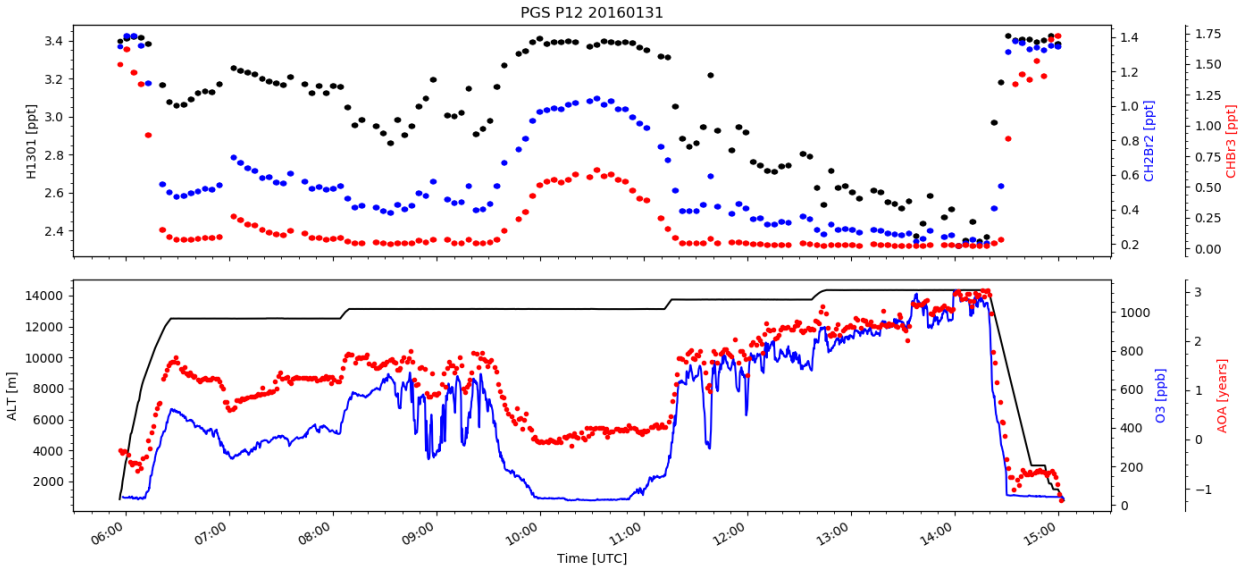

Figure 3: Example of data gathered during a single Flight of ~~the High Altitude and Long Range Research Aircraft~~HALO during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign. The flight PGS 12 started on 31 January 2016 from Kiruna in Northern Sweden. The upper panel shows measurements ~~(parts per trillion, ppt; 10^{-12})~~ of the long-lived brominated source gas Halon 1301 (CF_3Br) and the short-lived source gases CH_2Br_2 and CHBr3, all measured with GhOST MS. The lower panel shows flight altitude, as well as ozone (parts per billion, ppb; 10^{-9}; measured by the FAIRO instrument (Zahn et al., 2012) and of mean age of air derived from SF_6 measurements from the ECD channel of GhOST-MS (1 minute time resolution, see e.g. (Boenisch et al., 2009) for a description of the measurement technique). An air mass with low ozone and also low mean age of air was observed during the middle of the flight between about 10 and 11 UTC. High mixing ratios of all three source gases are found in this region, as well as during take-off and landing of the aircraft. $CHBr_3$ values are close to detection limit when flying in aged stratospheric air masses, indicating a complete conversion of the bromine to its inorganic form.

