Responses to reviewer #1

This study of airborne observations of halogenated VOCs (HVOCs) represents a valuable addition to the knowledge of these compounds over the Southern Ocean, where few data exist. The study confirms the current view that the main sources of CHBr3 and CH2Br2 are biological, and that CH3I has both biological and non-biological sources. The authors have put forward a novel concept of using enrichment ratios of HVOCs to O2 to infer the contribution or otherwise of ocean biological sources, and propose a new function to estimate non-biological emission fluxes of CH3I. The dataset has been used to evaluate the CAM-Chem HVOC emission scheme at high latitudes in the Southern Hemisphere. The take home message/s from this evaluation are rather opaque – they could do with being put in context. E.g., do they infer that fluxes from these regions are poorly known, or problems with the models mixing /convection schemes special to these latitudes, or issues with photo-oxidation rates?. In terms of presentation, the paper has a number of typographical and other errors, listed below, and needs a thorough reading (I doubt I captured all of them). However overall, I think this manuscript presents sufficiently novel results to be suitable for publication, once these matters have been attended to.

We appreciate the reviewer's time and comments. We have done our best to clarify the goals and findings of this study. We argue that emissions of HVOCs over the Southern Ocean are poorly known using mixing ratio comparisons with a global climate model and state of the art biogenic flux parameterizations based on chl *a* that show persistent model biases. Thereafter, we seek to address this problem by proposing new approaches to estimate regional HVOC fluxes using airborne observations. We demonstrate two additional approaches for deriving HVOC flux estimates using airborne observations, and model output. We hope that the reviewer finds our article suitable for publication following these revisions.

L34-38 The regional enrichment ratios should be put in context here - there is no explanation as their relevance.

We no longer report enrichment ratios in the abstract. We do however, attempt to explain the role of O_2-HVOC enrichment ratios in inferring a biological flux of HVOCs. This passage now reads, "The first approach takes advantage of the robust relationships that were found between airborne observations of O_2 and $CHBr_3$, CH_2Br_2, and $CHClBr_2$; we use these linear regressions with O_2 and modeled O_2 distributions to infer a biological flux of HVOCs." L30-33.

L51- 52 "Indeed, HVOCs may be among the most important sources of inorganic bromine to the whole atmosphere ..... (Murphy et al.,in review)." This is not conventional wisdom and thus quite a bold statement. Are the authors confident that the Murphy et al paper will be published soon?

Murphy et al. (2019) has now been published and the citation has been revised. We have also moderated the language to reflect that this statement challenges conventional wisdom. This passage L50-54 now reads, "In the marine boundary layer and lower troposphere, sea salt is the main source of reactive bromine (Finlayson-Pitts 1982, Simpson et al. 2019). Yet HVOCs may also be a more important source of inorganic bromine to the whole atmosphere than previously thought, according to a recent study, which indicates that sea salt is scarce and insufficient to control the bromine budget in the middle and upper troposphere (Murphy et al., 2019)."

L61-64 The anthropogenic sources of CH3Br have changed over time and now are dominated by quarantine and pre-shipment (QPS) applications (not controlled by the Montreal Protocol). Please stick to the most recent information from WMO 2018 (and update the reference).

Both the information and citation on anthropogenic sources of CH_3Br have been revised in L65-68: "CH_3I is also formed through non-biological reactions in surface seawater, and CH_3Br is emitted as a result of quarantine and pre-shipment activities, which are not regulated by the Montreal Protocol (e.g., Moore and Zafiriou; 1994, Engel and Rigby, 2018).

Elizabeth Asher 9/3/2019 11:46 AM
Deleted: WMO

L119- 130 The last paragraph of the introduction would benefit from an introduction to the concept of enrichment ratios of HVOCs to O2, which feature prominently in the abstract.

We have revised this passage in L122-139 to read, "In Section 3.1 and 3.2, we report new airborne observations of $CHBr_3$, CH_2Br_2, CH_3I, $CHClBr_2$, $CHBrCl_2$, and CH_3Br from high latitudes in the Southern Hemisphere, where data are scarce, and large-scale regional mixing ratio comparisons for HVOCs with the community earth system model (CESM) atmospheric component with chemistry (CAM-Chem). In section 3.4, we present two novel approaches to estimate regional fluxes of HVOCs for comparison with global climate models' parameterizations or climatologies. One approach uses correlations of HVOCs to marine, oxygen (O_2) of marine origin, as measured by deviations in the ratio of O_2 to nitrogen (N_2) ($\delta(O_2/N_2)$ see Sect. 2.1.2 and 3.1.2) to determine the importance of regional biological HVOC sources. The robust correlations of $CHBr_3$ and CH_2Br_2 with $\delta(O_2/N_2)$ are indicative of a strong biological source. Our first approach exploits the ratio of HVOCs to oxygen (O_2) determined from linear regressions (i.e. the enrichment ratio), and the ocean flux of O_2 from CESM's ocean component, to estimate the marine biogenic flux of several HVOCs. The second approach relies on observed HVOC mixing ratios, the Stochastic Time-Inverted Lagrangian Transport (STILT) particle dispersion model and geophysical datasets (see Sect. 2.3 and 3.3). We assess contributions from previously hypothesized regional sources for the Southern Ocean, and estimate HVOC fluxes based on regressions between upstream influences and observed mixing ratios and distributions of remotely sensed data."

L235-245 The fact that the polyhalogenated bromocarbons are likely co-emitted is not new – there are numerous papers that show this, and the discussion could elaborate on those a bit more. What is also missing from this paragraph is a discussion of macroalgal sources of these compounds, although this is presumably not relevant for the Antarctic.

We have expanded the discussion of previous findings of co-emitted polyhalogenated bromocarbons and cited several additional studies. This passage L390 - 401 now reads, "Previous studies have documented co-located source regions of $CHBr_3$ and CH_2Br_2 in the Southern Ocean (e.g. Hughes et al., 2009; Carpenter et al., 2000; Nightingale et al. 1995; Laturnus et al. 1996), and laboratory studies have demonstrated that phytoplankton and their associated bacteria cultures, including a cold water diatom isolated from coastal waters along the Antarctic Peninsula and common to the Southern Ocean, produce both $CHBr_3$ and CH_2Br_2 (Hughes et al., 2013; Tokarczyk and Moore 1994, Sturges et al., 1993). The non-linearity observed in ratios of these two gases at low $CHBr_3$ may reflect the different rates of their production or loss in seawater, or possibly, the influence of air masses from distant, more productive low-latitude source regions. Several studies have documented bacterially mediated loss of CH_2Br_2, but not

$CHBr_3$, and report distinct ratios of CH_2Br_2 to $CHBr_3$ in seawater during the growth and senescent phases of a phytoplankton bloom (e.g. Carpenter et al. 2009, Hughes et al 2013). ”

L244-245 “For instance, Huges et al. (2013) also report distinct seawater slopes between CH2Br2 to CHBr3 , when chl a was increasing.” It is not clear what is meant by this. Please rephrase

This statement has been rephrased on L398, “Several studies have documented bacterially mediated loss of CH_2Br_2, but not $CHBr_3$, and report distinct ratios of CH_2Br_2 to $CHBr_3$ in seawater during the growth and senescent phases of a phytoplankton bloom (e.g. Carpenter et al. 2009, Hughes et al 2013).”

L361- 366 “In both regions, the model under predicts CH3I above the MBL, which may indicate slower observed photochemical loss than the model predicts.” Has this been found in other CAM-Chem studies – e.g. is it a general result? If not, could a different source emission distribution (i.e. more homogeneous source) explain these results?

We have revised the text to reflect that indeed this result has been found in other CAM-Chem studies, and that the observed difference at high latitudes in the SH at ~10 km altitude may be due to the zonal transport of air masses from lower latitudes, where differences in CH_3I in the UTLS have also been observed. For instance, in Ordonez et al. (2012), Fig. 10 illustrates the consistent under prediction of the observed CH_3I mixing ratios, and these authors attribute this discrepancy to the strength of convective cells rapidly transporting air masses to the UTLS. This section L494-499 now reads as follows: “In both regions, the model most likely under predicts CH_3I in the upper troposphere and lower stratosphere (UTLS), likely stemming from the poleward transport of lower latitude air masses, where CAM-Chem also exhibits a negative bias. Mixing ratio comparisons with CAM-Chem over the tropics (see Ordonez et al. Figure 10) depict similar or larger discrepancies, and have been attributed to stronger than anticipated convective cells in the tropics.”

L555-L560 onwards. There is no mention in Moore and Zarifou 1994 nor Richter and Wallace 2004 as far as I can see on the influence of iron availability – do the authors mean iodide availability?!

We have both fixed a typo and clarified the discussion on proposed non-biological chemical mechanisms for CH_3I production in the ocean, which include the radical recombination reaction proposed by Moore and Zarifou (1994), and the substitution reaction, requiring an oxidant such as iron III, proposed by Williams et al. (2007). This passage L563-569 now reads, “This non-biological source, though not fully understood, requires light, a humic like substance at the surface ocean supplying a carbon source and methyl group, and reactive iodine (Moore and Zarifou 1994; Richter and Wallace 2004). Thus far, two chemical mechanisms have been proposed for the non-biological production of methyl iodide, one – a radical recombination of a methyl group and iodine involving UV photolysis (e.g. Moore and Zarifou 1994), and the second, a substitution reaction involving the reduction of an oxidant, such as iron III (e.g. Williams et al. 2007).”

L1036 – Note that units should be pmol m-2 hr-1 (not m2). Please state whether the values given for the observations are means or medians. It would be also be good to include their ranges.

We have corrected this typo on L1068. The units on Table 1 now read "pmol m^{-2} hr^{-1}."

Ln 82. atmopsheric Ln 213. "oppose" should be "opposed" Ln 213. "Huges" should be "Hughes" Ln 242 : "HOVCs" Ln 469. "Zafarou" should be "Zafariou" Ln 980. "includind" LN 1015. "fluxed"

L81, L253, L391, L518, L1171- Typos have been corrected to read, "Atmospheric," "opposed," "HVOCs," "Zafiriou," and "fluxes." Other typos previously listed have been deleted from the text.

Response to Reviewer #2

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 understudies region and applies new concepts for source determinations related to measurements of O2 and CO2 and geophysical datasets. It underlines current knowledge of the biological sources of CHBr3 and CH2Br2 by applying their ratio to oceanic oxygen emissions. CH3I 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. 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.

We appreciate the reviewer's constructive criticism. We have refocused our paper on the approaches and concepts outlined here, rather than our results. We also argue that emissions of HVOCs over the Southern ocean are poorly known and seek to address this problem by proposing new approaches to estimate regional HVOC fluxes using airborne observations. We have sought to better outline the two novel approaches to estimate HVOC fluxes and explain why these approaches represent an important step forward in the field. We have also done our best to improve the presentation by reorganizing the structure of the paper, simplified the language and corrected typos and grammar errors. We hope that the reviewer finds our article suitable for publication following these revisions.

L22- 25 We also use CH3Br 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 could be abandoned for the abstract and only explained later in the text.

We agree with the reviewer and have revised the text to include less detail on instrumentation. This section on L22-25 now reads: "We present observations of $CHBr_3$, CH_2Br_2, CH_3I, $CHClBr_2$, $CHBrCl_2$,

and CH_3Br during the O_2/N_2 Ratio and CO_2 Airborne Southern Ocean (ORCAS) study and the 2nd Atmospheric Tomography mission (ATom-2), in January and February of 2016 and 2017."

L32-38 Based on these relationships What does this refer to?... it is unclear

We have done our best to clarify how the regressions of HVOC mixing ratios with upwind influences and O_2 are used to estimate basin-wide fluxes on L30-33: "… we demonstrate two novel approaches to estimate HVOC fluxes; the first approach takes advantage of the robust relationships that were found between airborne observations of O_2 and $CHBr_3$, CH_2Br_2, and $CHClBr_2$; we use these linear regressions with O_2 and modeled O_2 distributions to infer a biological flux of HVOCs."

L49-53 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.

We have added a sentence to reflect that sea salt aerosol is critical to the bromine budget in the lower troposphere, and have moderated the language of the sentence regarding the contribution of bromocarbons to the middle and upper troposphere to reflect that this statement challenges conventional wisdom. This passage L50-54 now reads, "In the marine boundary layer and lower troposphere, sea salt is the main source of reactive bromine (Finlayson-Pitts 1982, Simpson et al. 2019). Yet HVOCs may also be a more important source of inorganic bromine to the whole atmosphere than previously thought, according to a recent study, which indicates that sea salt is scarce and insufficient to control the bromine budget in the middle and upper troposphere (Murphy et al., 2019)."

L75-80 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 CHBr3 and CH2Br2 at high latitudes in the Southern Hemisphere, and refer to Mattsson., possibly in line 79.

This passage has been revised on L79-84: "Mattsson et al. (2013) noted that the ocean also acts as a sink for HVOCs, when HVOC undersaturated surface waters equilibrate with air masses transported from source regions. The spatially heterogeneous ocean sources of $CHBr_3$ and CH_2Br_2 at high latitudes in the Southern Hemisphere are often underestimated in global atmospheric models (Hossaini et al., 2013; Ordoñez et al., 2012; Ziska et al., 2013)."

L94-103 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. . .

This passage has been rewritten to reflect this on L99-103, "As a result of limited vertical transport in these regions, however, air-sea fluxes lead to strong vertical gradients. Zonal transport from lower latitudes has a large impact on the vertical gradients of trace gas mixing ratios over polar regions (Salawitch 2010). Given their extended photochemical lifetimes at high latitudes (see Sect. 2.3 for a brief discussion), many HVOC distributions are particularly sensitive to zonal transport at altitude."

L105-106 Few constraints on HVOC mixing ratios or emissions based on airborne data exist at high latitudes in the Southern Hemisphere. What does this mean?

This sentence has been rewritten (L108-109) and is hopefully more clear: "Few airborne observations of HVOCs exist at high latitudes in the Southern Hemisphere."

L117 This is pmol. . . not nmol mol -1

The correction has been made on 119, "ACE-1 measurements of CH_3I in the MBL indicate a strong ocean source between 40° S and 50° S in austral summer, with mixing ratios above 1.2 pmol below ~1 km (Blake et al., 1999)."

L131 – 136 Here you could (you need to do it somewhere) elaborate on the O2/N2 concept and why you chose to relate the HVOHCs to those.

We now discuss the concept and purpose of relating HVOCs to O_2/N_2 in L126-L134: "In section 3.4, we present two novel approaches to estimate regional fluxes of HVOCs for comparison with global climate models' parameterizations or climatologies. One approach uses correlations of HVOCs to marine, oxygen (O_2) of marine origin, as measured by deviations in the ratio of O_2 to nitrogen (N_2) ($\delta(O_2/N_2)$ see Sect. 2.1.2 and 3.1.2) to determine the importance of regional biological HVOC sources. The robust correlations of $CHBr_3$ and CH_2Br_2 with $\delta(O_2/N_2)$ are indicative of a strong biological source. Our first approach exploits the ratio of HVOCs to oxygen (O_2) determined from linear regressions (i.e. the enrichment ratio), and the ocean flux of O_2 from CESM's ocean component, to estimate the marine biogenic flux of several HVOCs."

L141-144 Please include the regions into Figure 1.

We now include the regions in Fig. 1.

L144-152 If you only refer to two flights from ATom-2, the sentence could be easier to read.

This sentence has been revised to read, "On Feb. 10 and 13, 2017 the sixth and seventh ATom-2 research flights passed over the eastern Pacific sector poleward of 60° S (defined here as Region 1) and over the Patagonian Shelf between 40° S and 55° S and between 70° W and 55° W (defined here as Region 2), respectively."

L204 Model is missing

Although this passage has bee revised, "Model" has been added when CESM is first introduced in the introduction on L126: "In Section 3.1 and 3.2, we report new airborne observations of $CHBr_3$, CH_2Br_2, CH_3I, $CHClBr_2$, $CHBrCl_2$, and CH_3Br from high latitudes in the Southern Hemisphere, where data are scarce, and large-scale regional mixing ratio comparisons for HVOCs with the community earth system model (CESM) atmospheric component with chemistry (CAM-Chem)."

L207 You did not introduce CAM.

