

## ***Interactive comment on “Using airborne observations to improve estimates of short-lived halocarbon emissions during summer from Southern Ocean” by E. Asher et al.***

### **Anonymous Referee #2**

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The paper presented by Asher et al., provides a valuable contribution to the understanding of the distribution and sources of halogenated organic substances from the Southern Ocean. The work publishes airborne observations of VHOC in an understudied region and applies new concepts for source determinations related to measurements of O<sub>2</sub> and CO<sub>2</sub> and geophysical datasets. It underlines current knowledge of the biological sources of CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> by applying their ratio to oceanic oxygen emissions. CH<sub>3</sub>I appears to have a dominant biological source in the area of the Patagonian shelf, while closer to Antarctica a photochemical source appears to be dominant. The paper also compares the derived emissions of the novel concepts to the output of a global climate model.

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I agree that the presentation of data from several compounds and several campaigns is a difficult task. Also the loaded content of the paper: evaluation of model predictions, calculation of biogenic enrichment ratios, identification of regional sources, and novel means of parameterizing ocean fluxes, which was only summarized clearly in the conclusion section of the paper, makes the task of writing not easier. While the authors present their results and outcomes, which are not totally exciting and sometimes are also not very convincing due to poor correlations, their novel approaches and novel concepts are more exciting, but are poorly presented. They could do a much better job in explaining and presenting their concepts and the overall goal of the paper, which for me remains more a concept than a result paper. The results underline the novel approaches, as they do not contradict earlier studies and the novel approaches can be more useful and should be tested for and in future studies.

The authors should think about a different setup of their paper, putting their concepts more into the focus, but clearly their approaches need be described more clearly and in more detail throughout the text. Also they authors should think about the title. Also technically the paper needs improvement, as abbreviations are sometimes not introduced, sometimes edits are not clearly overworked, which led to typos and grammar mistakes and also I wonder if it would be possible to make some sentences less bulky and loaded. Some figures are too small, some legends appear odd and there appear to be misunderstandings with some references .

Overall I think the work behind the paper is very valuable and should be published in ACP, but the presentation of the work needs prior strong improvement.

Detailed comments below:

23-24: We also use CH<sub>3</sub>Br from the University of Miami Advanced Whole Air Sampler(AWAS) on ORCAS and from the UC Irvine Whole Air Sampler (WAS) on ATom-2.

In connection with the first and the third sentence, this is a strange sentence. I think there is too much detail in the first two sentences about the instrumentation , which

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could be abandoned for the abstract and only explained later in the text.

37: Based on these relationships

What does this refer to?... it is unclear

49-50: Indeed, HVOCs may be among the most important sources of inorganic bromine to the whole atmosphere, since recent evidence indicates that sea salt is scarce..

This is not true, as there is enough literature out to show how sea salt aerosol dominates the bromine in the lower troposphere. If the authors want to keep this sentence they have to provide more evidence, than just an upcoming paper. I suggest rewriting and specifying the statement to the known literature.

69 to 74: There is an important observational paper missing which the authors need to relate to in the discussion of their results later on in the paper. It is: Regional sinks of bromoform in the Southern Ocean from 2013 from Mattsson et al. in GRL, where he shows the heterogeneity of the sources, which make the ocean a sink at times. Therefore also the next sentence needs to be revised: These studies indicate moderate ocean sources of CHBr<sub>3</sub> and CH<sub>2</sub>Br<sub>2</sub> at high latitudes in the Southern Hemisphere, and refer to Mattsson., possibly in line 79.

86 to 94: Here you need to relate to Salawitch (2011?).. –most trace gases in tropospheric air enter the stratosphere in the tropics, move poleward and descend to the troposphere at middle and high latitudes. Salawitch claims, that the polar bromine can be influenced by large scale subsidence from the lower latitudes. . .

97-98: Few constraints on HVOC mixing ratios or emissions based on airborne data exist at high latitudes in the Southern Hemisphere. What does this mean?