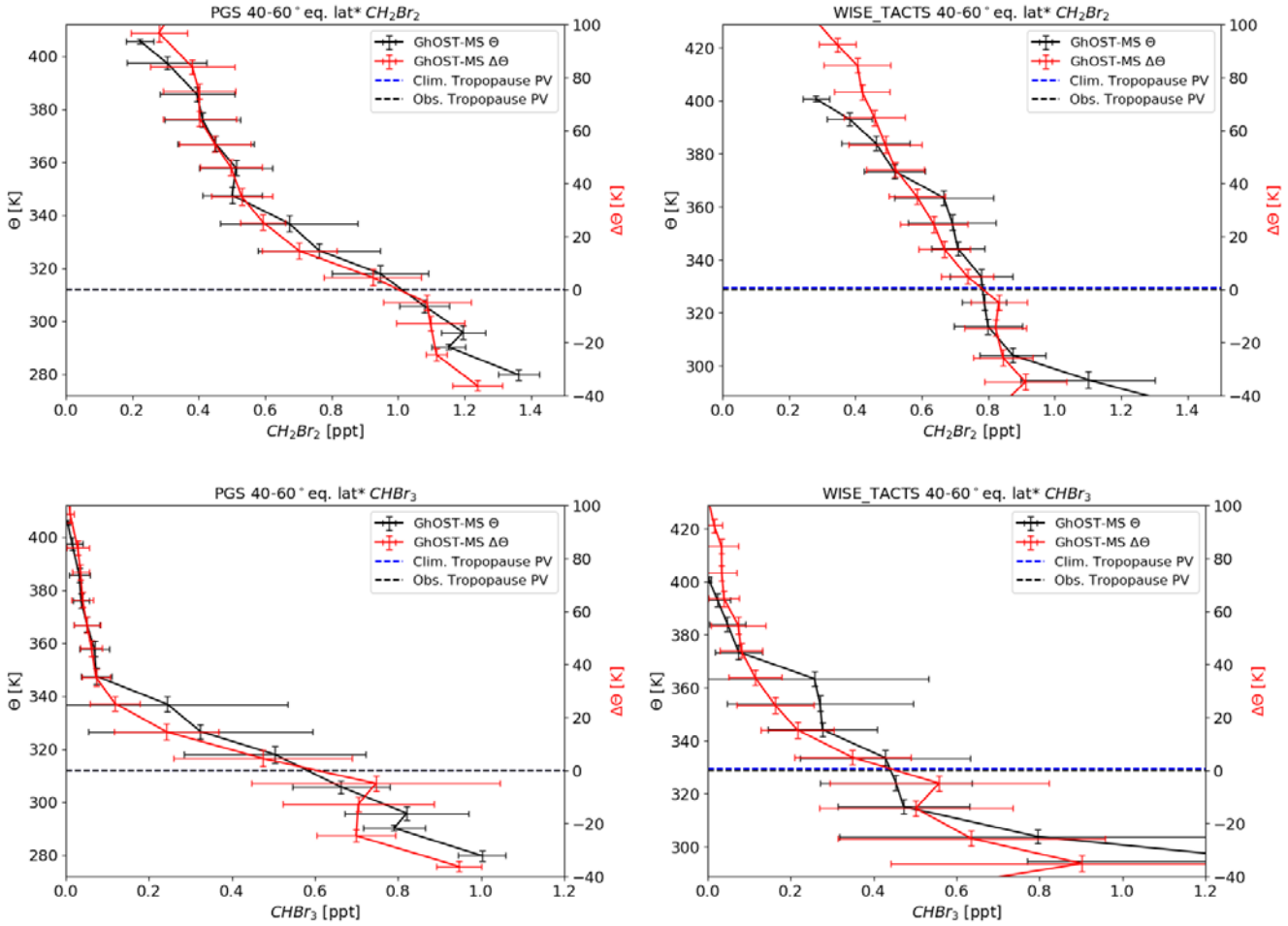

Figure 4: Vertical profiles of CH_2Br_2 (top) and $CHBr_3$ (bottom)~~(parts per trillion, ppt; 10^{-12})~~ averaged over 40-60° of equivalent latitude* and all flights during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign (left, late December 2015 to March 2016) and from the merged data set from the ~~Transport and Composition in the Upper Troposphere/Lowermost Stratosphere and Wave driven isentropic exchange~~TACTS and WISE campaigns (right, representative of late summer to fall). The data are displayed as function of potential temperature and potential temperature above the tropopause. The ~~dotted~~ dashed blue line shows the zonal mean dynamical tropopause derived from ERA Interim during September and October of the respective years in the Northern Hemisphere between 40 and 60° latitude, while the black dashed line is the average dynamical tropopause derived for the times and locations of our observations. Both vertical and horizontal error bars denote 1 sigma variability.

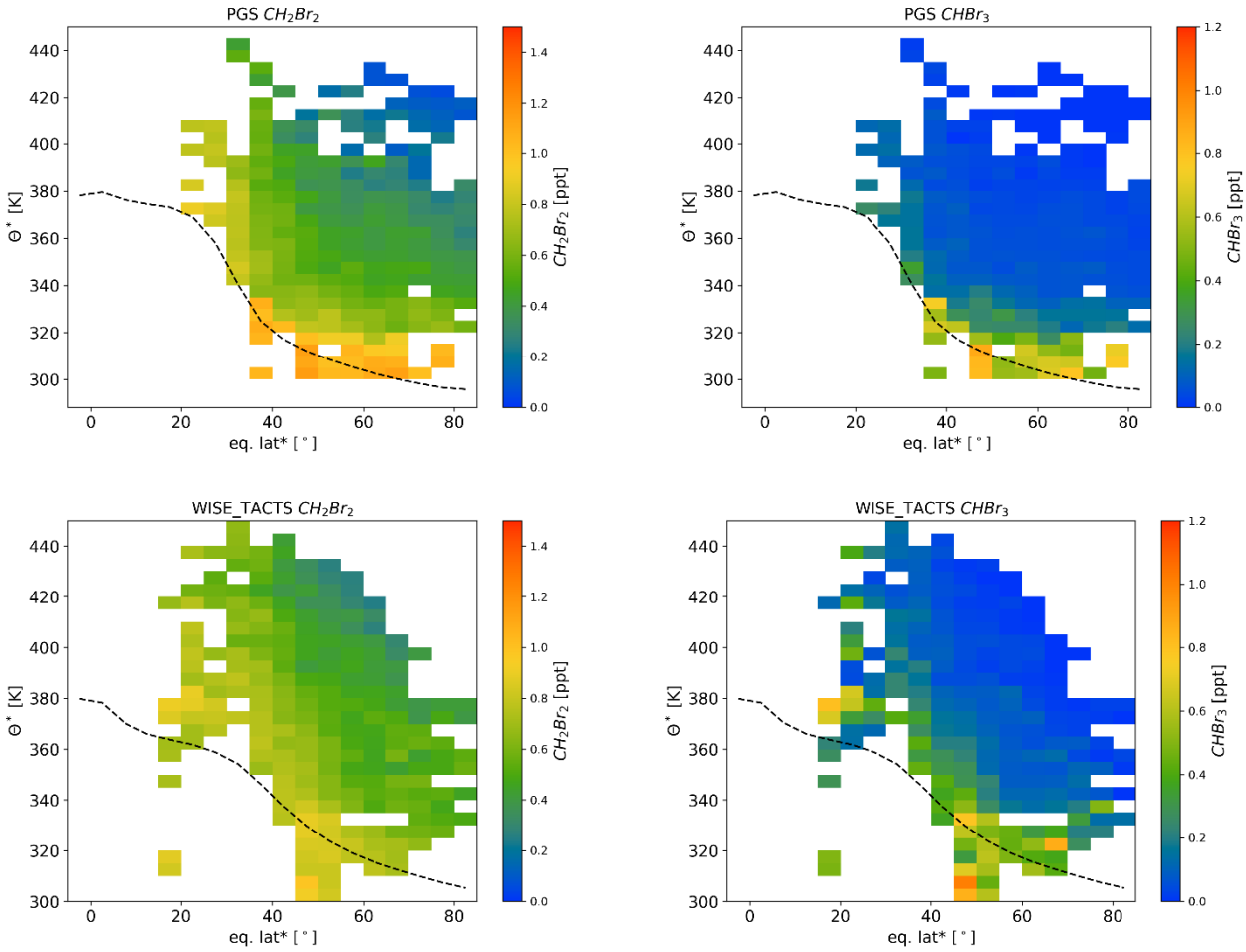

Figure 5: Altitude latitude cross sections of CH_2Br_2 (top) and $CHBr_3$ (bottom)~~(parts per trillion, ppt; 10^{-12})~~ compiled from all flights during the during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign from late December 2015 to March 2016 (left) and the ~~Transport and Composition in the Upper Troposphere/Lowermost Stratosphere (~~TACTS~~) and Wave driven isentropic exchange (~~WISE~~)~~ campaigns representative of late summer/early fall conditions (right). The data are displayed as function of $\boldsymbol{\theta}^*$ (see description in Section 2) and equivalent latitude*. The dynamical tropopause (dashed line) has been derived from ERA-Interim reanalysis, providing a climatological mean zonal mean value of the tropopause.