CAM is now referred to here as "CESM's atmosphere component. Please see above comment.

L1215 What is a broadening effect?

L217 We have specified "pressure broadening effect" on the CO2 and CH4 spectrum in cavity ring down instruments, which has been observed in several studies due to the influence of water vapor (e.g. Chen et al. 2013). This sentence now reads, "Dry-air mole fractions were calculated using empirical corrections to account for dilution and pressure broadening effects as determined in the laboratory before and after the campaign deployments, and in-flight calibrations were used to determine an offset correction for each flight."

L243-L252 We note that the non-linearity observed in ratios of these two gases at low CHBr3 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 (CH2Br2) over the shorter- lived compound (CHBr3) which is emitted in larger quantities in a biological source region (refer to Yokouchi, 20xx) but more rapidly degraded during transport.

Our analysis focuses on the bottom 2 km of the atmosphere, and as such largely reflects recent enhancements in HVOCs. Nevertheless, we have clarified this passage to reflect that contributions from zonal transport from low latitude regions cannot fully be ruled out, and have further expanded on the differences in CH2Br2 and CHBr3 production and loss rates in surface waters. This passage L395-405 now reads, "The non-linearity observed in ratios of these two gases at low $CHBr_3$ may reflect the different rates of their production or loss in seawater, or possibly, the influence of air masses from distant, more productive low-latitude source regions. Several studies have documented bacterially mediated loss of CH_2Br_2, but not $CHBr_3$, and report distinct ratios of CH_2Br_2 to $CHBr_3$ in seawater during the growth and senescent phases of a phytoplankton bloom (e.g. Carpenter et al. 2009, Hughes et al 2013). Although this analysis is restricted to the bottom 2 km of the atmosphere, zonal transport of air masses with lower ratios of CH_2Br_2 to $CHBr_3$ ratios, as have been observed in the MBL over productive, low-latitude regions, may also have influenced our observations (Yokouchi et al. 2005)."

L246-248 For instance, Huges et al. (2013) also report distinct seawater slopes between CH2Br2 to CHBr3 , when chl a was increasing. This is a weak sentence; can you give it more meaning?

This sentence has been rewritten on L398, "Several studies have documented bacterially mediated loss of CH_2Br_2, but not $CHBr_3$, and report distinct ratios of CH_2Br_2 to $CHBr_3$ in seawater during the growth and senescent phases of a phytoplankton bloom (e.g. Carpenter et al. 2009, Hughes et al 2013)."

L257-258 please explain the concept: What do you expect from the ratio of the HVOHCs and the marine oxygen.

L415-418 We have revised this passage, "We sought to test if the biologically mediated production of bromocarbons and oxygen result in similar atmospheric distributions. Conversely, we expected HVOC atmospheric distributions and CO_2 distributions to anticorrelate because CO_2 fixation in surface waters is proportional to the production of oxygen."

L288 238/241-242: Where did you get this equilibration times? Support them by reference or evidence. And also the air-sea fluxes of O2 and CHBr3 are not very similar. Revise. L444 This sentence now reads, "The bulk air-sea equilibration time for an excess of $CHBr_3$ and other HVOCs is less than two weeks, although the photochemical loss of HVOCs will alter their ratio over time (see Supplement for details on calculations of bulk sea air equilibration times)." The section in the supplement (L1177-1185) reads as follows: "To support the interpretation of our results, we calculate nominal equilibration times. For estimates of bulk sea air equilibration times for HVOCs, O_2, and CO_2, we assume a mixed layer depth of 30 m, a temperature of 0° C, a salinity of 35 PSU, and carbonate buffering according to eq. 8.3.10 in Sarmiento and Gruber (2006), and transfer velocities according to Nightingale et al., (2000). The Schmidt number (i.e. the ratio of the kinematic viscocity of a gas, divided by the molecular diffusivity) for O_2, CO_2 and CH_3Br were calculated according to Wanninkof (2014), and the Schmidt numbers for $CHBr_3$ and CH_3I were calculated according to Quack and Wallace (2003) and Moore and Groszko (1999), respectively. The results are provided in Sect. 3.1.2."

L291-300 This paragraph is a little back and forth between compounds and regions; it can be sorted for easier reading.

We have done our best to clarify this paragraph in L455-465: "Our observations suggest a biological source for $CHBr_3$ and CH_2Br_2 in both Region 1 and Region 2 (Fig. 4). Interestingly, the slope of the regression between $CHBr_3$ and O_2 appears distinct in Region 1 and Region 2, but between CH_2Br_2 is the same. Molar enrichment ratios are 0.20 ± 0.01, and 0.07 ± 0.004 pmol : mol for $CHBr_3$ and CH_2Br_2 to O_2 in Region 1, and 0.32 ± 0.02, and 0.07 ± 0.004 pmol : mol in Region 2. We observe a weaker relationship between CH_3I and $CHClBr_2$ and O_2 in Region 1 (Fig. 4c, d), consistent with the existence of other, non-biological sources of CH_3I in this region. Figure 4f illustrates a strong relationship between CH_3I and O_2, as well as $CHClBr_2$ and O_2, in Region 2, however, which implies that the dominant sources of CH_3I and $CHClBr_2$ emissions over the Patagonian Shelf are biological. The corresponding molar enrichment ratios of CH_3I to O_2 and $CHClBr_2$ to O_2 in Region 2 are 0.38 ± 0.03 pmol : mol and 0.19 ± 0.04 pmol: mol, respectively."

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

L44 We now refer the reader to the supplement here for further reading on the calculation of equilibration times. Please see two responses up for details.

L336 – 337 FINN and MEGAN 2.1 products. I guess the abbreviations need to be explained a bit as well as the products

L247 "The model uses chemistry described by Tilmes et al. (2016), biomass burning and biogenic emissions from the Fire INventory of NCAR (FINN; Wiedinmyer et al. 2011) and MEGAN (Model of Emissions of Gasses and Aerosols from Nature) 2.1 products (Guenther et al., 2012) with additional tropospheric halogen chemistry described in Fernandez et al. (2014) and Saiz-Lopez et al. (2014), including ocean emissions of $CHBr_3$, CH_2Br_2, $CHBr_2Cl$, and $CHBrCl_2$, with parameterized emissions based on chlorophyll *a* (chl *a*) concentrations and scaled by a factor of 2.5 over coastal regions, as opposed to open ocean regions (Ordoñez et al. 2012)."

L341 from this sentence it is not clear where the oceanic emissions are derived from. I guess its Ordonez, 2012? Done. Ordonez et al. (2012) has been cited. Please see above.

L343 Ordonez, 2012 does not include CH3Br. Revise

We respectfully disagree with the reviewer. Indeed, Ordonez does prescribe a lower boundary condition for CH_3Br and show mixing ratio comparisons for this compound. There is not a biogenic flux prescribed for CH_3Br.

L393 GDAS has to be introduced.

L271 "STILT was run using 0.5º Global Data Assimilation System (GDAS) reanalysis winds to investigate the transport history of air sampled along the flight track (Stephens et al., 2018)."

416-418 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. Given median wind speeds in this domain, this corresponds to a possible error of 260 km/day possible error. Here is also something wrong.

L287 We have revised this passage to read, "For wind speed, a small bias may be present, where we find a median difference between observations and reanalysis of 0.68 m/s, a 5% relative bias. The 1-sigma of the wind speed difference is 2.3 m/s, corresponding to a 19% 1-sigma uncertainty in wind speed. In its simplest approximation, the surface influence strength error is perfectly correlated with the wind speed error, and thus we take 19% as an approximation of the surface influence strength uncertainty. The uncertainty in surface influence location depends on the error in the wind direction. We find a 1-sigma error of 14 degrees in wind speed, which corresponds to a possible error of 260 km/day."

L448- 449 OCI and GIOP have to be introduced. What does . . ..and its uncertainty . . .mean? 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.

OCI and GIOP are introduced, and we have done our best to clarify the meaning of GIOP absorption uncertainty in L350-362: "Due to persistent cloud cover over the Southern Ocean, which often precludes the retrieval of remotely sensed ocean color data, we used 8-day mean composite Aqua MODIS L3 distributions of chl *a* from the Ocean Color Index (OCI) algorithm and absorption due to gelbstoff and detrital material at 443 nm from the Generalized Inherent Optical Properties (GIOP) model (NASA Goddard Space Flight Center, 2014). Absorption due to gelbstoff and detrital material at 443 nm is used as a proxy for colored dissolved organic matter (CDOM; https://oceancolor.gsfc.nasa.gov/atbd/giop/). CDOM is hypothesized to be an important source of carbon for the photochemical production of CH_3I (Moore et al., 1994). The GIOP model also publishes an uncertainty in the absorption due to gelbstoff and detrital material at 443 nm. Raw 4 km x 4 km data were geometrically averaged, based on lognormal probability density functions, to a spatial resolution of 0.25° x 0.25° for use with gridded surface influences. We used the ratio of the 0.25° x 0.25° gridded uncertainty in the detrital material absorption to the absorption as the relative uncertainty for flux calculations (see Sect. 3.4.2)."

L477 and elsewhere – Is the new terminology geophysical influence function something different than the surface influence function? Or why do you change the wording? Its unclear.

We do not mean to confuse the reader with superfluous terminology: "geophysical influence function" has been replaced everywhere with "surface influence function."

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

H is the surface influence based on a sample's back trajectories in the boundary layer (ppt m^2 s $pmol^{-1}$). An example of s would be the distribution of chl. a at the ocean surface (μg m^{-3}) or the distribution of fractional sea ice at the ocean surface, which is unitless.

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

L316-L333 Yes Hs1 is the same as HS2. This passage has been revised and two capitalization typos have been corrected to clarify the role of upstream influence functions and geophysical source distributions in these regressions with surface influence functions. Also an example of a geophysical source distribution s, was given, Chl. *a*, now L304. The relative uncertainty of regression coefficients for Figure 9 is reported, and used to calculate the flux shown in Figure 11 as described in Sect. 3.4.2. To clarify, in

those regressions where a flux was not calculated based on the relationship (e.g. Fig 7-8), the uncertainty in the regression coefficients is not reported.

L501 why did you include. . . such as CH3I in Region 1? The second half sentence does not add information?

The phrase "such as CH3I in Region 1" has been deleted.

L500-501 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.

This statement on L521 has been revised to read, "We found no positive relationships between upstream sea-ice influence and any measured HVOC Region 1 (Fig. 7)."

L506 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 CHBr3, CH2Br2, 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.

The statements regarding land ice and overturned first-year ice have been deleted.

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

The temporal resolution of the input shortwave radiation data is every six hours and detrital data is every eight days, as specified elsewhere on L351 (a) and L365 (b).

a) "Due to persistent cloud cover over the Southern Ocean, which often precludes the retrieval of remotely sensed ocean color data, we used 8-day mean composite Aqua MODIS L3 distributions of chl *a* from the Ocean Color Index (OCI) algorithm and absorption due to gelbstoff and detrital material at 443 nm from the Generalized Inherent Optical Properties (GIOP) model (NASA Goddard Space Flight Center, 2014)."

b) "The National Center for Environmental Prediction (NCEP) provides Final Global Data Assimilation System (GDAS/FNL) global data of downward shortwave radiation at the surface at 0.25 degree and 6-hour resolution (NCEP, 2015)."

L557-562 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.

L565-569 A typo has been corrected and this passage has been revised and clarified. The role of iron is briefly explicitly discussed as a possible oxidant for one of two proposed abiotic CH_3I reactions: "This

non-biological source, though not fully understood, requires light, a humic like substance at the surface ocean supplying a carbon source and methyl group, and reactive iodine (Moore and Zarifou 1994; Richter and Wallace 2004). Thus far, two chemical mechanisms have been proposed for the non-biological production of methyl iodide, one – a radical recombination of a methyl group and iodine involving UV photolysis (e.g. Moore and Zarifou 1994), and the second, a substitution reaction involving the reduction of an oxidant, such as iron III (e.g. Williams et al. 2007)."

L564-565 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

L570 Done, this statement has been revised, "Several previous studies have correlated mixing ratios of CH_3I to satellite retrievals of PAR and surface ocean temperature, revealing a link to solar radiation (e.g. Happell et al., 1996; Yokouchi et al., 2001)."

L424 please introduce TUV. This section appears to beat 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.

TUV is now introduced. Note, this section L419-429 has been moved up as suggested to the end of Sect. 2.3 L295-306: "Finally, we note that photochemical loss during transport is not accounted for in this analysis. Low OH mixing ratios, cold temperatures, and lower photolysis rates due to angled sunlight at high latitudes lead to longer than average HVOC lifetimes. For instance, assuming an average diurnal OH concentration of 0.03 pptv, and average photochemical loss according to the Tropospheric Ultraviolet and Visible (TUV) radiation model and the Mainz Spectral data site (http://satellite.mpic.de/spectral_atlas) for Jan. 29 under clear sky conditions at 60° S, $CHBr_3$ has a lifetime of 30 days, CH_2Br_2 has a lifetime of 270 days, CH_3I has a lifetime of 7 days, and $CHClBr_2$ has a lifetime of 63 days. As such, the photochemical lifetimes of these gases are greater than or equal to the time of our back-trajectory analysis. Moreover, OH concentrations in this region have large uncertainties, the inclusion of which would lead to more, not less, uncertainty in surface influence based regression coefficients and estimated fluxes."

L571-576.

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?

Our goal was not to suggest the "correct" regional flux of HVOCs based on data from two austral summers (and relatively few measurements from the Atom-2 campaign in 2017), but to demonstrate that airborne data can be use to develop other empirically based parameterizations, which could work better. We argue that despite the its inherent uncertainties in the parameterization of biogenic HVOC fluxes based on O_2, the current CAM-Chem scheme based on chl. *a* leads to biases that exceed 50-100% for these compounds. Moreover, the uncertainties in remotely sensed chl.*a* are rarely considered in such parameterizations.

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?

O_2 and CO_2 fluxes are not well constrained at high latitudes in the southern hemispheres. In fact, the ORCAS campaign sought primarily to address this problem. Please see Stephens et al. (2018) for details. Although we agree with the reviewer that the simple downscaling is crude, this large discrepancy between observations and model or climatological mean values is due to inter-annual variability. The uncertainty discussed in L546-548 is meant to account for errors in the spatial variability in the fluxes, and does not include the mean absolute difference that is adjusted for in downscaling.

L632-634 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. Regression coefficients from the MLR with surface influence functions are now shown in here on L641-644 not in the legend of Fig. 9, "We used a multiple linear regression (± 1standard deviations; Equation 2), where Hs1 and Hs2 are the surface influence functions of downward shortwave radiation and detrital absorption, respectively, with an intercept b = 0.19 ± 0.01, and influence coefficients a_1 = 3.7E-5 ± 1.3E-5, a_2 = 3.5± 0.74, and an interaction term with the coefficient -5.2E-4 ± 1.5E-4 (c)."

Table 1. You need to indicate in table1 ,which method you used in "This study" to derive the reported flux, as there are several methods here.

The approaches (O_2 vs. MLR using surface influence functions) has been clarified here.

L678-680 this also appears true for CHBr3, CHClBr2 in region 1 ..and for the entire troposphere for CHBrCl2

We have rewritten this passage. L692-704: "Our flux estimates based on the relationship of HVOC mixing ratios to other airborne observations and remotely sensed parameters compared relatively well with those derived from global models and ship-based studies (Table 1). Our emission estimates of $CHBr_3$, CH_2Br_2, and $CHClBr_2$ are significantly higher than CAM-Chem's globally prescribed emissions in Region 1, where HVOC mixing ratios are under predicted (Table 1; Fig. 5). Similarly, our estimate of $CHClBr_2$ emissions is also significantly higher than CAM-Chem's in Region 2, where $CHClBr_2$ mixing ratios remained under predicted. Nevertheless, our emission estimates of $CHBr_3$, CH_2Br_2, CH_3I, are lower than most prior estimates based on either other models or localized studies using seawater-side measurements from the Antarctic polar region in summer. In the case of CH_3I, our estimated emissions suggest that the prescribed emissions in CAM-Chem may be too high in Region 1 and Region 2. Our parameterizations of the CH_3I flux could be used to explore inter-annual variability in emissions, which is not captured by the Bell et al. (2002) CH_3I climatology currently employed in CAM-Chem."