108: This is pmol. . . not nmol mol<sup>-1</sup>

110 to 117: Here you could (you need to do it somewhere) elaborate on the O<sub>2</sub>/N<sub>2</sub>

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concept and why you chose to relate the HVOHCs to those.

124 to 131: Please include the regions into Figure 1.

126-128: If you only refer to two flights from ATom-2, the sentence could be easier to read.

174: Model is missing

177: You did not introduce CAM.

185: what is a broadening effect?

211-212: We note that the non-linearity observed in ratios of these two gases at low CHBr<sub>3</sub> levels likely reflects the differences in emissions during strong phytoplankton blooms, as oppose to other periods.

The ratio may simply (and more likely) reflect other air masses from more distant source regions, which is reflected in a ratio which favors the longer lived compound ( CH<sub>2</sub>Br<sub>2</sub>) over the shorter- lived compound (CHBr<sub>3</sub>) which is emitted in larger quantities in a biological source region (refer to Yokouchi, 20xx) but more rapidly degraded during transport

213-214: For instance, Huges et al. (2013) also report distinct seawater slopes between CH<sub>2</sub>Br<sub>2</sub> to CHBr<sub>3</sub> , when chl a was increasing.

This is a weak sentence; can you give it more meaning?

219 . . . : please explain the concept: What do you expect from the ratio of the HVOHCs and the marine oxygen. 238/241-242: Where did you get this equilibration times? Support them by reference or evidence. And also the air-sea fluxes of O<sub>2</sub> and CHBr<sub>3</sub> are not very similar. Revise.

244-253: This paragraph is a little back and forth between compounds and regions; it can be sorted for easier reading.

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263...: This should have come earlier, when you start with the equilibria (238, 241). And do you also reference the atmospheric lifetimes?

284: FINN and MEGAN 2.1 products. I guess the abbreviations need to be explained a bit as well as the products

286: from this sentence it is not clear where the oceanic emissions are derived from. I guess its Ordonez, 2012?

289: Ordonez, 2012 does not include CH<sub>3</sub>Br. Revise

334: GDAS has to be introduced.

353-354: We consider the wind direction error to evaluate the possible size of spatial errors in footprint location.

There appears to be something wrong with the grammar? The sentence is not understandable.

355-356: Given median wind speeds in this domain, this corresponds to a possible error of 260 km/day possible error.

Here is also something wrong.

375 and 376: OCI and GIOP have to be introduced. What does ...and its uncertainty ...mean?

382: how do you obtain a 0.25° x 0.25° gridded uncertainty in the detrital material absorption? It is also not clear from section 5.2.

394: is the new terminology geophysical influence function something different than the surface influence function? Or why do you change the wording? Its unclear.

403 to 404. Can you give an example for H and s. What is the potential geophysical source distribution s?

412: here the potential source distributions is Hs1, Hs2...? And not s? Is HS1 ( line C5

406 ) the same as Hs1?

415-416: We used the standard deviation of the regression coefficients and the relative uncertainty in the source fields, added in quadrature, to estimate the uncertainty in these fluxes (see Fig. 7 and Sect. 5.2 for fractional uncertainties).

418: How did you calculate and do you report the relative uncertainty of the regression coefficients?

There is no standard deviation of the regression coefficients in Fig 7 and sect 5.2 does not explain fractional uncertainties and no explanation is found about relative uncertainties in source fields. Or are you relating to surface influence strength uncertainty here. There needs to be more explanation about this added here.

424: why did you include... such as CH<sub>3</sub>I in Region 1? The second half sentence does not add information?

425-426: Note, sea ice did not include land ice; however, we also found a negative correlation between upstream land ice influence and mixing ratios of HVOCs.

Why do you add the sentence starting with however? How did you get the correlations when it is not included and does it help the interpretation of the results? It appears misleading and redundant.

432-433: We note that over-turned first year sea-ice, which can expose under-ice algae colonies to the air, likely still present a local source of CHBr<sub>3</sub>, CH<sub>2</sub>Br<sub>2</sub>, or other VOHCs to the MBL.