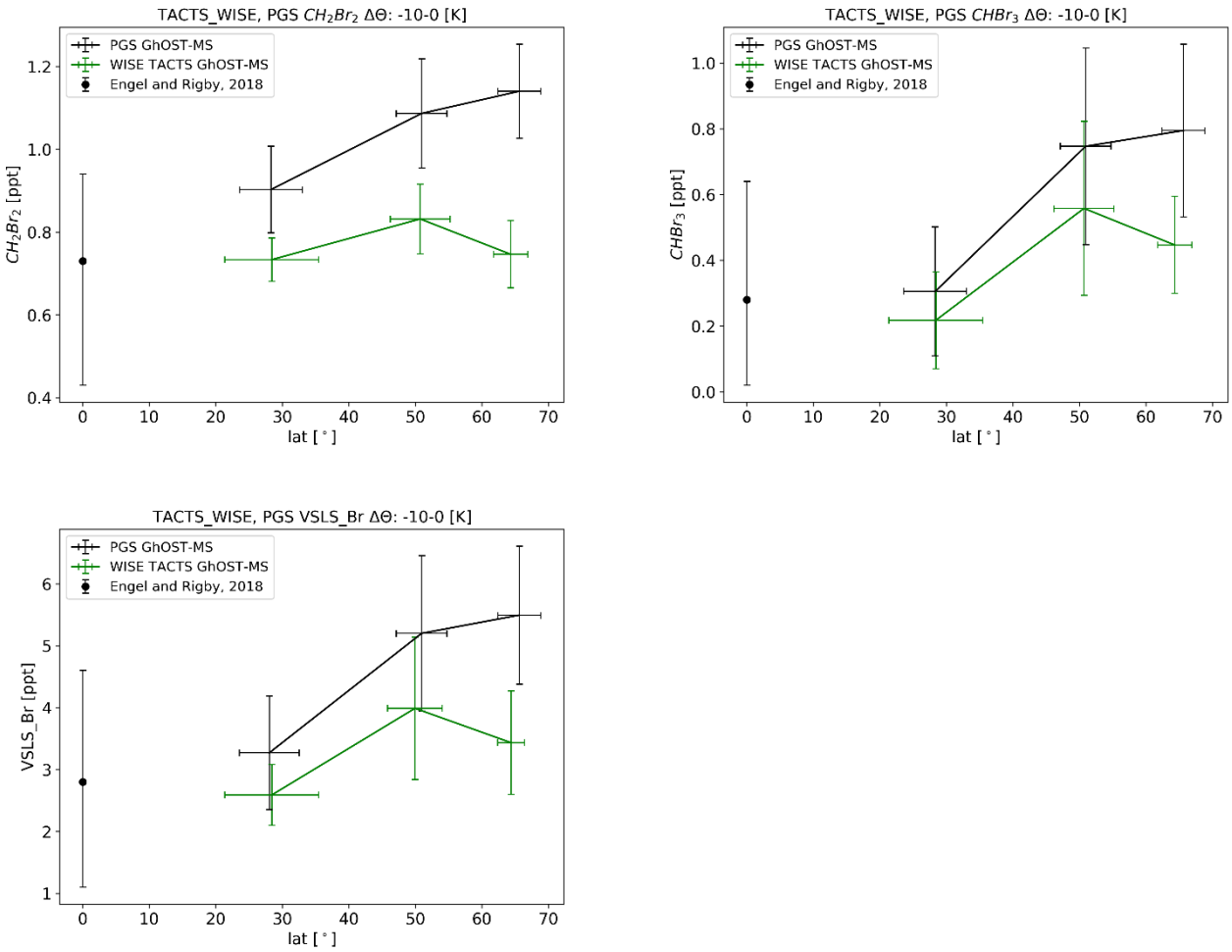

Figure 6: Latitudinal cross section of CH_2Br_2~~,~~ (to left), $CHBr_3$ (top right) and total organic VSLS bromine (bottom) ~~(parts per trillion, ppt; 10^{-12})~~ for all three campaigns, binned by latitude and averaged within 10 K below the local dynamical tropopause. Also included are the reference values for the tropical tropopause (Engel and Rigby, 2018).