L660-664 although they were significantly higher than CAM-Chem's prescribed emissions 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.

We have clarified these two passages. Please see above.

L675 – 684 parameterizations..these are different ..and you need to add which compounds you are referring to in this sentence. Here it would be good to extend on the methods and why they are appear so usefull and how you would extend them to other species.

L705-711 We have done our best to clarify this passage: "To extend these relationships to year-round and global parameterizations for use in global climate models, they must be studied using airborne observations in other seasons and regions. These approaches may help parameterize emissions of new species that can be correlated with surface influence functions or the biological production of oxygen or may improve existing emissions, where persistent biases exist. Finally, future airborne observations of HVOCs have the potential to further improve our understanding of air-sea flux rates and their drivers for these chemically and climatically important gases over the Southern Ocean."

Figure 2. Are the data of the campaigns merged? Detection limits need to be added. The label of CH3I is odd.

Yes, the data are merged. Detection limits have been added to the legend.

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.

All mentions of ATom are now listed as ATom-2.

Figure 4. There appears to be an old legend as d, g and h are missing as well as CHClBr2. 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 .

The legend has been revised, and a statement has been added to say that only regressions with $r^2 > 0.2$ 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.

CESM in all the figure axes has been relabeled CAM-Chem. The sentence regarding data below the DL has been revised to read, "Again, the binned mean includes measurements below the detection limit (DL), which for this calculation are assigned a value equal to the DL multiplied by the percentage of data below detection."

Figure 7,8. Talking of statistical significance with r2 « 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 help the statistics.

P-values listed on the plots have been replaced with p-value thresholds (e.g. $p < 0.001$).

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.

The size of figure labels is larger. The calculation is now shown in the text as discussed above.

Figure 10. The figures and labeling of a to c are too small. (I suggest single plots, resolution as Figure 1?. It must be pmol m-2 hr-1 also in the legend. Also clarify that these are model results. How do the mentioned CESM (CAM- Chem 1.2) O2 fluxes relate to the figure? And is this also 2016?

The labeling is now larger, and as now stated in the figure legend, represents the year 2016. CESM ocean component O_2 fluxes (not shown here) were multiplied by the regression coefficients shown in Fig. 4 to infer a biological flux of HVOCs, as explained in Sect. 5.1.

Figure 11. fluxes not fluxed

Done, and now reads, “fluxes.”

Response to Reviewer #3

Anonymous Referee #3 The manuscript of Asher et al. describes airborne observations of halogenated volatile organic compounds over the Southern Ocean and improved emission flux estimates, based on modeling studies and correlative O2 observations. This is an important and interesting study that should be published in Atmos. Chem. Phys. after consideration of the following points. The authors should consider improving the presentation by first presenting their data and methods and then discussing the results. This study contains important new methods and approaches compared to previous studies but the presentation is not always clear. As an example, a key result is the presentation of "regional enrichment ratios" for HVOCs, but it did not become sufficiently clear to me, how they are defined and how they were calculated.

We appreciate the reviewer's comments and suggestions. We have done our best to reorganize the paper accordingly, by first discussing our methods and data sources and discussing our results second. We have paid particular attention to clarifying the discussion of regional enrichment ratios for HVOCs in the abstract as well as in sections 3.12 and 3.31.

Specific Comments:

Specific comments: L32-34: in the same sentence "halogenated hydrocarbon" and "halogenated volatile organic compounds (HVOCs)" are used. If the two mean the same, use only one name. If there is a distinction, please define.

Indeed- these are the same. The wording has been revised. Only the term "halogenated volatile organic compounds (HVOCs)" is now used.

L47-49: Is there a particular logic for the order of the citations given? They are neither sorted according to year, nor alphabetically.

This has been corrected and special attention has been paid to the order of citations throughout the paper.

L50: "recent evidence indicates that sea salt is scarce and insufficient": this is a strong statement that should be backed up with more than a manuscript in review.

We appreciate the reviewer's comment. Although this study is now published, this statement has been amended to better reflect current understanding on L50 – 54: "In the marine boundary layer and lower troposphere, sea salt is the main source of reactive bromine. Yet HVOCs may also be a more important source of inorganic bromine to the whole atmosphere than previously thought, according to a recent study, which indicates that sea salt is scarce and insufficient to control the bromine budget in the middle and upper troposphere (Murphy et al., 2019)."

L66: You may cite Abrahamsson et al. (2018) already at this stage.

Done. L670: "Over the Southern Ocean specifically, hypothesized sources of HVOCs include: coastal macroalgae, phytoplankton, sea ice algae, and photochemical or dust stimulated non-biological production at the sea surface (e.g., Abrahamsson et al. 2018, Manley and Dastoor 1998; Moore and Zafiriou 1994; Moore et al., 1996; Richter and Wallace 2004; Williams et al., 2007; Tokarczyk and Moore 1994; Sturges et al., 1992)."

L96: The point "support quantitative air-sea flux estimates" is less obvious than the other points so a reference may be helpful here.

Thank you, we have revised this sentence on L106 to read, "Aircraft observations can rapidly map basin-wide vertical distributions, support quantitative flux estimates, and provide spatial constraints to atmospheric models (e.g. Xiang et al. 2010x; Stephens et al 2018; Wofsy et al. 2011)."

L211: "We note that the non-linearity observed in ratios of these two gases at low CHBr3 levels likely reflects the differences in emissions during strong phytoplankton blooms, as oppose to other periods." Could not the different lifetimes also effect this?

L395-409 Thank you, this passage has been amended to reflect this possibility, and we have done our best to clarify the wording: "The non-linearity observed in ratios of these two gases at low $CHBr_3$ may reflect the different rates of their production or loss in seawater, or possibly, the influence of air masses from distant, more productive low-latitude source regions. Several studies have documented bacterially mediated loss of CH_2Br_2, but not $CHBr_3$, and report distinct ratios of CH_2Br_2 to $CHBr_3$ in seawater during the growth and senescent phases of a phytoplankton bloom (e.g. Carpenter et al. 2009, Hughes et al 2013). Although this analysis is restricted to the bottom 2 km of the atmosphere, zonal transport of air masses with lower ratios of CH_2Br_2 to $CHBr_3$ ratios, as have been observed in the MBL over productive, low-latitude regions, may also have influenced our observations (Yokouchi et al. 2005)."

Fig. 3. Units missing for the axes

This has been corrected- thank you for brining it to our attention.

Fig. 4. Why are some units given as nmol/mol and others as ppt ?

This too has now been corrected, the axes all read ppt. Again, thank you for brining this to our attention.

L222: Sorry, but I don't know what a type II major axis regression is. A few more words may help.

L426-L431 We have added a short passage to clarify the meaning and utility of the type II major axis regression in this analysis: "We used a type II major axis regression model (bivariate) to balance the influences of uncorrelated processes and measurement uncertainty in HVOCs (on the y-axis) and uncorrelated processes and measurement uncertainty in O_2 and CO_2 (on the x-axis) on the regression slope (Ayers et al. 2001; Glover et al., 2011). As noted by previous studies, simple least squares linear regressions fail to account for uncertainties in predictor variables (e.g. Cantrell et al. 2008)."

L250: Please explain how the molar enrichment ratios are defined and/or calculated. This seems to be critical, but not well explained. Is this just the slope of the regression between CHBr3 (or CH2Br2) and O2?

Yes, the molar enrichment ratios are equivalent to the slope of the regression, although the units of O_2 must be converted from O_2/N_2 (per meg) to equivalent ppm (multiplying O2/N2 by the XO_2, in dry air = 0.2093).

L351: "In its simplest approximation, the wind speed error will correlate with surface influence error" I understand that this is in general may be a reasonable assumption, but it is not obvious to me why the error in the influence function (in ppt m2 s pmol-1) should be proportional to the error in wind speed. More justification of this argument would be needed here.

As explained in Xiang et al. 2010, now cited here, the STILT model error (E) represents a combination of source and model transport error. Although model transport error is difficult to quantify precisely, it is influenced first and foremost by differences in simulated and actual wind speed, wind direction, and boundary layer height. This passage L280-294 now reads, "Uncertainty in the surface influence value is strongly influenced by the accuracy of the underlying meteorological transport, as discussed in Xiang et al. (2010). We evaluated the GDAS reanalysis winds by comparing model winds interpolated in space and averaged between corresponding time points and pressure levels to match aircraft observations. By evaluating observed winds compared with modeled winds along the flight tracks we can estimate uncertainty in the surface influence values. We consider the observation-model differences in both wind speed and direction to approximate errors in surface influence strength and location. For wind speed, a small bias may be present, where we find a median difference between observations and reanalysis of 0.68 m/s, a 5% relative bias. The 1-sigma of the wind speed difference is 2.3 m/s, corresponding to a 19% 1-sigma uncertainty in wind speed. In its simplest approximation, the surface influence strength error is perfectly correlated with the wind speed error, and thus we take 19% as an approximation of the surface influence strength uncertainty. The uncertainty in surface influence location depends on the error in the wind direction. We find a 1-sigma error of 14 degrees in wind speed, which corresponds to a possible error of 260 km/day."

L389: PAR: please spell out (as far as I can see first defined in L476)

L369 Thank you. This is now done.

L431: "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 CHBr3, CH2Br2, or other HVOCs to the MBL." What is this statement based on?

As it is irrelevant to the main objective of the paper, this statement has been removed.

L499: Reference to Fig.9 in L499 was not clear to me. Was really Fig.9 meant here?

594 Fig. 10 is now referenced here, "For $CHBr_3$, CH_2Br_2, and $CHClBr_2$ we construct ocean emission inventories for January and February using a scaled version of gridded modeled air-sea O_2 fluxes and the slopes (i.e. molar ratios) of linear correlations between $\delta(O_2/N_2)$ and HVOC mixing ratios (Fig. 10)."

Fig. 9c: Caption not very clear, would be helpful if the description in the caption can be improved.

The wording of this caption has been rewritten. As now discussed elsewhere in the text (Sect. 2.3.1) the surface influence function (e.g. HS_1) is the product of the surface influence and a relevant surface source field.

5.2 Why are STILT based emission estimates presented only for CH3I? Why is it not possible to perform this for other HVOCs as well?

Indeed, it is possible to estimate STILT emissions for other gases such as CHBr3 and CH2Br2. At present, we have not done this, as the correlations with STILT surface influence functions were less strong than those with O_2/N_2, as now stated in the text L653-656.

Figure S4: "Consecutive samples in and out of dips into the MBL": Sorry, I don't really understand what is meant here, please re-word.

This has been reworded as requested to read, "Consecutive TOGA VOC sample locations, their back-trajectories and surface influences in the lower troposphere on two different flights (a-c; Jan. 21,2016, and d-f; Jan. 30, 2016)."

Technical corrections: L134: "low attitude" -> "low altitude"

Done.

L183: citation should be part of the sentence

Done.

Novel approaches to improve estimates of short-lived halocarbon emissions during summer from the Southern Ocean using airborne observations

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Abstract.

Fluxes of halogenated volatile organic compounds (VOCs) over the Southern Ocean remain poorly understood, and few atmospheric measurements exist to constrain modeled emissions of these compounds. We present observations of $CHBr_3$, CH_2Br_2, CH_3I, $CHClBr_2$, $CHBrCl_2$, and CH_3Br during the O_2/N_2 Ratio and CO_2 Airborne Southern Ocean (ORCAS) study and the 2nd Atmospheric Tomography mission (ATom-2), in January and February of 2016 and 2017. Good model-measurement correlations were obtained between these observations and simulations from the Community Earth System Model (CESM) atmospheric component with chemistry (CAM-Chem) for $CHBr_3$, CH_2Br_2, CH_3I, and $CHClBr_2$ but all showed significant differences in model:measurement ratios. The model:measurement comparison for CH_3Br was satisfactory and for $CHBrCl_2$ the low levels present precluded us from making a complete assessment. Thereafter, we demonstrate two novel approaches to estimate halogenated VOC fluxes; the first approach takes advantage of the robust relationships that were found between airborne observations of O_2 and $CHBr_3$, CH_2Br_2, and $CHClBr_2$; we use these linear regressions with O_2 and modeled O_2 distributions to infer a biological flux of halogenated VOCs. The second approach uses the Stochastic Time-Inverted Lagrangian Transport (STILT) particle dispersion model to explore the relationships between observed mixing ratios and the product of the upstream surface influence and sea ice, chl *a*, absorption due to detritus, and downward shortwave radiation at the surface, which in turn relate to various regional hypothesized sources of halogenated VOCs such as marine phytoplankton, phytoplankton in sea ice brines, and decomposing organic matter in surface seawater. These relationships can help evaluate the likelihood of particular halogenated VOC sources, and in the case of statistically significant correlations, such as was found for CH_3I, may be used to derive an estimated flux field. Our results are consistent with a biogenic regional source of $CHBr_3$, and both non-biological and biological sources of CH_3I over these regions.

1 Introduction

Emissions of halogenated volatile organic compounds (VOCs) influence regional atmospheric chemistry and global climate. Through the production of reactive halogen radicals at high latitudes, halogenated VOCs contribute to tropospheric and stratospheric ozone destruction, and alter the sulfur, mercury, nitrogen oxide and hydrogen oxide cycles (e.g. Schroeder et al., 1998; Boucher et al., 2003; Bloss et al., 2005; von Glasow and Crutzen; 2007; Saiz-Lopez et al., 2007; Obrist et al., 2011; Engel and Rigby, 2018). In the marine boundary layer and lower troposphere, sea salt is the main source of reactive bromine (Finlayson-Pitts 1982, Simpson et al., 2015). Yet halogenated VOCs may also be a more important source of inorganic bromine to the whole atmosphere than previously thought, according to a recent study, which indicates that sea salt is scarce and insufficient to control the bromine budget in the middle and upper troposphere (Murphy et al., 2019).

Phytoplankton and macroalgae in the ocean are the main sources to the atmosphere of several very short-lived bromocarbons, including bromoform ($CHBr_3$), dibromomethane (CH_2Br_2),

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dibromochloromethane ($CHClBr_2$), and bromodichloromethane ($CHBrCl_2$) (Moore et al., 1996; Carpenter et al. 2003; Butler et al., 2007; Raimund et al., 2011). Other halogenated VOCs, such as methyl iodide (CH_3I), and methyl bromide (CH_3Br) have many natural sources, such as coastal macroalgae, phytoplankton, temperate forest soil and litter, and biomass burning (e.g., Bell et al., 2002; Sive et al., 2007; Colomb et al. 2008; Drewer et al., 2008). CH_3I is also formed through non-biological reactions in surface seawater, and CH_3Br is emitted as a result of quarantine and pre-shipment activities, which are not regulated by the Montreal Protocol (e.g., Moore and Zafiriou; 1994, Engel and Rigby, 2018). Over the Southern Ocean specifically, hypothesized sources of halogenated VOCs include: coastal macroalgae, phytoplankton, sea ice algae, and photochemical or dust stimulated non-biological production at the sea surface (e.g., Abrahamsson et al. 2018, Manley and Dastoor 1998; Moore and Zafiriou 1994; Moore et al., 1996; Richter and Wallace 2004; Williams et al., 2007; Tokarczyk and Moore 1994; Sturges et al., 1992).

We largely owe our current understanding of marine halogenated VOC emissions over the Southern Ocean to ship-based field campaigns and laboratory process studies (e.g., Abrahamsson et al. 2004a,b; Atkinson et al., 2012; Carpenter et al., 2007; Moore et al., 1996; Chuck et al., 2005; Butler et al., 2007; Raimund et al., 2011; Hughes et al., 2009; Mattsson et al. 2013; Hughes et al., 2013). These studies have reported surface water and sea-ice halogenated VOC supersaturation and corresponding elevated levels of halogenated VOCs in the marine boundary layer (MBL) in summer, and have identified numerous biological and non-biological ocean sources for these compounds. Mattsson et al. (2013) noted that the ocean also acts as a sink for halogenated VOCs, when undersaturated surface waters equilibrate with air masses transported from halogenated VOC source regions. The spatially heterogeneous ocean sources of $CHBr_3$ and CH_2Br_2 at high latitudes in the Southern Hemisphere are often underestimated in global atmospheric models (Hossaini et al., 2013; Ordoñez et al., 2012; Ziska et al., 2013). Ship-based and Lagrangian float observations provide invaluable information on the sources and temporal variability of compounds in the surface ocean. These methods offer the advantage of simultaneous measurements of both air and seawater to evaluate the gases' saturation state in the surface ocean and calculate fluxes. Yet ship-based measurements onboard these slow moving platforms also have drawbacks: they under sample the spatial variability of halogenated VOCs (e.g., Butler et al., 2007) and require assumptions about gas-exchange rates to estimate fluxes.