How does this speculation relate to your study and how does it help your interpretations? It stands a bit loose currently.

461-464: What was the temporal resolution of the input data shortwave and detrital material- add in section 4.2.

468-474: This section is wrong. There is no study ( at least not the referenced ones)

which proves a relationship between iron availability and methyl iodide. The authors have misinterpreted the cited studies. Please check and revise.

476: citing the link between temperature and PAR to the solar radiation..this wording is strange..also add which temperature is needed. . .water . may be its easier to just write revealing the link to solar radiation ..or similar

483: please introduce TUV

480 to 490: this section appears to be in the wrong place. I would expect this earlier in the description of the model, e.g. in 4.1., where you also talk about uncertainties due to meteorology.

494-495: as explained earlier the concept needs to be introduced more clearly earlier..e.g. why do you not take the VOHC directly but apply their relationship to oxygen?

502 -518: How can a model and an observation based flux-estimate be wrong by around 50%? And why do you think that a simple down scaling of the calculated oxygen fluxes leads to a robust flux estimate for VOHC, respectively why is this better, than taking just the VOHC fluxes? Can you explain this concept in the text please? Also it is unclear why you calculate all your influence functions to the VOHC mixing ratios directly, and not to their relation to oxygen and why for the flux calculation this now appears better?

540: I strongly believe that the calculation of the regression surface influence functions need to be shown in the text not in the legend of figure 9.

543: You need to indicate in table 1 ,which method you used in "This study" to derive the reported flux, as there are several methods here.

564-565: this also appears true for CHBr<sub>3</sub>, CHClBr<sub>2</sub> in region 1 ..and for the entire troposphere for CHBrCl<sub>2</sub>

578: although they were significantly higher than CAM-Chem's prescribed emissions

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in Region 1, where VOHC mixing ratios are under predicted (Table 1; Fig. 5).

Can you please add the comparison to CAM- Chem at the beginning .It would be better structured if you don't jump between comparisons.

581: parameterizations..these are different ..and you need to add which compounds you are referring to in this sentence.

586-587: Nevertheless, these methods may facilitate parameterizing emissions of new species or improving existing emissions.

Here it would be good to extend on the methods and why they appear so useful..and how you would extend them to other species.

Figure 2: Are the data of the campaigns merged? Detection limits need to be added. The label of CH<sub>3</sub>I is odd.

Figure 3: Please specify one name for the campaigns and keep it. Here in one figure the authors switch between Atom-2, Atom and Atom. Line 937 to 939 in the legend : This sentence does not make sense.

Figure 4. There appears to be an old legend as d, g and h are missing as well as CHClBr<sub>2</sub>. The applied regressions appear to be the same , thus it would be good to elaborate in the text about the method to reduce the legend, e.g. what means. using variables scaled to their range? In the legend? Also here only regressions above 0.2 are shown .

Figure 5,6: Switching between CESM in the figure and CAM-Chem1.2 does not help clarity. . .multiplied by the percentage of data below detection.. .. was it used for calculating the mean? ..rephrase for clarity.

Figure 7: Talking of statistical significance with  $r^2 < 0.2$  and looking at the plots with scattered values and no surface influence, is a bold exaggeration. And the p-values can be abandoned from the figure and just the threshold mentioned, as they do not

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help the statistics.

Figure 9: The labeling of the figures is too small, the p- value redundant and the legend for figure c.) too intricate. I strongly believe that the calculation of the regression surface influence functions need to be shown in the text not in the legend of figure 9.

Figure 10: The figures and labeling of a to c are too small. ( I suggest single plots, resolution as Figure 1?. It must be  $\text{pmol m}^{-2} \text{ hr}^{-1}$  also in the legend. Also clarify that these are model results. How do the mentioned CESM (CAM- Chem 1.2) O<sub>2</sub> fluxes relate to the figure? And is this also 2016?

Figure 11: fluxes not fluxed

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-102>, 2019.