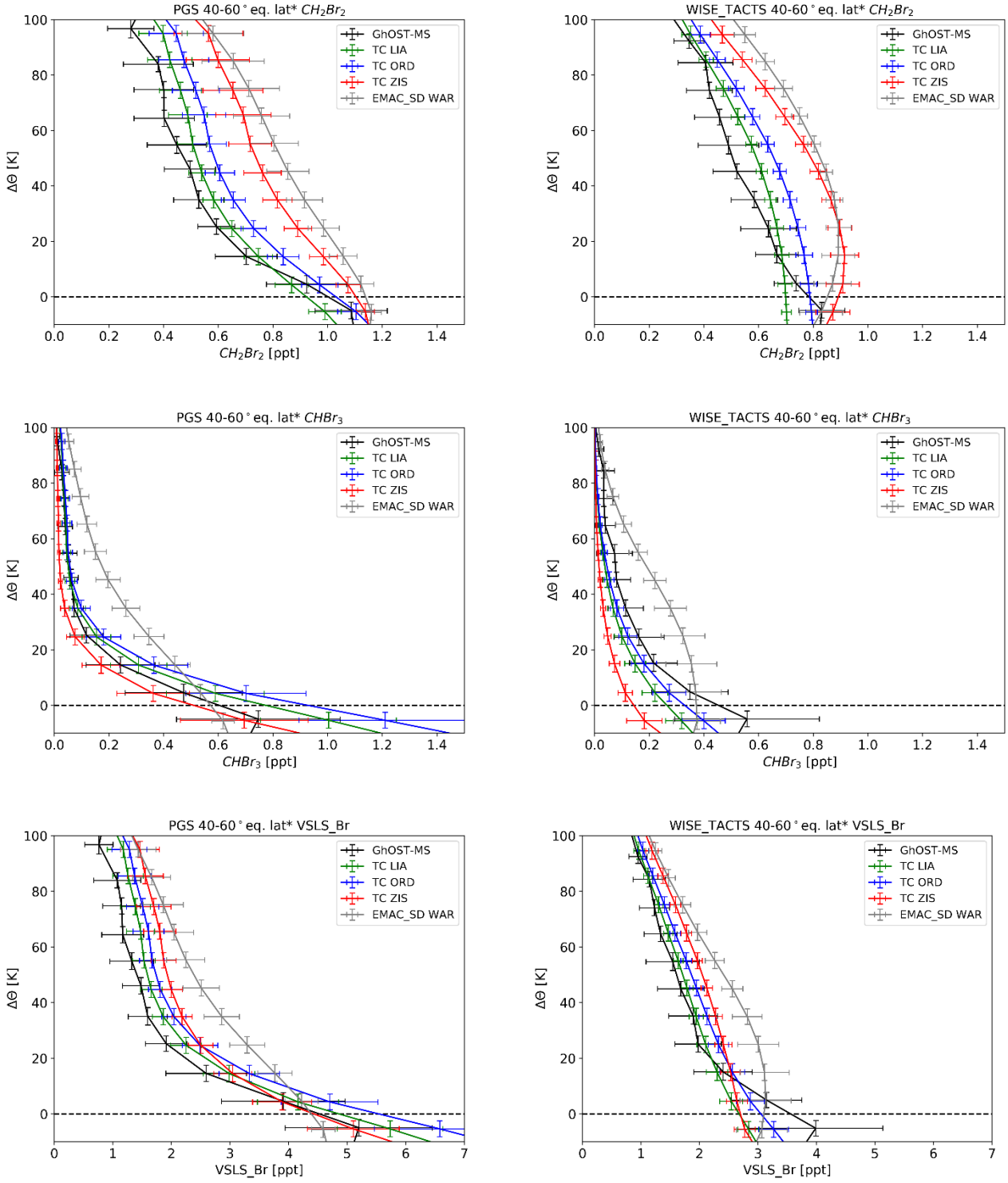

Figure 7: Vertical profiles of CH_2Br_2 (top),~~and~~ $CHBr_3$ (middle) and total organic VSLS bromine (bottom) ~~(parts per trillion, ppt; 10^{-12})~~ averaged over 40-60° of equivalent latitude* and all flights during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign from late December 2015 to March 2016 (left hand side) and from the combined WISE_TACTS ~~(Wave-driven isentropic exchange, WISE; and Transport and Composition in the Upper Troposphere/Lowermost Stratosphere, TACTS)~~ data set, representative of late summer to fall conditions. Also shown are model results from the ~~Toulouse Off-line Model of Chemistry And Transport (~~TOMCAT~~)~~ and ~~ECHAM/MESSy Atmospheric Chemistry (~~EMAC~~)~~ model using different emission scenarios (see text for details). ~~Data from some flight of the TACTS campaign have bene omitted due to some extremely high values, which are suspected to be a contamination.~~ The data are displayed as function of potential temperature above the dynamical tropopause. In case no model information on the tropopause altitude was available (TOMCAT), climatological tropopause values have been used (see text for details).

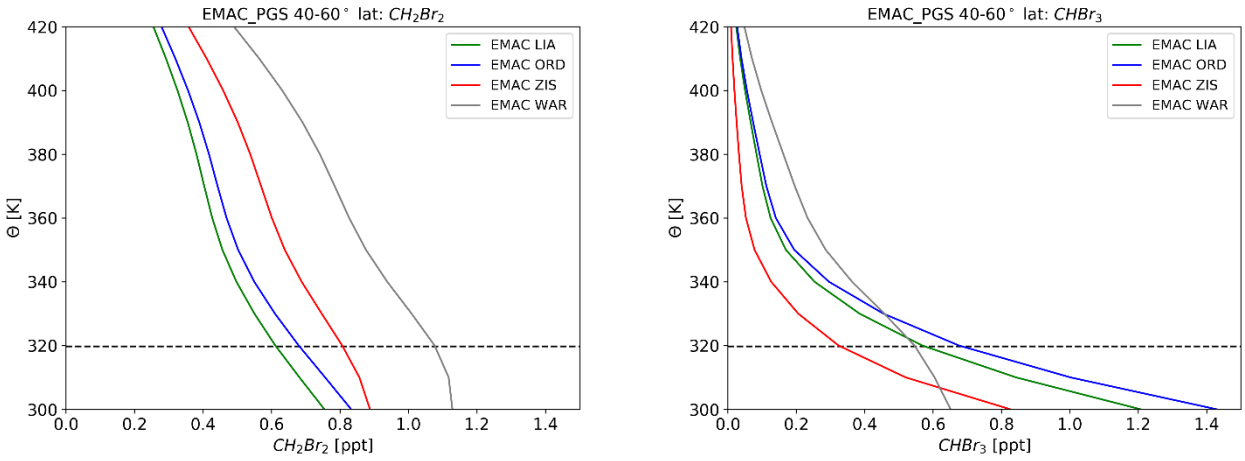

Figure 8: Vertical profiles of CH_2Br_2 (left) and $CHBr_3$ (right)~~(parts per trillion, ppt; 10^{-12})~~ averaged over 40-60° latitude from four model simulations with the EMAC model using the emission scenarios by (Liang et al., 2010;Warwick et al., 2006;Ordóñez et al., 2012;Ziska et al., 2013). The data have been averaged for January/February and March, i.e. representative of the time period covered by the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign. The dashed line represents the model tropopause. Model results are for nudged simulations of EMAC but do not cover the time period of our observations.