To disentangle the roles of atmospheric transport and spatial variability of emissions on halogenated VOC distributions requires large-scale atmospheric observations. At low latitudes, large-scale convection at the intertropical convergence zone carries bromocarbons and other halogenated VOCs into the free troposphere and lower stratosphere (e.g., Liang et al., 2014; Navarro et al., 2015). Polar regions are characterized by stable boundary layers in summer. Wind shear, frontal systems, and internal gravity waves create turbulence and control vertical mixing within and across a stable polar boundary layer (e.g. Anderson et al., 2008), and small, convective plumes may form over the marginal sea ice zone, related to sea ice leads as well as winds from ice-covered to open-ocean waters (e.g. Schnell et al., 1989). As a result of limited vertical transport in these regions, however, air-sea fluxes lead to strong vertical gradients. Zonal transport from lower latitudes has a large impact on the vertical gradients of trace gas

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mixing ratios over polar regions (Salawitch 2010). Given their extended photochemical lifetimes at high latitudes (see Sect. 2.3 for a brief discussion), many halogenated VOC distributions are particularly sensitive to zonal transport at altitude.

Aircraft observations can rapidly map basin-wide vertical distributions, support quantitative flux estimates, and provide spatial constraints to atmospheric models (e.g. Xiang et al., 2010; Stephens et al., 2018; Wofsy et al., 2011). Few airborne observations of halogenated VOCs exist at high latitudes in the Southern Hemisphere. Two earlier aircraft campaigns that have measured summertime halogenated VOCs in this region are the first Aerosol Characterization Experiment (ACE-1; Bates et al., 1999) and the first High-performance Instrumented Airborne Platform for Environmental Research (HIAPER) Pole-to-Pole Observations (HIPPO; Wofsy, 2011) campaign. For these two aircraft campaigns, whole air samples were collected onboard the NSF/NCAR C-130 and the NSF/NCAR Gulfstream V (GV) during latitudinal transects over the Pacific Ocean as far south as 60° S and 67° S, respectively. However, the ACE-1 and HIPPO campaigns obtained relatively few whole air samples in this region, with ≤100 samples poleward of 60° S combined (e.g., Blake et al., 1999; Hossaini et al., 2013). ACE-1 measurements of CH_3I in the MBL indicate a strong ocean source between 40° S and 50° S in austral summer, with mixing ratios above 1.2 pmol below ~1 km (Blake et al., 1999).

Halogenated VOC emissions are frequently incorporated into earth system models, using either climatologies or parameterizations based on satellite observations of chlorophyll and geographical region and evaluated using mixing ratio comparisons with airborne observations. In Section 3.1 and 3.2, we report new airborne observations of $CHBr_3$, CH_2Br_2, CH_3I, $CHClBr_2$, $CHBrCl_2$, and CH_3Br from high latitudes in the Southern Hemisphere, where data are scarce, and large-scale regional mixing ratio comparisons for halogenated VOCs with the community earth system model (CESM) atmospheric component with chemistry (CAM-Chem). In section 3.4, we present two novel approaches to estimate regional fluxes of halogenated VOCs for comparison with global climate models' parameterizations or climatologies. One approach uses correlations of halogenated VOCs to marine, oxygen (O_2) of marine origin, as measured by deviations in the ratio of O_2 to nitrogen (N_2) ($\delta(O_2/N_2)$ see Sect. 2.1.2 and 3.1.2). We exploit robust ratios of halogenated VOCs to oxygen (O_2) determined from linear regressions (i.e. the enrichment ratio), and the ocean flux of O_2 from CESM's ocean component, to estimate the marine biogenic flux of several halogenated VOCs. The second approach relies on observed halogenated VOC mixing ratios, the Stochastic Time-Inverted Lagrangian Transport (STILT) particle dispersion model and geophysical datasets (see Sect. 2.3 and 3.3). We assess contributions from previously hypothesized regional sources for the Southern Ocean, and estimate halogenated VOC fluxes based on regressions between upstream influences and observed mixing ratios and distributions of remotely sensed data.

2 Methods

2.1 Measurements

Atmospheric measurements for this study were collected at high latitudes in the Southern Hemisphere as part of the O_2/N_2 Ratio and CO_2 Airborne Southern Ocean (ORCAS) study

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(Stephens et al., 2018), and the second NASA Atmospheric Tomography Mission (ATom-2), near Punta Arenas, Chile (Fig. 1). The ORCAS field campaign took place from Jan. 15 – Feb. 29, 2016 onboard the NSF/NCAR GV. On Feb. 10 and 13, 2017 the sixth and seventh ATom-2 research flights passed over the eastern Pacific sector poleward of 60° S (defined here as Region 1) and over the Patagonian Shelf between 40° S and 55° S and between 70° W and 50° W (defined here as Region 2), respectively. The two regions for this study are defined based loosely on dynamic biogeochemical provinces identified using bathymetry, algal biomass, sea surface temperature and salinity (Reygondeau et al., 2013).

Both projects featured en route vertical profiling from near the ocean surface (~ 150 m) to the upper-troposphere, with 74 ORCAS and seven ATom-2 (during the sixth and seventh flights) low-altitude level legs in the MBL. These campaigns shared a number of instruments, including the NCAR Trace Gas Organic Analyzer (TOGA), the NCAR Atmospheric Oxygen (AO2) instrument, a Picarro cavity ringdown spectrometer operated by NOAA, discussed below. More information about individual instruments may be found in Stephens et al., 2018 and at https://www.eol.ucar.edu/field_projects/orcas and https://espo.nasa.gov/atom/content/ATom.

2.1.1 Halogenated VOCs

During ORCAS and ATom-2 TOGA provided mixing ratios of over 60 organic compounds, including halogenated VOCs. The instrument, described in Apel et al. (2015), continuously collects and analyzes samples for $CHBr_3$, CH_2Br_2, $CHClBr_2$, $CHBrCl_2$, and CH_3I among other compounds, with a 35-second sampling period and repeats the cycle every two-minutes using online fast gas chromatography and mass spectrometry. This study also leverages measurements of CH_3Br from whole air samples from the U. Miami / NCAR Advanced Whole Air Sampler (AWAS; Schauffler et al., 1999) onboard the GV during the ORCAS campaign and the UC Irvine Whole Air Sampler (WAS; Blake et al., 2001) onboard the DC-8 during the ATom-2 campaign. Halogenated VOCs reported here have an overall ±15% accuracy and ±3% relative precision, and detection limits of 0.03 ppt for CH_3I, 0.2 ppt for $CHBr_3$, 0.03 ppt for CH_2Br_2, 0.03 ppt for $CHClBr_2$, 0.05 ppt for $CHBrCl_2$, and 0.2 ppt for CH_3Br – 0.2 ppt. In addition, comparisons between onboard collected whole air samples and in-flight TOGA measurements, when sharing over half of their sampling period with TOGA measurements, showed good correlations for $CHBr_3$, CH_2Br_2, CH_3I, and $CHClBr_2$, although there were some calibration differences (Fig. S1 and Fig. S2). In addition to the comparison between co-located atmospheric measurements, we also conducted a lab inter-comparison following the campaign between NOAA's programmable flask package (PFP) and TOGA (Table S1; see supplement for details).

2.1.2 $\delta(O_2/N_2)$ and CO_2

The AO2 instrument measures variations in atmospheric O_2, which are reported as relative deviations in the oxygen to nitrogen ratio ($\delta(O_2/N_2)$), following a dilution correction for CO_2 (Keeling et al., 1998; Stephens et al., 2018). The instrument's precision is ±2 per meg units (one

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in one million relative) for a 5 second measurement (Stephens et al., 2003; Stephens et al., manuscript in preparation, 2019). Anthropogenic, biogenic, and oceanic processes introduce O_2 perturbations that are superimposed on the background concentrations of O_2 in air (XO_2, in dry air = 0.2095). Air-sea O_2 fluxes are driven by both biological production and consumption of O_2 and by heating and cooling of surface waters. O_2 is consumed when fossil fuels are burned and produced and consumed during terrestrial photosynthesis and respiration. Seasonal changes in the ocean heat content lead to small changes in atmospheric N_2. As others have done, we isolated the air-sea O_2 signal by subtracting model estimates of the terrestrial O_2, fossil-fuel O_2, and air-sea N_2 flux influences from the $\delta(O_2/N_2)$ measurements (Equation 1; Keeling et al., 1998; Garcia and Keeling, 2001; Stephens et al., 2018). The difference of the $\delta(O_2/N_2)$ measurement and these modeled components is multiplied by XO_2 to convert to ppm equivalents as needed (ppm eq; Keeling et al., 1998; Equation 1).

$$O_{2\text{-ppm-equiv}} = [\delta(O_2/N_2) - \delta(O_2/N_2)_{Land} - \delta(O_2/N_2)_{Fossil\ Fuel} - \delta(O_2/N_2)_{N2}] \times XO_2 \quad (1)$$

We obtained the modeled $\delta(O_2/N_2)$ signal terrestrial influences from the land model component of the CESM, the fossil fuel combustion influences from the Carbon Dioxide Information Analysis Center (CDIAC; Boden et al. 2017), and the air-sea N_2 influences from the oceanic component of CESM. These fluxes were all advected through the specified dynamics version of CESM's atmosphere component, as described below in Sect. 2.2 and in Stephens et al. (2018).

CO_2 measurements were provided by NOAA's Picarro G2401-m cavity ring down spectrometer modified to have a ~1.2 sec measurement interval and a lower cell pressure of 80 Torr, which enabled the instrument to function at the full range of GV altitudes. (McKain et al. manuscript in preparation, 2019). Dry-air mole fractions were calculated using empirical corrections to account for dilution and pressure broadening effects as determined in the laboratory before and after the campaign deployments, and in-flight calibrations were used to determine an offset correction for each flight. Corrected CO_2 data have a total average uncertainty of 0.07 ppm (McKain et al. manuscript in preparation, 2019). To merge them with the TOGA data, these faster O_2 and CO_2 measurements were arithmetically averaged over TOGA's 35-s sampling periods (Stephens et al., 2017 and https://espo.nasa.gov/atom/content/ATom).

2.2 CAM-Chem model configuration

The CESM version 1, atmospheric component with chemistry (CAM-Chem) is a global three-dimensional chemistry climate model that extends from the Earth's surface to the stratopause. CAM-Chem version 1.2 includes all the physical parameterizations of Neale et al. (2013) and a finite volume dynamical core (Lin, 2004) for tracer advection. The model has a horizontal resolution of 0.9° latitude × 1.25° longitude, with 56 vertical hybrid levels and a time-step of 30 minutes. Meteorology is specified using the NASA Global Modeling and Assimilation Office (GMAO) Goddard Earth Observing System Model, version 5 (GEOS-5; Rienecker et al., 2008) (GEOS-5), following the specified dynamic procedure described by Lamarque et al. (2012). Winds, temperatures, surface pressure, surface stress, and latent and sensible heat fluxes are

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nudged using a 5-hour relaxation timescale to GEOS-5 1° × 1° meteorology. The sea surface temperature boundary condition is derived from the Merged Hadley-NOAA Optimal Interpolation Sea Surface Temperature and Sea-Ice Concentration product (Hurrell et al., 2008). The model uses chemistry described by Tilmes et al. (2016), biomass burning and biogenic emissions from the Fire INventory of NCAR (FINN; Wiedinmyer et al., 2011) and MEGAN (Model of Emissions of Gasses and Aerosols from Nature) 2.1 products (Guenther et al., 2012) and additional tropospheric halogen chemistry described in Fernandez et al. (2014) and Saiz-Lopez et al. (2014). These include ocean emissions of $CHBr_3$, CH_2Br_2, $CHBr_2Cl$, and $CHBrCl_2$, with parameterized emissions based on chlorophyll *a* (chl *a*) concentrations and scaled by a factor of 2.5 over coastal regions, as opposed to open ocean regions (Ordoñez et al., 2012). The model used an existing CH_3I flux climatology (Bell et al., 2002), and CH_3Br was constrained to a surface lower boundary condition, also described by Ordoñez et al. (2012). This version of the model was run for the period of the ORCAS field campaign (January and February 2016), following a 24-month spin-up. To facilitate comparisons to ORCAS observations, output included vertical profiles of modeled constituents from the two nearest latitude and two nearest longitude model grid-points (four profiles in total) to the airborne observations at every 30-min model time-step. Following the run, simulated constituent distributions were linearly interpolated to the altitude, latitude and longitude along the flight track, yielding co-located modeled constituents and airborne observations. This version of the model has not yet been run for the ATom-2 period.

2.3 STILT model configuration

The Stochastic Time-Inverted Lagrangian Transport (STILT; Lin et al., 2003) particle dispersion model uses a receptor oriented framework to infer surface sources or sinks of trace gases from atmospheric observations collected downstream, thus simulating the upstream influences that are ultimately measured at the receptor site. The model tracks ensembles of particle trajectories backward in time and the resulting distributions of these particles can be used to define surface influence maps for each observation. STILT was run using 0.5º Global Data Assimilation System (GDAS) reanalysis winds to investigate the transport history of air sampled along the flight track (Stephens et al., 2018). For each TOGA observation, an ensemble of 4,096 particles was released from the sampling location and followed over a backwards simulation period of seven days. Particles in the lower half of the simulated MBL are assigned a surface influence value, which quantitatively links observed mixing ratios to surface sources (Lin et al., 2003). The average surface influence of all 4,096 particles per sampling location yields an hourly and spatially gridded surface influence value (ppt m^2 s $pmol^{-1}$) at a spatial resolution of 0.25º x 0.25º for each sample point.

Uncertainty in the surface influence value is strongly influenced by the accuracy of the underlying meteorological transport, as discussed in Xiang et al. (2010). We evaluated the GDAS reanalysis winds by comparing model winds interpolated in space and averaged between corresponding time points and pressure levels to match aircraft observations. By evaluating observed winds compared with modeled winds along the flight tracks we can estimate

uncertainty in the surface influence values. We consider the observation-model differences in both wind speed and direction to approximate errors in surface influence strength and location. For wind speed, a small bias may be present, where we find a median difference between observations and reanalysis of 0.68 m/s, a 5% relative bias. The 1-sigma of the wind speed difference is 2.3 m/s, corresponding to a 19% 1-sigma uncertainty in wind speed. In its simplest approximation, the surface influence strength error is perfectly correlated with the wind speed error, and thus we take 19% as an approximation of the surface influence strength uncertainty. The uncertainty in surface influence location depends on the error in the wind direction. We find a 1-sigma error of 14 degrees in wind speed, which corresponds to a possible error of 260 km/day.

Finally, we note that photochemical loss during transport is not accounted for in this analysis. Low OH mixing ratios, cold temperatures, and lower photolysis rates due to angled sunlight at high latitudes lead to longer than average halogenated VOC lifetimes. For instance, assuming an average diurnal OH concentration of 0.03 ppt, and average photochemical loss according to the Tropospheric Ultraviolet and Visible (TUV) radiation model and the Mainz Spectral data site (http://satellite.mpic.de/spectral_atlas) for Jan. 29 under clear sky conditions at 60° S, $CHBr_3$ has a lifetime of 30 days, CH_2Br_2 has a lifetime of 270 days, CH_3I has a lifetime of 7 days, and $CHClBr_2$ has a lifetime of 63 days. As such, the photochemical lifetimes of these gases are greater than or equal to the time of our back-trajectory analysis. Moreover, OH concentrations in this region have large uncertainties, the inclusion of which would lead to more, not less, uncertainty in surface influence based regression coefficients and estimated fluxes (see Sect. 2.3 and 3.3 for details).