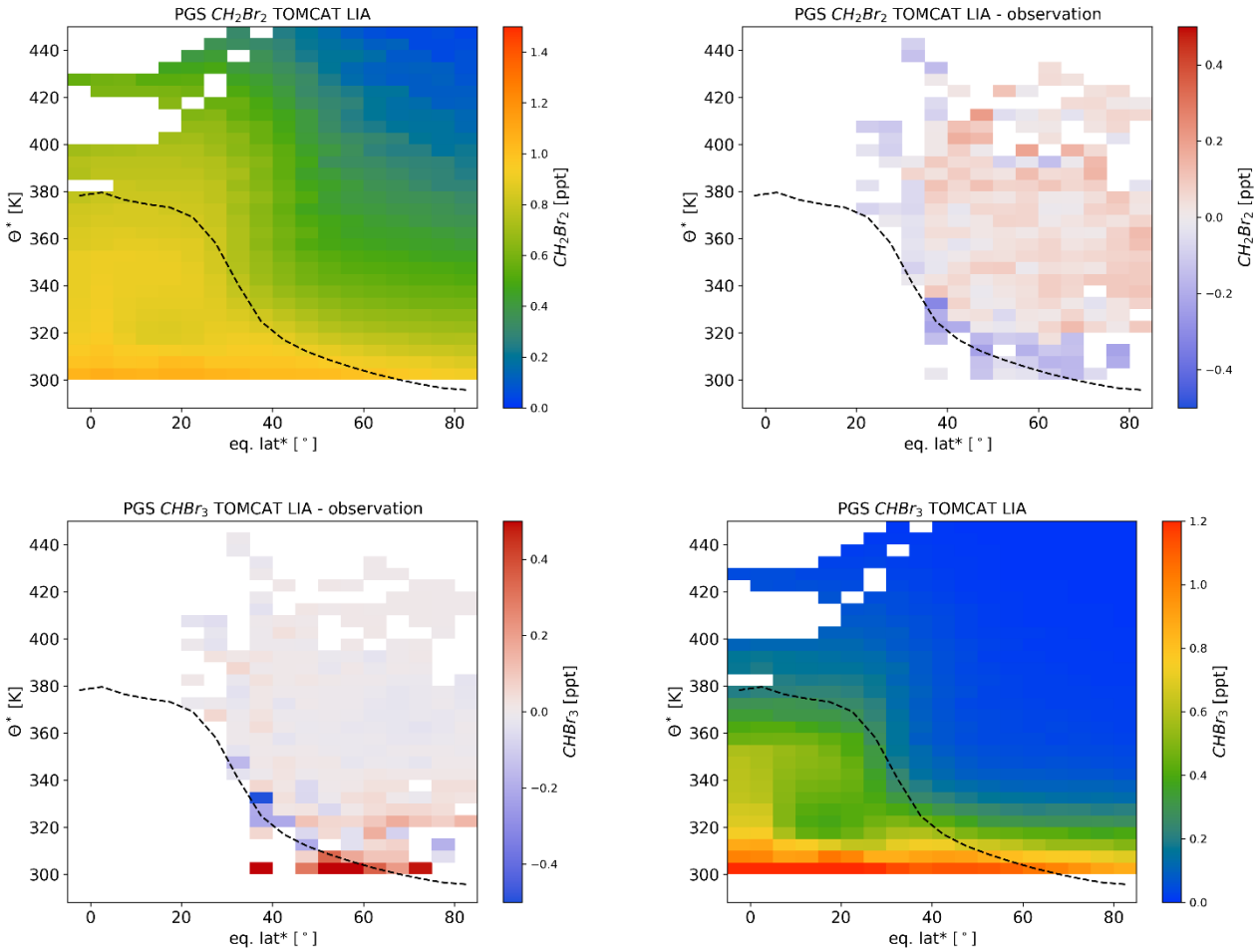

Figure 9: Latitude altitude cross section of CH_2Br_2 (top) and $CHBr_3$ (bottom)~~(parts per trillion, ppt; 10^{-12})~~ for the ~~Toulouse Off-line Model of Chemistry And Transport (~~TOMCAT~~)~~ model using the Liang et al. (2010) emission scenario (left) and differences to the observations (right) for all flights during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign from late December 2015 to March 2016. The data are binned using equivalent latitude* and $\boldsymbol{\theta}^*$as coordinates (see text for details). Also shown in the climatological mean tropopause (see text for details; dashed line). Boxes in which due to the vertical resolution of the model no values are available are left blanc.

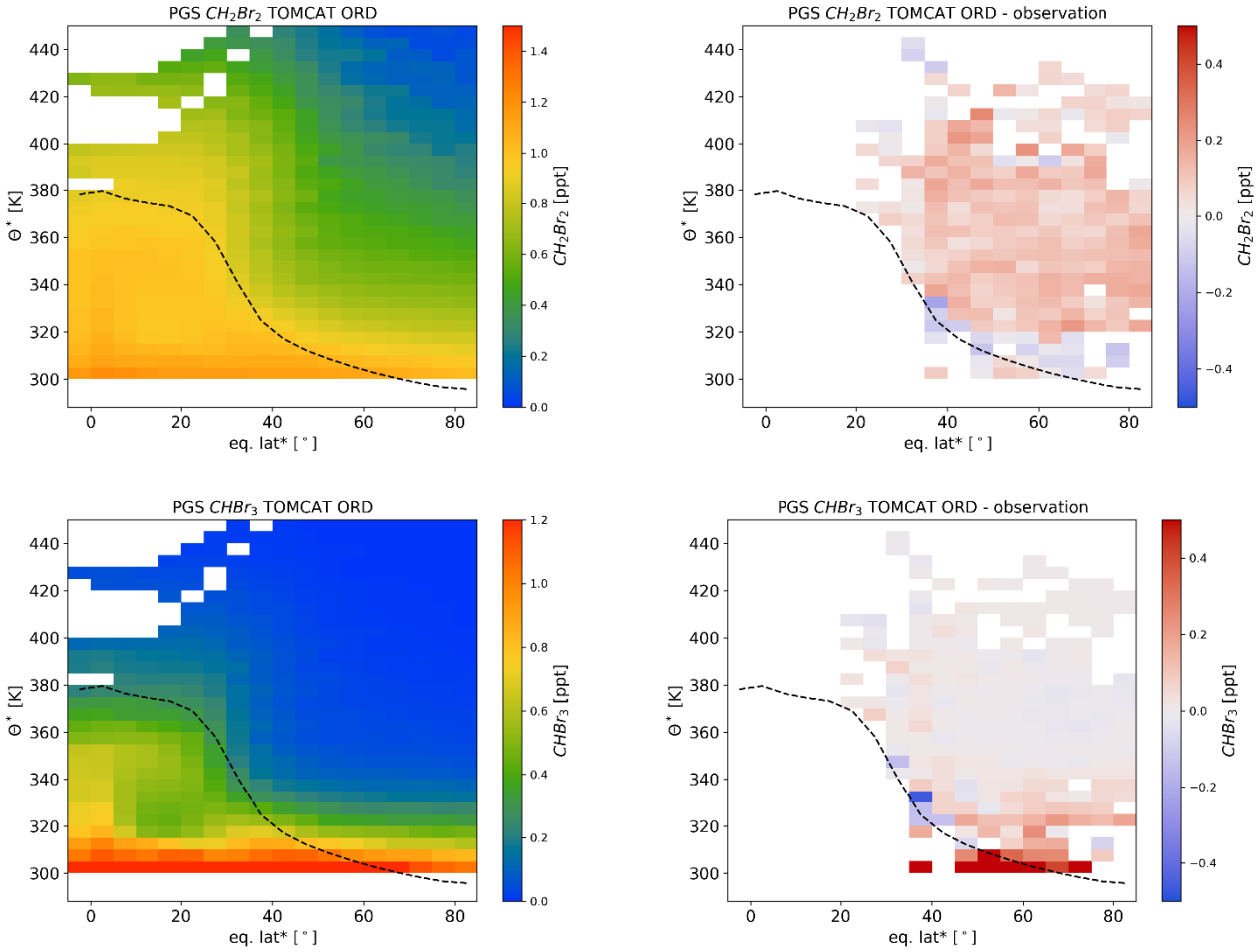

Figure 10: Latitude altitude cross section of CH_2Br_2 (top) and $CHBr_3$ (bottom) ~~(parts per trillion, ppt; 10^{-12})~~ for the ~~Toulouse Off-line Model of Chemistry And Transport (~~TOMCAT~~)~~ model using the ~~Ordonez et al. (2012)~~ Ordóñez et al. (2012) emission scenario (left) and differences to the observations (right) for all flights during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign from late December 2015 to March 2016. The data are binned using equivalent latitude* and $\boldsymbol{\theta}^*$as coordinates (see text for details). Also shown in the climatological mean tropopause (see text for details; dashed line). Boxes in which due to the vertical resolution of the model no values are available are left blanc.

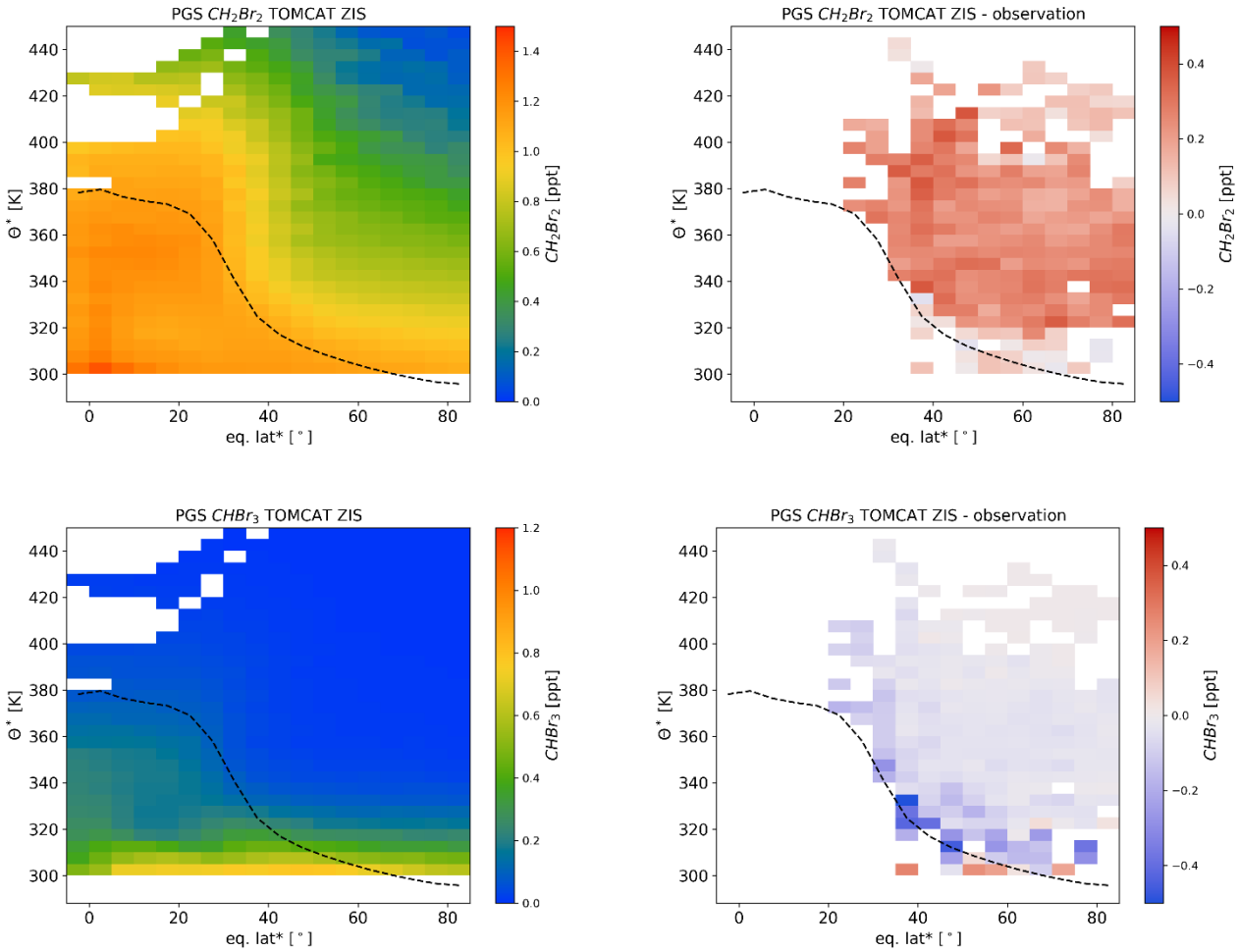

Figure 11: Latitude altitude cross section of CH_2Br_2 (top) and $CHBr_3$ (~~parts per trillion, ppt; 10^{-12}~~bottom) for the ~~Toulouse Off-line Model of Chemistry And Transport (~~TOMCAT~~)~~ model using the Ziska et al. (2013) emission scenario (left) and differences to the observations (right) for all flights during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign from late December 2015 to March 2016. The data are binned using equivalent latitude* and $\boldsymbol{\theta}^*$as coordinates (see text for details). Also shown in the climatological mean tropopause (see text for details; dashed line). Boxes in which due to the vertical resolution of the model no values are available are left blanc.