2.3.1 STILT surface influence functions

For this study, we used STILT surface influence distributions with remotely sensed ocean surface and reanalysis data (i.e. surface source fields) in linear and multi-linear regressions to generate empirical STILT influence functions. Surface influence functions can help explain observed mixing ratios of $CHBr_3$, CH_2Br_2, CH_3Br and CH_3I, evaluate the likelihood of particular halogenated VOC sources, and in the case of statistically significant correlations, may be used to derive an estimated flux field (See Sect. 3.3 and 3.4.2 for details).

We tested whether observed mixing ratios (Z) could be explained by a linear relationship in which the predictor variable is a surface influence function, equal to the product of the surface influence (H) and a potential geophysical surface source field(s), such as chl *a*, as well as an intercept (b), a slope (a), and error term ξ (Equation 2; Fig. S5). This relationship can be generalized as a multiple linear regression with multiple surface influence functions (Hs_1, Hs_2…) and slope coefficients (a_1, a_2; Equation 3), when multiple sources contribute to observed halogenated VOC mixing ratios. The multiple linear regression may also include an interaction term (Hs_2) between predictor variables (e.g. Hs_1 and Hs_2) with a slope coefficient (a_3) to improve the fit. Statistical correlations between mixing ratios and surface influence functions may be

used to support or reject hypothesized sources. A flux (μmol m^{-2} s^{-1}) may then be estimated for each grid cell based on the product of the slopes (a_1, $a_{2...}$) and the potential source fields (s_1, $s_{2...}$). Grid cell fluxes are averaged over a geographical region to yield the average regional flux. We used the standard deviation of the regression coefficients and the relative uncertainty in the surface source, added in quadrature, to estimate the uncertainty in the flux (see Sect. 3.4.2 for fractional uncertainties). We note that the uncertainty in STILT transport (see Sect. 2.3 for details) is inherently reflected in the relative uncertainty of the regression coefficients (a_1, $a_{2...}$).

$$Z = aHs + b + \xi \quad (2)$$

$$Z = a_1 Hs_1 + a_2 Hs_2 + (a_3 Hs_1 Hs_2) \ldots + b + \xi \quad (3)$$

2.3.2 Surface Source Fields

Geophysical surface source fields of remotely sensed and reanalysis data included a combination of sea ice concentration, chl *a*, absorption due to ocean detrital material, and downward shortwave radiation at the ocean surface.

We used daily sea ice concentration data (https://nsidc.org/data/nsidc-0081) at a 25 km x 25 km spatial resolution between 39.23° S and 90° S, 180° W – 180° E from the NASA National Snow and Ice Data Center Distributed Active Archive Center (NSIDC; Maslanik et al., 1999). This data reports the fraction of sea-ice cover, land-ice cover, and open water. Unfortunately, these data do not provide any information on sea ice thickness, or the presence of brine channels or melt ponds, which may modulate emissions from sea-ice covered regions. Sea ice concentration data were calculated using measurements of near-real-time passive microwave brightness temperature from the Special Sensor Microwave Image/Sounder (SSMIS) on the Defense Meteorological Satellite Program (DMSP) satellites. NSIDC sea ice concentration data were arithmetically averaged to yield 0.25° x 0.25° binned sea ice fraction for use with gridded surface influences.

Due to persistent cloud cover over the Southern Ocean, which often precludes the retrieval of remotely sensed ocean color data, we used 8-day mean composite Aqua MODIS L3 distributions of chl *a* from the Ocean Color Index (OCI) algorithm and absorption due to gelbstoff and detrital material at 443 nm from the Generalized Inherent Optical Properties (GIOP) model (NASA Goddard Space Flight Center, 2014). Absorption due to gelbstoff and detrital material at 443 nm is used as a proxy for colored dissolved organic matter (CDOM; https://oceancolor.gsfc.nasa.gov/atbd/giop/). CDOM is hypothesized to be an important source of carbon for the photochemical production of CH_3I (Moore et al., 1994). The GIOP model also publishes an uncertainty in the absorption due to gelbstoff and detrital material at 443 nm. Raw 4 km x 4 km data were geometrically averaged, based on lognormal probability density functions, to a spatial resolution of 0.25° x 0.25° for use with gridded surface influences. We used the ratio of the 0.25° x 0.25° gridded uncertainty in the detrital material absorption to the absorption as the relative uncertainty for flux calculations (see Sect. 3.4.2).

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The National Center for Environmental Prediction (NCEP) provides Final Global Data Assimilation System (GDAS/FNL) global data of downward shortwave radiation at the surface at 0.25 degree and 6-hour resolution (NCEP, 2015). We chose downward shortwave radiation for use with gridded surface influences because the photo-production of CH_3I has been observed at all visible wavelengths (Moore et al., 1994). This reanalysis data is available at a higher temporal resolution and better spatial coverage than satellite retrievals of photosynthetically active radiation (PAR) or temperature.

3 Results and discussion

3.1 Observed halogenated VOC patterns and relationships

Zonal cross-sections of halogenated VOC data collected on ORCAS and ATom-2 illustrate unprecedented spatial sampling across our study area between the surface and 12 km (Fig. 2). Above average mixing ratios of CH_3I, $CHBr_3$, and $CHClBr_2$ typically remain confined to the lower ~2-4 km of the atmosphere (Fig. 2a, b, d). These compounds have lifetimes of approximately two months or less. Conversely, weak sources and longer lifetimes (≥ 3 months) may have contributed to similar concentrations of CH_2Br_2 and $CHBrCl_2$ throughout the troposphere and above average mixing ratios as high as 8 km (Fig. 2c, e). Unfortunately, the availability of data above the detection limit and absence of BL enhancements for $CHBrCl_2$ preclude the identification of strong regional sources at this time. Meridional distributions also indicate lower latitude sources of CH_3I and CH_3Br (< 50° S), potentially resulting from terrestrial and anthropogenic contributions, and higher latitude sources (> 60° S) of $CHBr_3$, CH_2Br_2, and $CHClBr_2$ (Fig. 2a-d,f).

3.1.1 Observed halogenated VOC interrelationships

Across our study area in both 2016 and 2017, we found that $CHBr_3$ and CH_2Br_2 exhibit a consistent enhancement ratio with each other in the bottom 2 km of the atmosphere both in Region 1 and Region 2, which suggests that these bromocarbon fluxes are closely coupled. Previous studies have documented co-located source regions of $CHBr_3$ and CH_2Br_2 in the Southern Ocean (e.g. Hughes et al., 2009; Carpenter et al., 2000; Nightingale et al., 1995; Laturnus et al., 1996), and laboratory studies have demonstrated that phytoplankton and their associated bacteria cultures, including a cold water diatom isolated from coastal waters along the Antarctic Peninsula and common to the Southern Ocean, produce both $CHBr_3$ and CH_2Br_2 (Hughes et al., 2013; Tokarczyk and Moore 1994, Sturges et al., 1993). The non-linearity observed in ratios of these two gases at low $CHBr_3$ may reflect the different rates of their production or loss in seawater, or possibly, the influence of air masses from distant, more productive low-latitude source regions. Several studies have documented bacterially mediated loss of CH_2Br_2, but not $CHBr_3$, and report distinct ratios of CH_2Br_2 to $CHBr_3$ in seawater during the growth and senescent phases of a phytoplankton bloom (e.g. Carpenter et al., 2009, Hughes et al., 2013). Although this analysis is restricted to the bottom 2 km of the atmosphere, zonal

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transport of air masses with lower ratios of CH_2Br_2 to $CHBr_3$ ratios, as have been observed in the MBL over productive, low-latitude regions, may also have influenced our observations (Yokouchi et al. 2005). Mixing ratios of $CHBr_3$ and $CHClBr_2$ were also correlated (Fig. 3d) in Region 2, and, a similar, weaker relationship was observed in Region 1 (Fig. 3b). $CHClBr_2$ is a less well-studied compound than CH_2Br_2. Yet these consistent relationships suggest that $CHBr_3$ and $CHClBr_2$ may either share some of the same sources or have sources that co-vary.

3.1.2 Observed halogenated VOC relationships to $\delta(O_2/N_2)$ and CO_2

We sought to test if the biologically mediated production of bromocarbons and oxygen result in similar atmospheric distributions. Conversely, we expected halogenated VOC atmospheric distributions and CO_2 distributions to anticorrelate because CO_2 fixation in surface waters is proportional to the production of oxygen.

For these comparisons, both O_2 and CO_2 mixing ratios from the upper troposphere (5-7 km) were subtracted from the data to detrend for seasonal and inter-annual variability (Fig. 4; Fig. S3). To isolate the contribution of ocean O_2 fluxes, the ORCAS $\delta(O_2/N_2)$ values reported here represent the $\Delta\delta(O_2/N_2)$ to observed values between 5-7 km adjusted for CESM O_2 land and fossil fuel contributions and the influence of air-sea N_2 fluxes. In Fig. 4 we present type II major axis regression fits to data (fits were calculated using data scaled to their full range) between the ocean surface and the lowest 7 km for bromocarbons with photochemical lifetimes of ≥ 1 month and from the lowest 2 km for CH_3I with a photochemical lifetime of ~ 1 week. We used a type II major axis regression model to balance the influences of uncorrelated processes and measurement uncertainty in halogenated VOCs (on the y-axis) and uncorrelated processes and measurement uncertainty in O_2 and CO_2 (on the x-axis) on the regression slope (Ayers et al., 2001; Glover et al., 2011). As noted by previous studies, simple least squares linear regressions fail to account for uncertainties in predictor variables (e.g. Cantrell et al., 2008).

The robust correlations of $CHBr_3$ and CH_2Br_2 with $\delta(O_2/N_2)$, in both 2016 and 2017 and in Region 1 and Region 2, provides support for a regional biogenic source of these two halogenated VOCs (Fig. 4a, b and Fig. 4d, e). The air-sea exchange of O_2 during summer in the Southern Ocean is driven by net community production (the excess of photosynthesis over respiration) in the surface mixed layer, surface warming, and to a lesser extent ocean advection and mixing (e.g. Stephens et al., 1998; Tortell and Long 2009; Tortell et al., 2014). Note that we adjust for influences on the $\delta(O_2/N_2)$ from thermal N_2 fluxes (see Equation 1, Sect. 2.1.2 for details). Biological O_2 supersaturation in the surface mixed layer develops quickly in the first several days of a phytoplankton bloom and diminishes as community respiration increases and air-sea gas exchange equilibrates the surface layer with the atmosphere on a timescale of ~ 1 week. $CHBr_3$ and CH_2Br_2 are emitted from phytoplankton during the exponential growth phase (Hughes et al., 2013), which often coincides with high net community production and the accumulation of O_2 in surface waters. The bulk air-sea equilibration time for an excess of $CHBr_3$ and other halogenated VOCs is less than two weeks, although the photochemical loss of

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halogenated VOCs will alter their ratio over time (see Supplement for details on calculations of bulk sea air equilibration times).

Our observations suggest a biological source for $CHBr_3$ and CH_2Br_2 in both Region 1 and Region 2 (Fig. 4). Interestingly, the slope of the regression between $CHBr_3$ and O_2 appears distinct in Region 1 and Region 2, but between CH_2Br_2 is the same. Molar enrichment ratios are 0.20 ± 0.01, and 0.07 ± 0.004 pmol : mol for $CHBr_3$ and CH_2Br_2 to O_2 in Region 1, and 0.32 ± 0.02, and 0.07 ± 0.004 pmol : mol in Region 2. We observe a weaker relationship between CH_3I and $CHClBr_2$ and O_2 in Region 1 (Fig. 4c, d), consistent with the existence of other, non-biological sources of CH_3I in this region. Figure 4f illustrates a strong relationship between CH_3I and O_2, as well as $CHClBr_2$ and O_2, in Region 2, however, which implies that the dominant sources of CH_3I and $CHClBr_2$ emissions over the Patagonian Shelf are biological. The corresponding molar enrichment ratios of CH_3I to O_2 and $CHClBr_2$ to O_2 in Region 2 are 0.38 ± 0.03 pmol : mol and 0.19 ± 0.04 pmol: mol, respectively.

In contrast to O_2, air-sea fluxes of CO_2 over the Southern Ocean during summer reflect the balance of opposing thermal and biological drivers (e.g. Stephens et al., 1998; 2018). Ocean buffering chemistry results in CO_2 equilibration across the air-sea interface on a timescale of several months. ORCAS observations showed a depletion of CO_2 in the MBL, indicating that uptake driven by net photosynthesis dominated over thermally driven outgassing during the several months preceding the campaign (Stephens et al., 2018). $CHBr_3$ and CH_2Br_2 in the lowest 7 km were negatively correlated with CO_2 in both years in Region 1 and Region 2 (Fig. S3a, b, d, e). Interestingly, CH_3I was not correlated with CO_2 in Region 1, likely due to the long air-sea equilibration timescale of CO_2 compared with a 9-day air-sea equilibration time and a ~7-day photochemical lifetime for CH_3I. For longer lived species, correlations for halogenated VOCs to CO_2 have similar r^2-values as those for halogenated VOCs to $\delta(O_2/N_2)$, but model and climatological estimates of Southern Ocean CO_2 fluxes are much less certain than for O_2 (Anav et al., 2015; Nevison et al., 2016). As a result, we use modeled O_2 fluxes as the basis for our halogenated VOC flux estimates (see Sect. 3.4.1 for details).

3.2 Model-observation comparisons

The ORCAS dataset provides an exceptional opportunity to evaluate the CAM-Chem halogenated VOC emission scheme (Ordoñez et al., 2012) at high latitudes in the Southern Hemisphere. We compared modeled halogenated VOC constituents to corresponding observations along the ORCAS flight track (Fig. 5; Fig. 6). In these figures, we used type II major axis regression models to balance the measurement uncertainty (on the y-axis) and the inherent, yet difficult to quantify representativeness and errors in a global atmospheric chemistry model (on the x-axis). We note that this comparison may favor constituents with longer photochemical lifetimes, when transport and mixing dominate over source heterogeneity.

In Region 1 and Region 2, both the model and observations indicate that elevated mixing ratios of CH_3I remain confined to the MBL (Fig. 5a and Fig. 6a), presumably due to its relatively short

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photochemical lifetime. Modeled and observed CH_3I are poorly correlated in Region 1 (r^2 = 0.20; Fig. 5b) and better correlated in Region 2 (r^2 = 0.70; Fig. 6b). In both regions, the model most likely under predicts CH_3I in the upper troposphere and lower stratosphere (UTLS), likely stemming from the poleward transport of lower latitude air masses, where CAM-Chem also exhibits a negative bias. Mixing ratio comparisons with CAM-Chem over the tropics (see Figure 10 in Ordoñez et al., 2012) depict similar or larger discrepancies, and have been attributed to stronger than anticipated convective cells in the tropics. We found strong correlations and agreement to within a factor of ~2 between modeled and observed $CHBr_3$ and CH_2Br_2 (Fig. 5c-f and Fig. 6c-f). Relatively long lifetimes (≥ 1 month) in Region 1 likely enable vertical and zonal transport of $CHBr_3$ and CH_2Br_2 to the mid and upper troposphere (Fig. 5c and e). The model was biased low with respect to measurements of CH_3Br by ~25% in Region 1 and Region 2 (Fig. 5g-h and Fig. 6g-h), potentially as a result of an incorrect surface lower boundary condition. The model underpredicted the mean vertical gradient in $CHClBr_2$, although it did a reasonable job of representing the mean vertical gradient in $CHBrCl_2$, in both Region 1 and Region 2. In both cases, however, the model failed to capture the spatial variability in both $CHClBr_2$ and $CHBrCl_2$ observations (Fig. 5i-l and Fig. 6i-l). Region 2 contains stronger sources of halogenated VOCs than Region 1, which has been documented in numerous ship-based campaigns and archived in the Halocarbons in the Ocean and Atmosphere database (HalOcAt; https://halocat.geomar.de/). Region 2 also has much higher chl *a* (Fig. S4), supporting biogenic sources for these gases.