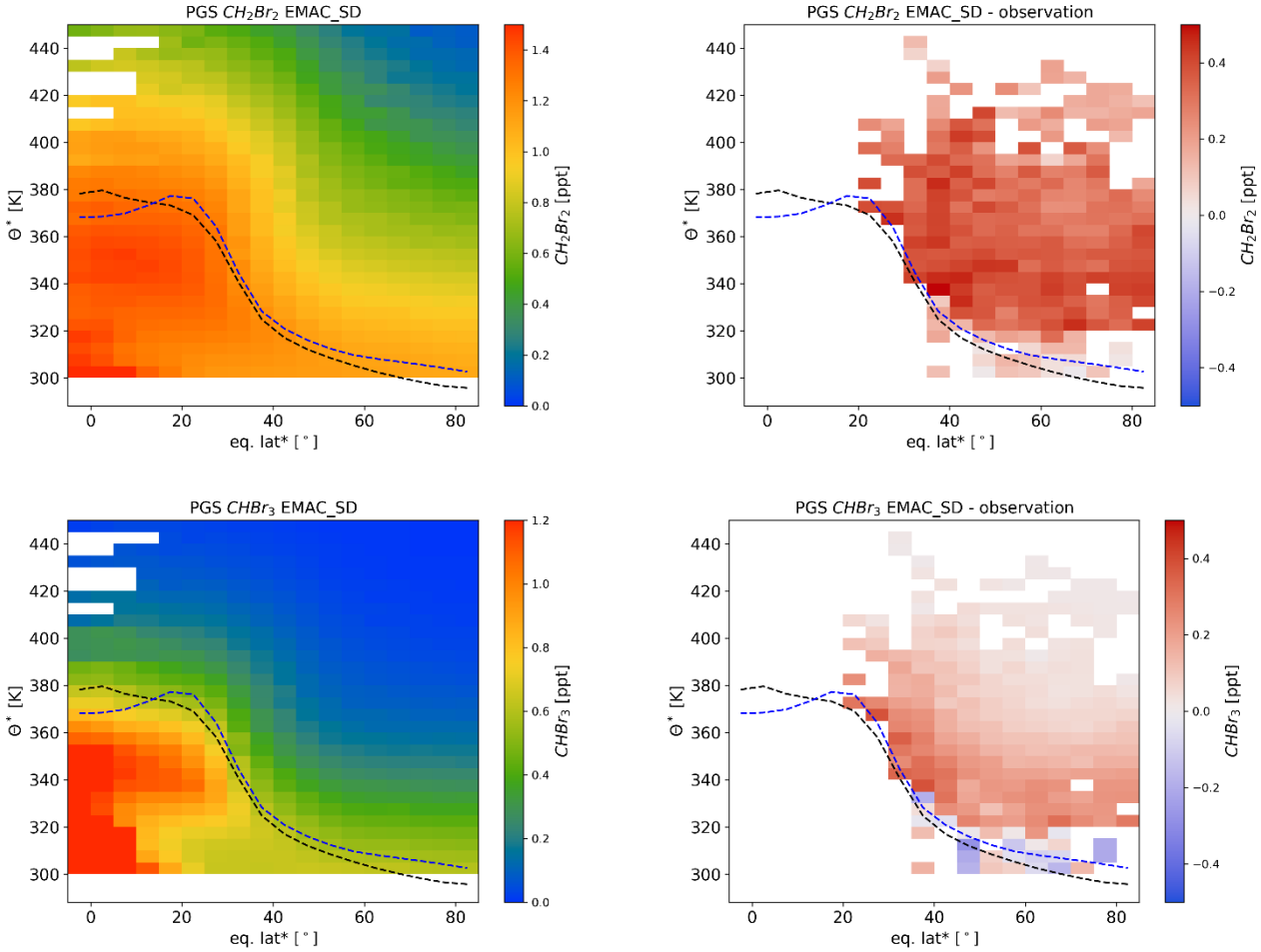

Figure 12: Latitude altitude cross section of CH_2Br_2 (top) and $CHBr_3$ (~~parts per trillion, ppt; 10^{-12}~~bottom) for the ~~ECHAM/MESSy Atmospheric Chemistry (~~EMAC~~)~~ model using the Warwick et al. (2006) emission scenario (left) and differences to the observations (right) for all flights during the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign from late December 2015 to March 2016. The data are binned using equivalent latitude* and $\boldsymbol{\theta}^*$as coordinates (see text for details). Also shown in the climatological mean tropopause (black dashed line, see text for details) and the model tropopause (dashed blue line, see text for details). Boxes in which due to the vertical resolution of the model no values are available are left blanc.

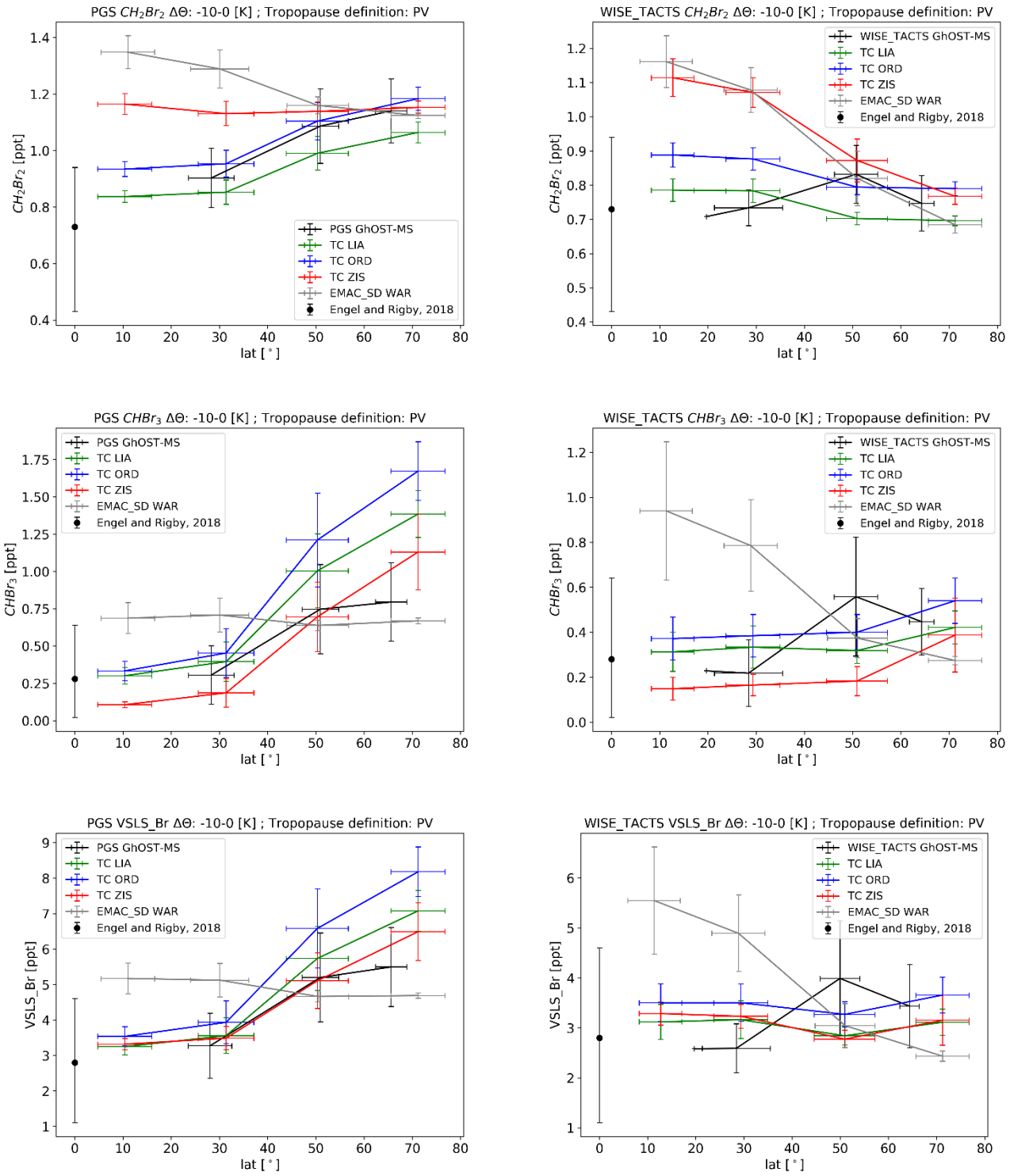

Figure 13: Latitude cross section of tropopause representative values of CH_2Br_2~~,~~ (top) $CHBr_3$ (middle) and total organic VSLS bromine (top)~~(parts per trillion, ppt; 10^{-12})~~ for all the measurements from the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign (left) and WISE_TACTS ~~(Wave driven isentropic exchange, WISE; and Transport and Composition in the Upper Troposphere/Lowermost Stratosphere, TACTS)~~ dataset (right) from observations in comparison to all model emissions scenario combinations. Data are binned by latitude and averaged over 10 K below the tropopause. Due to the different sampling of the observations and the models the centers of the different latitude bins are not the same for observations and models.