3.3 Relationships between STILT surface influence functions and observations

We used the STILT model to explore the relationships between observed mixing ratios and the upstream surface influence functions (Equations 2-3) of sea ice, chl *a*, absorption due to detritus, and downward shortwave radiation at the surface, which relate to various regional hypothesized sources of halogenated VOCs such as marine phytoplankton, phytoplankton in sea ice brines, and decomposing organic matter in surface seawater (e.g. Moore and Zafiriou 1994; Moore et al., 1996; Tokarczyk and Moore 1994; Sturges et al., 1992).

We found no positive relationships between upstream sea-ice influence and any measured halogenated VOC Region 1 (Fig. 7). We interpret this result to mean that increased summertime sea ice acts either to reduce the production of halogenated VOCs by blocking sunlight or as a physical barrier to oceanic emissions of halogenated VOCs from under-ice algae. Both of these mechanisms are also consistent with a link between enhanced $CHBr_3$ and CH_2Br_2 emissions due to sea-ice retreat and surface sea-ice melt water (Carpenter et al., 2007).

In other studies, it has also been proposed that sea ice could be an important source for $CHBr_3$ and other halogenated VOCs, since high mixing ratios of $CHBr_3$ have been observed at the sea-ice and ice-snow interface in the austral winter (Abrahamsson et al., 2018) and in under-ice algae in the austral spring (Sturges et al., 1993). At present, CAM-Chem v1.2 with very short-lived halogen chemistry does not include a regional flux of halogenated VOCs over sea-ice covered waters in summer, and our results do not indicate a need to include one. Our data, which were

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collected in January and February, however, cannot assess the importance of sea ice as a source of halogenated VOCs in other seasons, such as winter or spring (Abrahamsson et al., 2018; Sturges et al., 1993). More field campaigns are needed to further study the seasonality and regional strength of sea ice related halogenated VOC emissions.

We observed a statistically significant positive correlation between the surface influence function of 8-day satellite composites of chl *a* concentration, which is widely used as a proxy for near-surface phytoplankton biomass, and mixing ratios of $CHBr_3$ and CH_2Br_2 in Region 1 (Fig. 8a, b). This finding corroborates previous findings from ship-borne field campaigns and laboratory studies that have suggested a biogenic source for these two bromocarbons (e.g., Moore et al., 1996; Hughes et al., 2013), and further substantiates the current CAM-Chem parameterization of regional bromocarbon emissions using satellite retrievals of chl *a* in polar regions. CH_3Br mixing ratios were not significantly correlated with chl *a* surface influence functions (Fig. 8c). Although potentially suggesting that marine phytoplankton and microalgae were not a strong regional source of CH_3Br during ORCAS, it is also possible that the relatively long lifetime of CH_3Br precludes a definitive analysis of its origin based on chl *a* using 7-day back-trajectories. Neither $CHClBr_2$ nor $CHBrCl_2$ were significantly correlated with chl *a* composite surface influence functions (data not shown); however, more observations of these short-lived species in the remote MBL are needed to substantiate this result.

Similar to Lai et al. (2011), we observed a significant correlation between mixing ratios of CH_3I and total weekly upstream influence functions of 8-day chl *a* composites (Fig. 8d). Weaker correlations were observed with upstream influence functions on shorter timescales than seven days. We found that CH_3I, particularly in Region 1, was better explained by a multi-linear regression with two predictors: 1) the influence function of downward shortwave radiation at the surface (Fig. 9a) and 2) the absorption of light due to detrital material (Fig. 9b), yielding improved agreement between predicted and observed CH_3I (Fig. 9c). Several previous studies have correlated mixing ratios of CH_3I to satellite retrievals of PAR and surface ocean temperature, revealing a link to solar radiation (e.g. Happell et al., 1996; Yokouchi et al., 2001).

Although certain species of phytoplankton are capable of producing CH_3I (e.g. Manley and de la Cuesta 1997; Hughes et al., 2011), several studies also indicate a non-biological source for CH_3I in the surface ocean. This non-biological source, though not fully understood, requires light, a humic like substance at the surface ocean supplying a carbon source and methyl group, and reactive iodine (Moore and Zarifou 1994; Richter and Wallace 2004). Thus far, two chemical mechanisms have been proposed for the non-biological production of methyl iodide, one – a radical recombination of a methyl group and iodine involving UV photolysis (e.g. Moore and Zarifou 1994), and two, a substitution reaction involving the reduction of an oxidant, such as iron III (e.g. Williams et al. 2007).

3.4 Flux estimation

3.4.1 O_2-based emission estimates

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We present a novel approach that facilitates a basin-wide halogenated VOC flux estimate using the robust relationship between airborne observations of O_2 and halogenated VOCs combined with modeled O_2 fluxes. Unlike the existing CAM-Chem halogenated VOC biogenic flux parameterization, this method does not rely on weekly retrievals of chl *a* at high latitudes, which are often patchy. In addition, our study indicates that $CHBr_3$, CH_2Br_2, and $CHClBr_2$ and CH_3I are better correlated with marine derived O_2 than the upstream influence of chl *a*.

For $CHBr_3$, CH_2Br_2, and $CHClBr_2$ we construct ocean emission inventories for January and February using a scaled version of gridded modeled air-sea O_2 fluxes and the slopes (i.e. molar ratios) of linear correlations between $\delta(O_2/N_2)$ and halogenated VOC mixing ratios (Fig. 10). O_2 fluxes were obtained from simulations using a configuration of the CESM model nudged to reanalysis temperatures and winds as described in Stephens et al. (2018). An earlier free running version of CESM was one of the best evaluated for reproducing the seasonal cycle of $\delta(O_2/N_2)$ over the Southern Ocean (Nevinson et al., 2015; 2016). To date, the north-south gradient in atmospheric O_2 has not been well reproduced by any models (Resplandy et al., 2016). Vertical gradients in O_2 on ORCAS indicate that CESM overestimated gradients by 47% on average; accordingly, O_2 fluxes were adjusted downward by 47% to better match the observations. This is obviously a very simple adjustment to the modeled fluxes, and the actual air-sea O_2 flux biases in CESM likely have a great deal of spatial and temporal heterogeneity. We calculated an uncertainty for the CESM flux using a second, independent estimate of O_2 fluxes based on dissolved O_2 measurements in surface seawater. The Garcia and Keeling (2001) climatology has much smoother temporal and spatial patterns than CESM flux estimates but also results in overestimated atmospheric O_2 spatial gradients. We calculate the relative uncertainty in O_2 flux as the ratio of the mean absolute difference between gridded Garcia and Keeling values (2001; also adjusted down by 51 % everywhere to better match ORCAS observations) to the CESM model flux estimates in Regions 1 and 2 (adjusted down by 47% everywhere). These disagreements were 7.3 % and 3.4 % for Regions 1 and 2, respectively. Based on the ratios of halogenated VOC to O_2 mixing ratios in bivariate least squares regressions and these adjusted O_2 fluxes, we estimate mean emissions of $CHBr_3$ and CH_2Br_2 in Region 1 and Region 2. Relative uncertainty in the slopes (i.e., the standard deviation of the slopes) from these regressions and the mean relative uncertainties in regional O_2 fluxes were added in quadrature to yield uncertainties in calculated halogenated VOC emission rates.

Figure 10 shows the mean emissions for Jan. and Feb. of $CHBr_3$, CH_2Br_2, and $CHClBr_2$ in Region 1 and Region 2. Mean regional emissions of $CHBr_3$ and CH_2Br_2 and $CHClBr_2$ are 91 ± 8, 31 ± 17, and 11 ± 4 pmol m^{-2} hr^{-1} in Region 1 and 329 ± 23, 69 ± 5, and 24 ± 5 pmol m^{-2} hr^{-1} in Region 2 (Table 1). The mean flux of CH_3I in Region 2 is 392 ± 32 (Table 1). Table 1 also lists the mean Jan. and Feb. CAM-Chem emissions from Region 1 and Region 2, as well as emissions from several other observational and modeling Antarctic polar studies. Our estimates fall within the range of these other studies, which span every month of the year and whose estimated fluxes range from negative (i.e. from the atmosphere into the ocean) to 3500 pmol m^{-2} hr^{-1} $CHBr_3$ in a coastal bay during its peak in primary production. CAM-Chem emissions for all species are

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significantly lower than our observationally derived values in Region 1, with the exception of CH_3I. Conversely, CAM-Chem emissions are significantly higher than our estimated emissions in Region 2, with the exception of $CHClBr_2$ in Region 1, which remains underpredicted by the model (Table 1). We note that in Region 2, CAM-Chem fluxes of $CHBr_3$ and CH_2Br_2, although still significantly different, are more similar to our estimated fluxes.

3.4.2 STILT-based emission estimates

Similar to our O_2-based emission estimates, we used the relationship between surface influence functions and CH_3I mixing ratios (Fig. 9) to predict a flux field in Region 1 (Fig. 11). We used a multiple linear regression (± 1standard deviations; Equation 2), where Hs_1 and Hs_2 are the downward shortwave radiation and detrital absorption surface influence functions, respectively, with an intercept b = 0.19 ± 0.01, and influence coefficients a_1 = 3.7E-5 ± 1.3E-5, a_2 = 3.5± 0.74, and an interaction term with the coefficient a_3 = -5.2E-4 ± 1.5E-4 (Fig.9c). These regression coefficients and interaction term were used to estimate an average non-biological flux of CH_3I (Fig. 11; Table 1). This method could be used in place of the current Bell et al. (2002) climatology to update near weekly (~8 day) emissions of CH_3I in future versions of CAM-Chem. Our estimated mean CH_3I flux in Region 1 (35 ± 29 pmol m^{-2} hr^{-1}) is significantly lower than the current CAM-Chem estimated emissions (Table 1). As noted in Sect. 3.2, our observations of CH_3I are also much lower than the modeled mixing ratios. As discussed above, the strong correlations between CH_3I and O_2 in Region 2 also suggest a dominant biological source for this compound in this region. As a result, we have not used this relationship to parameterize a flux for CH_3I in Region 2 (see Sect. 3.1.2 and 3.4.1 for details). We note that although it would be possible to provide STILT-based emission estimates for other halogenated VOCs (e.g. $CHBr_3$ and CH_2Br_2), the correlations these compounds were less strong with surface influence functions than those with O_2/N_2.

4 Conclusions

Our work combined TOGA and AWAS halogenated VOC airborne observations from the ORCAS and ATom-2 campaigns, with coincident measurements of O_2 and CO_2, geophysical datasets and numerical models, including the global atmospheric chemistry model CAM-Chem, and the Lagrangian transport model, STILT. We evaluated model predictions, calculated molar enrichment ratios, inferred regional sources, and provided novel means of parameterizing ocean fluxes. We found that the Southern Ocean MBL is enriched in halogenated VOCs, but that these MBL enhancements are less pronounced at higher latitudes, i.e., poleward of 60° S (Region 1) than over the productive Patagonian shelf (Region 2). Overall, our results indicated that the Southern Ocean is a moderate regional sources of $CHBr_3$, CH_2Br_2, and CH_3I, and a weak source of $CHClBr_2$ and $CHBrCl_2$ in January and February. Good model-measurement correlations were obtained between our observations and simulations from the Community Earth System Model (CESM) atmospheric component with chemistry (CAM-Chem) for $CHBr_3$, CH_2Br_2, CH_3I, and $CHClBr_2$ but all showed significant differences in model:measurement ratios. The

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model:measurement comparison for CH_3Br was satisfactory and for $CHBrCl_2$ the low levels present precluded us from making a complete assessment.

$CHBr_3$ and CH_2Br_2 exhibited strong and robust correlations with each other and with O_2 and weaker but statistically significant correlations with the influence of chl *a*, which is a proxy for phytoplankton biomass. $CHClBr_2$ and $CHBr_3$ were well correlated with one another, particularly in Region 2. Together, these correlations suggested a biological source for these gases over the Southern Ocean. We found that CH_3I mixing ratios in Region 1 were best correlated with a non-biological surface influence function, although biogenic CH_3I emissions appear important in Region 2.

Our flux estimates based on the relationship of halogenated VOC mixing ratios to O_2 and remotely sensed parameters (for CH_3I) were compared with those derived from global models and ship-based studies (Table 1). Our emission estimates of $CHBr_3$, CH_2Br_2, and $CHClBr_2$ are significantly higher than CAM-Chem's globally prescribed emissions in Region 1, where halogenated VOC mixing ratios are under predicted (Table 1; Fig. 5). Similarly, our estimate of $CHClBr_2$ emissions is also significantly higher than CAM-Chem's in Region 2, where $CHClBr_2$ mixing ratios remained underpredicted. Yet, to the best of our knowledge, CAM-Chem's global parameterization of halogenated VOC fluxes has not been compared with data at high latitudes. Indeed, our emission estimates of $CHBr_3$, CH_2Br_2, CH_3I fall within a range of CAM-Chem's esimtates (on the low end) and most prior estimates based on either other models or localized studies using seawater-side measurements from the Antarctic polar region in summer (on the high end). In the case of CH_3I, our estimated emissions suggest that the prescribed emissions in CAM-Chem may be too high in Region 1 and Region 2. Our parameterizations of the CH_3I flux could be used to explore inter-annual variability in emissions, which is not captured by the Bell et al. (2002) CH_3I climatology currently employed in CAM-Chem.

To extend these relationships to year-round and global parameterizations for use in global climate models, they must be studied using airborne observations in other seasons and regions. These approaches may help parameterize emissions of new species that can be correlated with surface influence functions or the biological production of oxygen or may improve existing emissions, where persistent biases exist. Finally, future airborne observations of halogenated VOCs have the potential to further improve our understanding of air-sea flux rates and their drivers for these chemically and climatically important gases over the Southern Ocean.

Data Availability. The ORCAS and ATom-2 datasets are publically available at https://doi.org/10.5065/D6SB445X ; (www.eol.ucar.edu/field_projects/orcas) and https://doi.org/10.3334/ORNLDAAC/1581

Author Contributions. EA is responsible for the bulk of the conceptualization, formal analysis, writing, review, and editing with contributions from all authors. BBS and ECA were instrumental in the investigation and supervision related to this manuscript. RSH contributed to the conceptualization, as well as the investigation and halogenated VOC data curation for this project. BBS, EJM, and RFK were responsible for the data curation of $\delta(O_2/N_2)$ data and contributed to formal analysis involving these data. MSHM along with EAK were responsible for STILT data curation and formal analysis, and the conceptualization and formal analysis of

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SITLT-based geostatistical influence functions and flux estimates were also informed by these two. DK, along with ST, JFL and ASL were responsible for constructing CAM halogenated VOC emissions and conducting CAM runs. MCL was responsible for CESM simulations yielding O_2 fluxes and comparing this product alongside the Garcia and Keeling O_2 climatology in CAM. KMC and CM were responsible for the data curation of CO_2 observations. AJH contributed to the investigation for halogenated VOC data.

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Tables

Table 1. Mean ± uncertainty (see Sect. 3.4.1 and 3.4.2 for details) halogenated VOC emission estimates (pmol m^{-2} hr^{-1}) in Region 1 and Region 2 calculated in this study (with method indicated below each value), from CAM-Chem (Ordoñez et al., 2012) and from several other modeling and ship-based observational studies.

Region/Months	$CHBr_3$	CH_2Br_2	CH_3I	$CHClBr_2$	Reference
Region 1 (JF) < 60° S	91 ± 8 O_2 Regr.	31 ± 18 O_2 Regr.	35 ± 29 MLR	11 ± 4 O_2 Regr.	This Study
Region 2 (JF) >55° S and <40° S	329 ± 23 O_2 Regr.	69 ± 5 O_2 Regr.	392 ±32 O_2 Regr.	25 ± 5 O_2 Regr.	This Study
Region 1 (JF)	10	1.9	120	0.38	CAM-Chem
Region 2 (JF)	360	44	800	8.7	CAM-Chem
Southern Ocean (≥50°S), (DJ)	200	200	200	----------	Ziska et al. 2013 (model)
Marguerite Bay (DJF)	3500	875	----------	----------	Hughes et al. 2009 (obs)
70°S-72°S Antarctica	1300	----------	----------	----------	Carpenter et al. 2007 (obs)
Southern Ocean (≥50°S) (Feb. - April)	225	312	708	----------	Butler et al. 2007 (obs)
40°S-52°S S. Atlantic (Sept.-Feb.)	-1670	----------	250	----------	Chuck et al. 2005
Southern Ocean (≥50°S), (DJ)	-330	----------	----------	----------	Mattson et al. 2013 (model)

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Figures

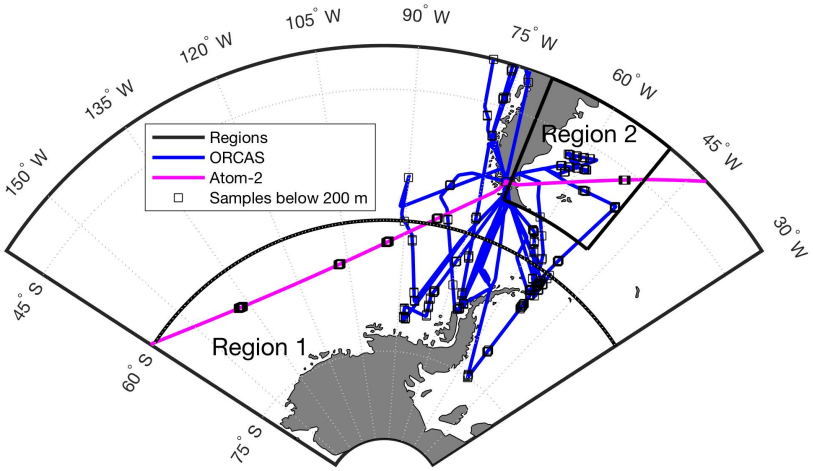

Figure 1. Overview map ORCAS and ATom-2 flight tracks in the study regions: 1) high latitudes in the Southern Hemisphere poleward 60° S and 2) the Patagonian Shelf. The ORCAS and ATom-2 aircraft flights and dips below 200 m that took place within these regions are also shown.

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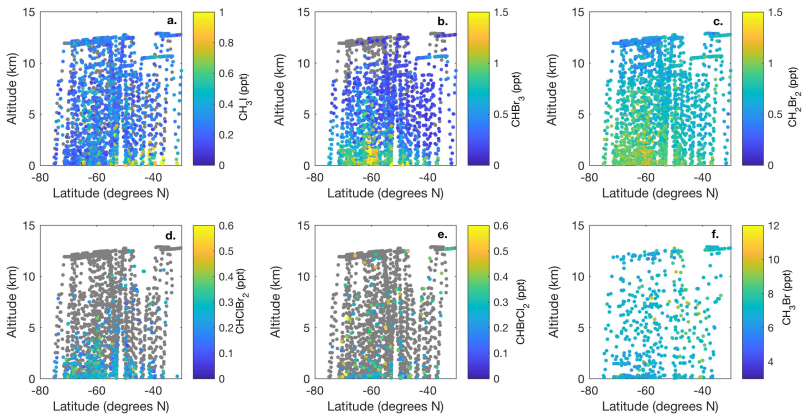

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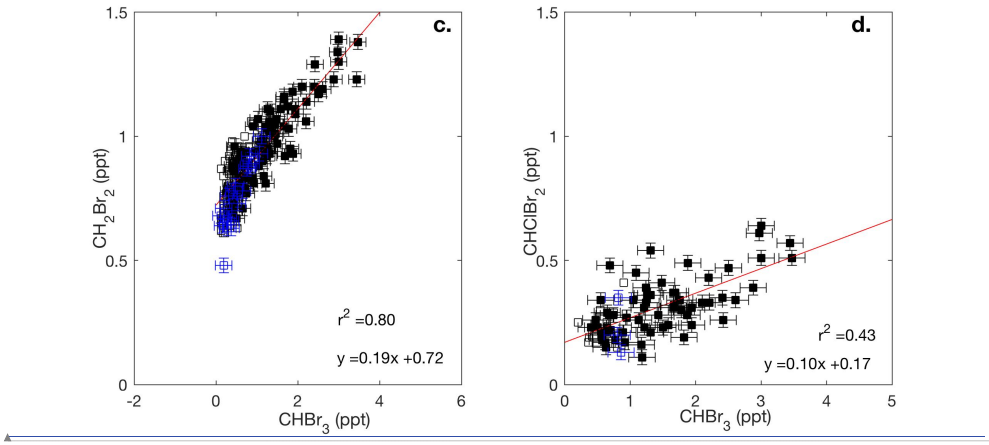
Figure 2. Meridional-altitudinal cross-sections of mixing ratios of a) CH_3I , b) $CHBr_3$, c) CH_2Br_2, d) $CHClBr_2$, and e) $CHBrCl_2$ from the TOGA and mixing ratios of f) CH_3Br from AWAS and WAS in 2016 and 2017, respectively, during the ORCAS and ATom-2 campaigns over the Southern Ocean in the austral summer. Note the different color bar scales. Gray points denote measurements below the detection limit of each species (CH_3I - 0.03 ppt, $CHBr_3$ – 0.2 ppt, CH_2Br_2 – 0.03 ppt, $CHClBr_2$ – 0.03 ppt, $CHBrCl_2$ – 0.05 ppt, CH_3Br – 0.2 ppt).



c.
d.
CH_2Br_2 (ppt)
$CHClBr_2$ (ppt)
$CHBr_3$ (ppt)
r^2 =0.80
y =0.19x +0.72
r^2 =0.43
y =0.10x +0.17

Figure 3. Mixing ratios of $CHBr_3$ vs. CH_2Br_2 and $CHClBr_2$ across the ORCAS and ATom-2 campaigns in Region 1 (Fig.3a,b) and in (Fig.3c,d), respectively. Type II major axis regression model (bivariate least squares regressions) are based on ORCAS data below 2 km and illustrate regional enhancement ratios. Error bars represent the uncertainty in halogenated VOC measurements.

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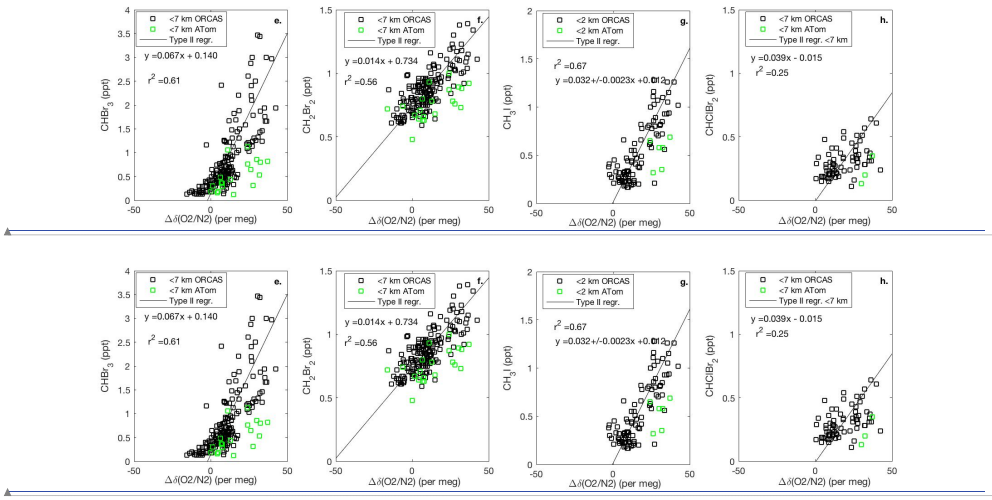

Figure 4. Mixing ratios of $CHBr_3$, CH_2Br_2, and CH_3I vs. O_2 on ORCAS and ATom-2 in Region 1, poleward of 60° S (a-d) and Region 2 over the Patagonian Shelf (e-h). Slopes ± standard errors from type II major axis regression model (bivariate least squares regression) fits of ORCAS data for regressions with $r^2 > 0.2$ (fits were calculated on variables scaled to their full range). The slopes reported in the figure are converted to pmol:mol ratios prior to estimating biogenic halogenated VOC fluxes based on modeled CESM O_2 fluxes. Data from above 7 km were excluded due to the influence of air masses transported from further north.

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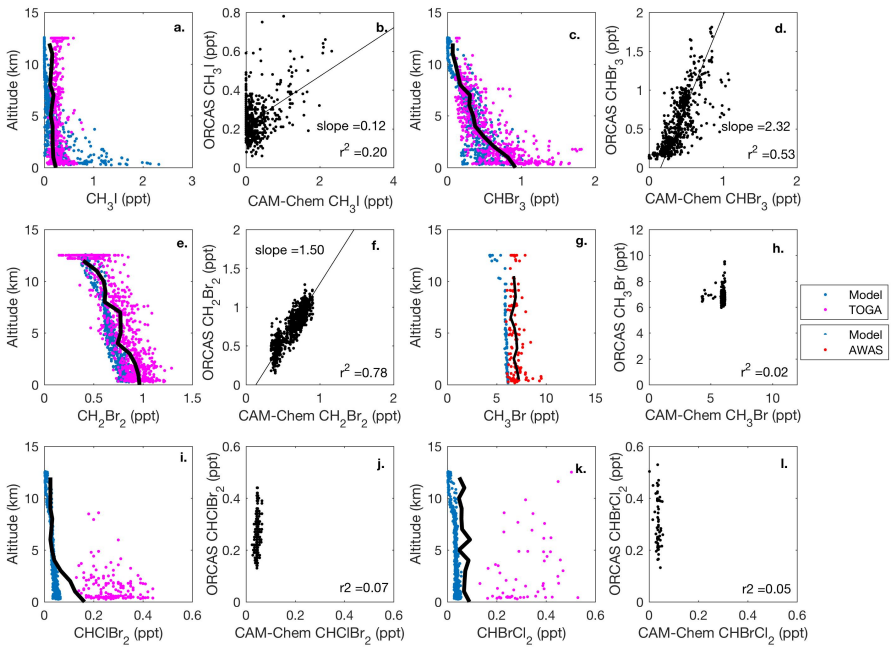

Fig 5. CAM-Chem1.2 model-aircraft measurement comparison during the ORCAS campaign between 1-12 km in Region 1, high latitudes in the Southern Hemisphere poleward 60° S. All regressions are type II major axis regression models bivariate least squares regressions (slopes are shown when the $r^2 \geq 0.2$). The bold, black line in each vertical profile represents the binned (mean) mixing ratio of halogenated VOC measurements at that altitude. The binned mean includes measurements below the detection limit (DL), which for this calculation are assigned a value equal to the DL multiplied by the percentage of data below detection. Modeled values include locations where observations were below the DL.

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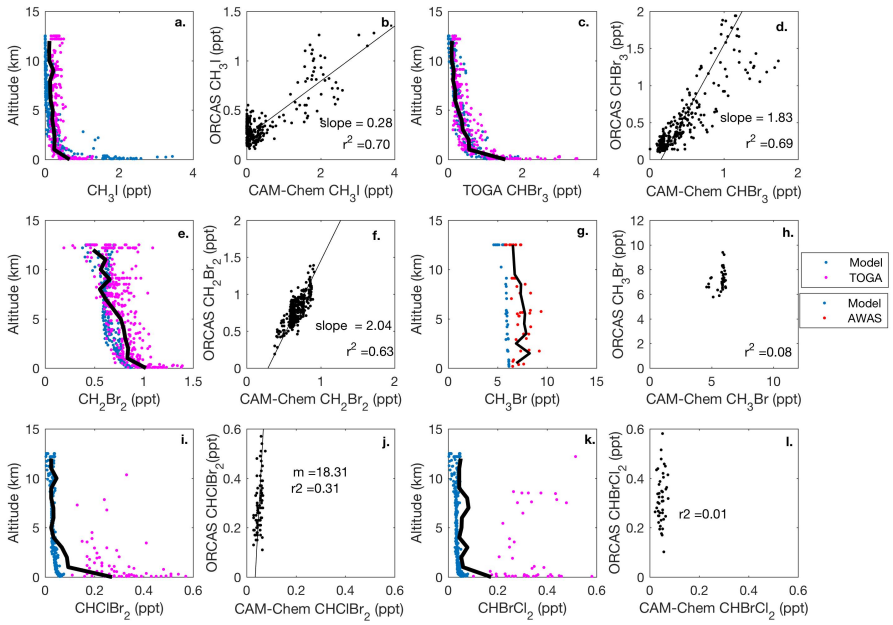

Figure 6. CAM-Chem 1.2 model-aircraft measurement (TOGA and AWAS) comparison during ORCAS campaign between 1-12 km in Region 2, the Patagonian Shelf. All regressions are type II major axis regression models bivariate least squares regressions (slopes are shown when the r^2 ≥ 0.2). The bold, black line in each vertical profile represents the binned (mean) mixing ratio of halogenated VOC measurements at that altitude. Again, the binned mean includes measurements below the detection limit (DL), which for this calculation are assigned a value equal to the DL multiplied by the percentage of data below detection. Modeled values include locations where observations were below the DL.

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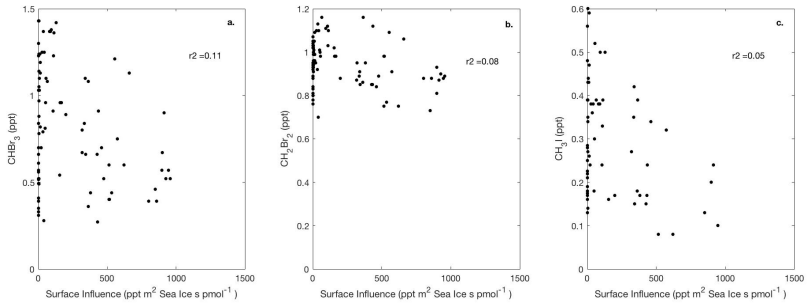

Figure 7. Linear type II regressions between influence functions convolved with sea ice distributions, which exclude land ice, and mixing ratios for $CHBr_3$, CH_2Br_2, and CH_3I in Region 1, poleward of 60° S. Surface influence (ppt m^2 s $pmol^{-1}$) in each grid cell was multiplied by fractional sea ice concentration surface field, which is unit-less, yielding sea ice surface influence function units of ppt m^2 s $pmol^{-1}$, as shown on the x-axis. Linear regression lines are not shown, as $p \geq 0.001$.

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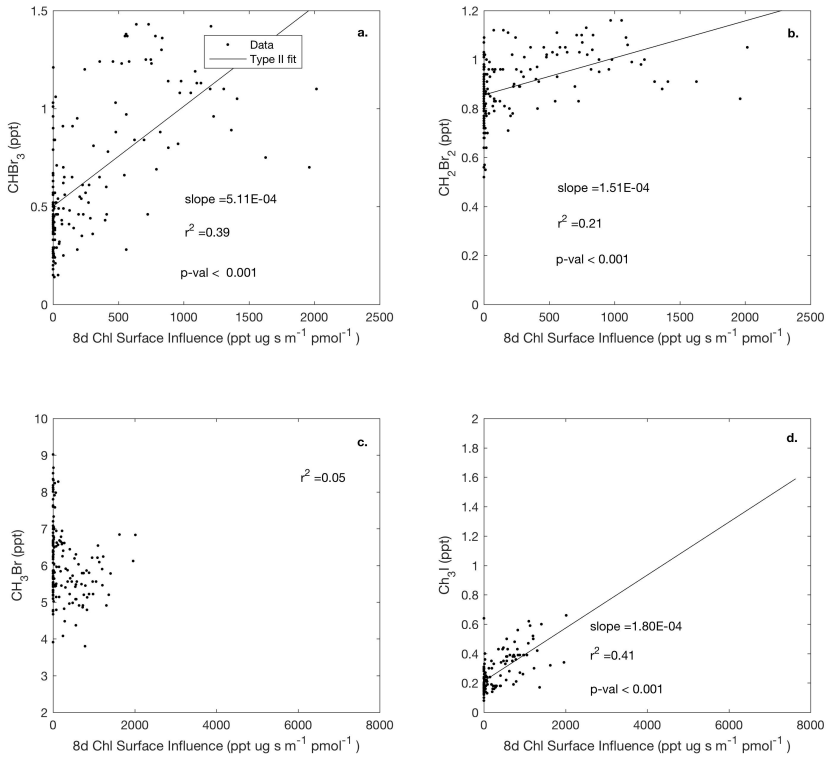

Figure 8. Linear type II regressions between influence functions of eight day composites of chl *a* and mixing ratios of halogenated VOCs (a-d) poleward of 60° S (Region 1). Surface influence (ppt m^2 s $pmol^{-1}$) in each grid cell was multiplied by the chl *a* (µg m^{-3}) surface field, resulting in surface influence function units of µg ppt s $pmol^{-1}$ m^{-1}, shown on the x-axis. Linear regression lines are shown where when $p < 0.001$.