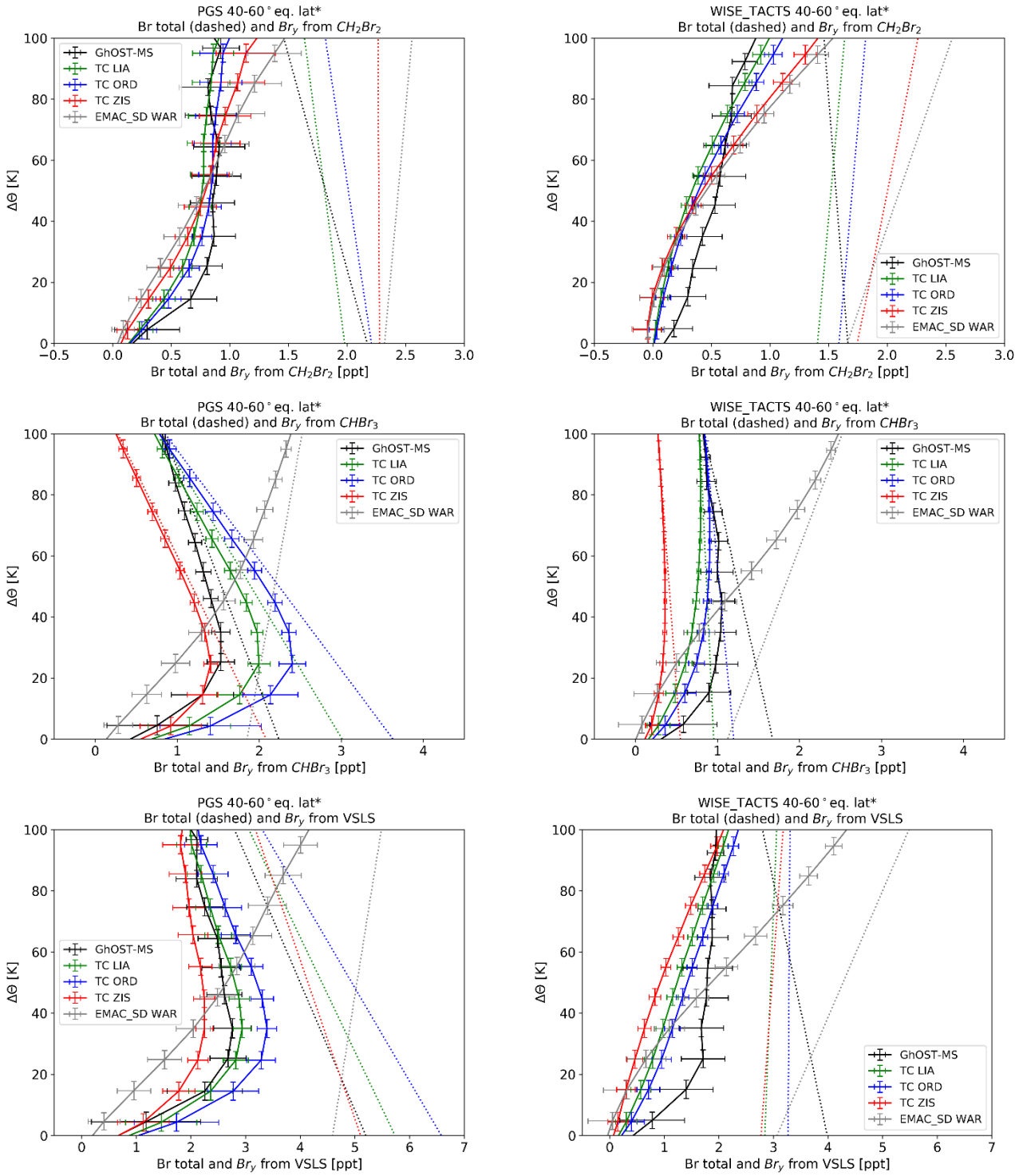

Figure 14 Vertical profiles of Br_y (solid lines~~; parts per trillion, ppt, 10^{-12}~~) and total Bromine (dotted lines~~; ppt~~) from CH_2Br_2, from $CHBr_3$ and from total organic VSLS bromine averaged over 40-60° of equivalent latitude* for the winter PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign (left, late December 2015 to March 2016) and for late summer to early fall period (right, ~~Wave driven isentropic exchange (~~WISE~~)~~ and ~~Transport and Composition in the Upper Troposphere/Lowermost Stratosphere (~~TACTS~~)~~ campaigns) in comparison to model results from the ~~Toulouse Off line Model of Chemistry And Transport (~~TOMCAT~~)~~ and the ~~ECHAM/MESSy Atmospheric Chemistry (~~EMAC~~)~~ model using different emission scenarios (see text for details on calculation of Br_y). Total Bromine is calculated from data at the tropical and extratropical tropopause and using assumptions about fractional input from these two source regions (see text for details). The data are displayed as function of potential temperature above the tropopause. In case no model information on the tropopause altitude was available (TOMCAT), climatological tropopause values have been used (see text for details).

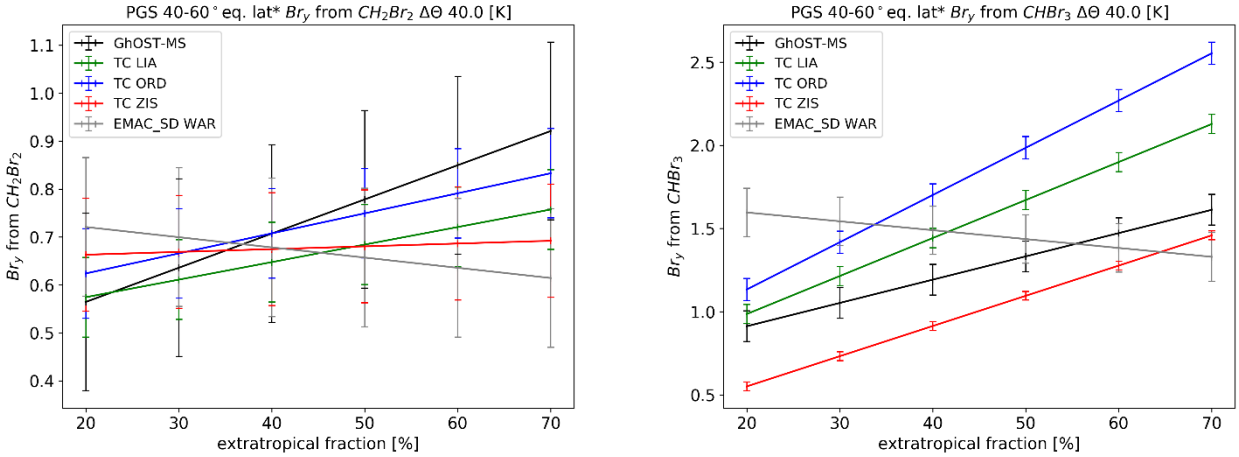

Figure 15: Sensitivity of Br_y from CH_2Br_2 and $CHBr_3$ ~~(parts per trillion, ppt; 10^{-12})~~ at $\Delta\theta$ ~~of =~~ 40 K as a function of the fraction of extratropical air for the PGS ~~(Polar Stratosphere in a Changing Climate, Investigation of the Life cycle of gravity waves and Seasonality of Air mass transport and origin in the Lowermost Stratosphere)~~ campaign from January to April 2016 for observations in comparison to the different model calculation.