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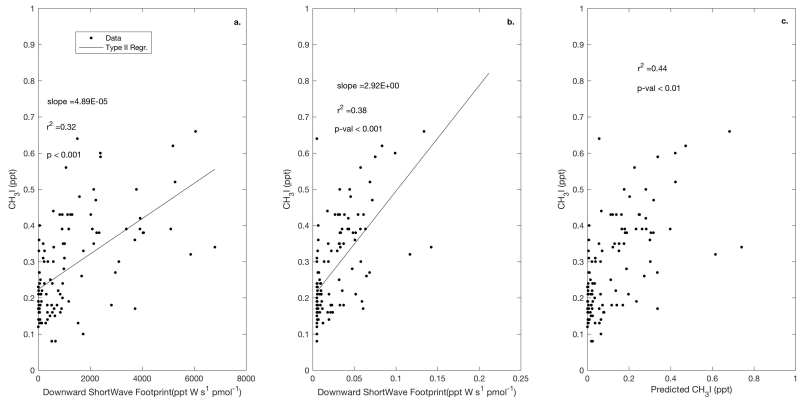

Figure 9. Observed CH_3I plotted against the surface influence functions of downward shortwave radiation (a) and absorption due to detritus (b). Predicted mixing ratios of CH_3I based on a multiple linear regressions (MLR) using these two predictors in Region 1 are shown in Fig. 9c according to Equation 3. Surface influence (ppt m^2 s $pmol^{-1}$) in each grid cell was multiplied by the surface source field, such as shortwave radiation at the surface (W m^{-2}), yielding units of ppt Ws $pmol^{-1}$, and the surface ocean's detrital absorption (m^{-1}), yielding units of ppt m s $pmol^{-1}$, shown on the x-axes.

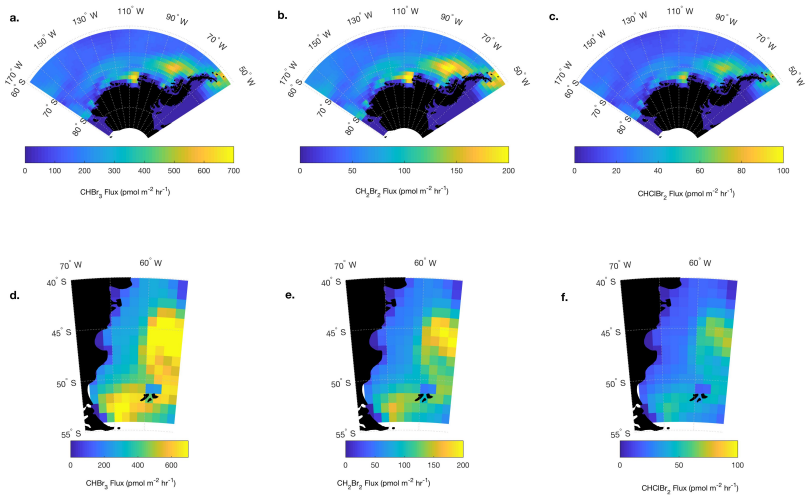

Figure 10. Resulting mean Jan. – Feb. 2016 O_2-based (parameterized) $CHBr_3$ and CH_2Br_2 and $CHClBr_2$ fluxes (pmol m^{-2} s^{-1}) in Region 1 (a-c) poleward of 60° S and Region 2 (d-f) over the Patagonian Shelf. CESM modeled O_2 fluxes are scaled by the slope between the oceanic contribution to $\delta(O_2/N_2)$ and $CHBr_3$ and CH_2Br_2, and $CHClBr_2$ reported in Fig. 4. Note that these fluxes represent mean estimated biogenic fluxes in Jan. -Feb. 2016 (see Sect. 3.4.1 for details).

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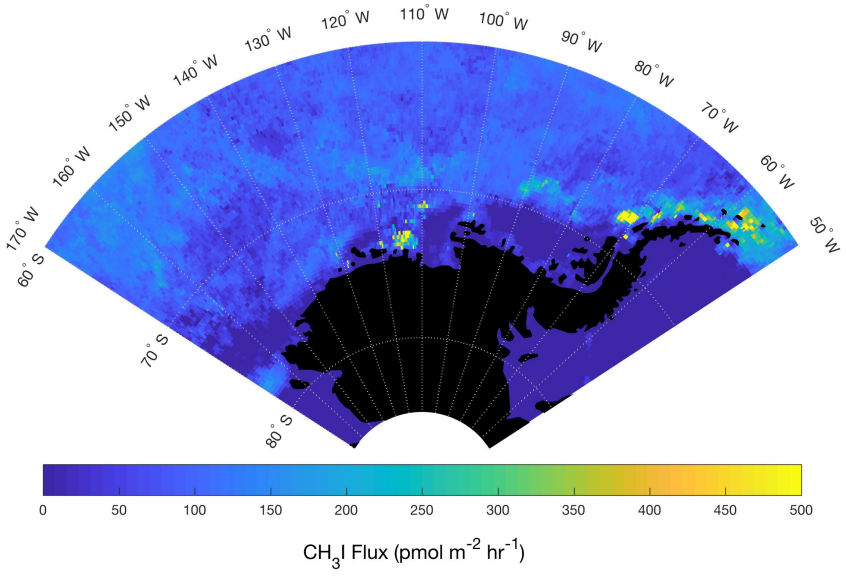

Figure 11. Mean estimated CH_3I fluxes for Jan. – Feb. The multilinear regression in Fig. 9 between CH_3I mixing ratios and geophysical influence functions related to shortwave radiation and detrital material at the sea surface was used to derive a mean flux field in Jan.-Feb., 2016 for Region 1.

Supplementary Text

Sea air exchange calculations

To support the interpretation of our results, we calculate nominal equilibration times. For estimates of bulk sea air equilibration times for halogenated VOCs, O_2, and CO_2, we assume a mixed layer depth of 30 m, a temperature of 0° C, a salinity of 35 PSU, and carbonate buffering according to eq. 8.3.10 in Sarmiento and Gruber (2006), and transfer velocities according to Nightingale et al., (2000). The Schmidt number (i.e. the ratio of the kinematic viscocity of a gas, divided by the molecular diffusivity) for O_2, CO_2 and CH_3Br were calculated according to Wanninkof (2014), and the Schmidt numbers for $CHBr_3$ and CH_3I were calculated according to Quack and Wallace (2003) and Moore and Groszko (1999), respectively. The results are provided in Sect. 3.1.2.

Comparisons of TOGA, WAS and PFP

Despite overall good agreement between co-located inflight AWAS, WAS, and PFP samples and TOGA measurements, we observed notable discrepancies in several cases (e.g. Fig. S1b; Fig. S2a-b). On ORCAS, we observed a non-linear relationship between inflight TOGA measurements and co-located AWAS samples of CH_3I (Fig. S1b), driven by a few samples with high mixing ratios. Close inspection of upwind and downwind flights over Region 2 with the campaign's high mixing ratios of CH_3I indicated that TOGA measurements were consistent with a modest flux of CH_3I from the ocean to the atmosphere. On ATom-2, TOGA measurements agreed better with co-located PFP samples than with co-located WAS samples; and differences on the sixth and seventh research flights (i.e. the data used here) were relatively small. Nevertheless these differences motivated an instrument inter-comparison following the ATom campaign between these instruments. Thus far, results of this inter-comparison show that TOGA and PFP measurements differ by < 25%.

Supplementary Tables

Table S1. The TOGA-PFP instrument comparison was done by sampling a 50L SS pontoon, created at NCAR from a humidified dilution of the TOGA ATom standard. Data were analyzed and reported by Rebecca Hornbrook (NCAR, TOGA) and Steve Montzka (NOAA, PFP).

Pontoon Inter-comparison	Concentration (dilution-based calc.)	TOGA (10/12/2018)	PFP (10/24/2018)
$CHBr_3$	34	21.0 ± 0.1	26.6 ± 0.8
$CHClBr_2$	26	19.9 ± 1.0	22.9 ±0.1
CH_2Br_2	52	47.7 ± 0.2	51.7 ± 2.0

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Supplementary Figures

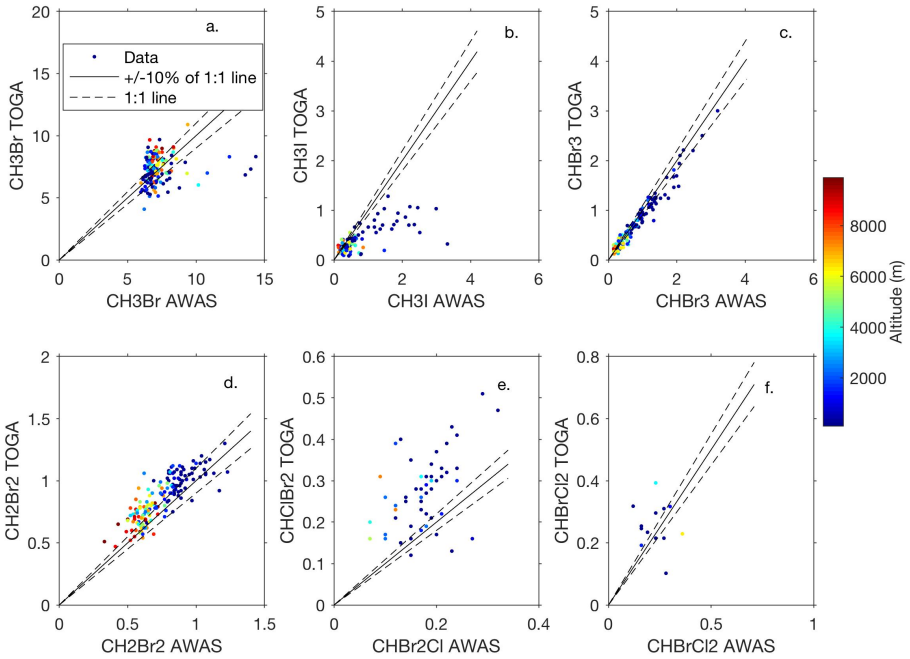

Figure S1. Comparison between AWAS samples and TOGA measurements during ORCAS below 10 km, when these two shared over half their sampling period Points are colored by altitude. Dashed lines represent ± 10% of the 1:1 line. Sample points below the DL are not included in this quantitative comparison.

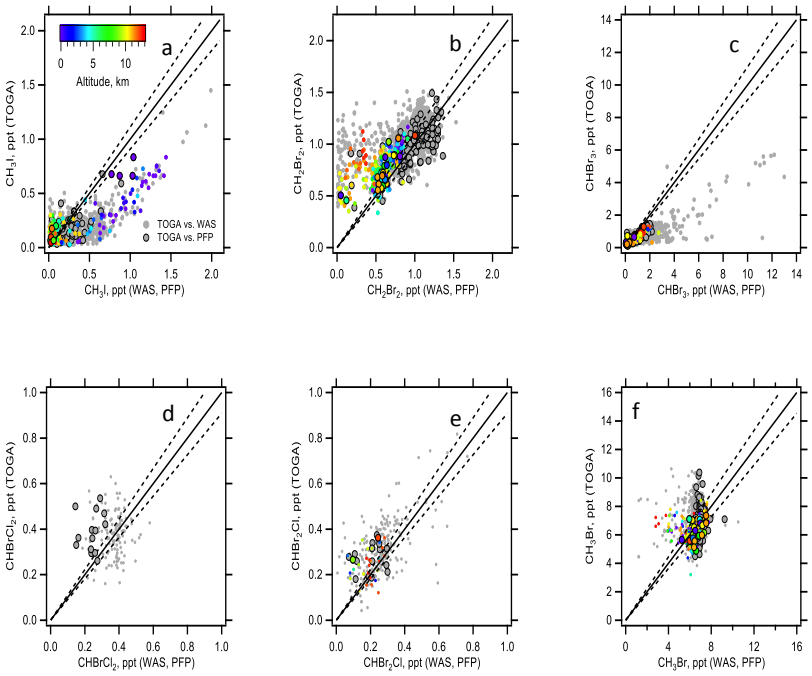

Figure S2. Comparison between WAS, PFP and TOGA measurements during ATom-2 below 10 km, when these instruments shared over half their sampling period. WAS measurements are shown in larger circles, PFP measurements in smaller circles, and measurements from the research flights six and seven used in this analysis are shown in color, while measurements on other research flights in ATom-2 are shown in gray. Dashed lines represent ± 10% of the 1:1 line. Sample points below the DL are not shown.

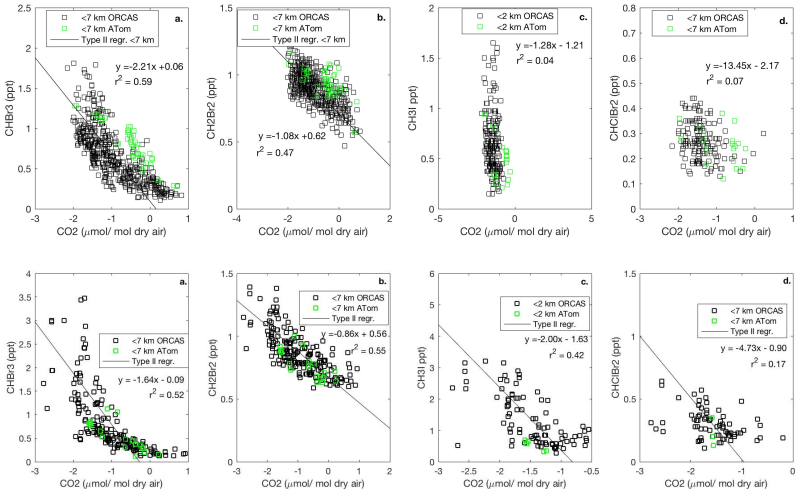

Figure S3. Mixing ratios of $CHBr_3$, CH_2Br_2 and CH_3I vs. CO_2 in Region 1 (a-c) and Region 2 (d-f). Type II major axis regression model (bivariate least squares regression) fits are shown for combined ORCAS and ATom-2 data, using data below 7 km for $CHBr_3$, CH_2Br_2, and below 2 km for CH_3I.

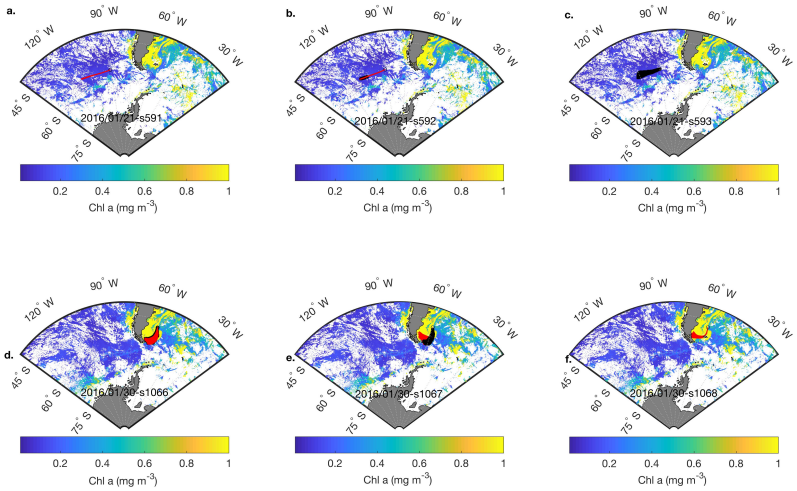

Figure S4. Two sets of three consecutive TOGA VOC sample locations, their back-trajectories and surface influences in the lower troposphere on two different flights (a-c; Jan. 21,2016, and d-f; Jan. 30, 2016). For illustrative purposes, sampling locations are denoted by a black circle, 24-hour back trajectories are shown in red, and surface influences are shown with black squares in each subpanel, overlying weekly composites of remotely sensed chl *a*. Surface influence is multiplied by the underlying chl *a* (or other) surface field and averaged for each sample to yield a surface influence function.