Using airborne observations to improve estimates of short-lived halocarbon emissions during summer from Southern Ocean

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Abstract.

We present observations of CHBr$_3$, CH$_2$Br$_2$, CH$_3$I, CHClBr$_2$, and CHBrCl$_2$ from the Trace Gas Organic Analyzer (TOGA) during the O$_2$/N$_2$ Ratio and CO$_2$ Airborne Southern Ocean (ORCAS) study and the 2$^{nd}$ Atmospheric Tomography mission (ATom-2), in January and February of 2016 and 2017. We also use CH$_3$Br from the University of Miami Advanced Whole Air Sampler (AWAS) on ORCAS and from the UC Irvine Whole Air Sampler (WAS) on ATom-2. We compare our observations with simulations from the Community Atmosphere Model with Chemistry (CAM-Chem). We report regional enrichment ratios of CHBr$_3$ and CH$_2$Br$_2$ to O$_2$ of 0.19 ± 0.01, and 0.07 ± 0.004 pmol : mol, poleward of 60° S between 180° W and 55° W, and of 0.32 ± 0.02, 0.07 ± 0.004 pmol : mol over the Patagonian Shelf, between 40° S and 55° S and between 70° W and 55° W where we also report enrichment ratios of CH$_3$I to O$_2$ of 0.38 ± 0.03 pmol : mol and of CH$_2$ClBr$_2$ to O$_2$ of 0.19 ± 0.04 pmol : mol. Using the Stochastic Time-Inverted Lagrangian Transport (STILT) particle dispersion model, we use correlations between halogenated hydrocarbon mixing ratios and the upwind influences of chlorophyll $a$, sea ice, solar radiation, and dissolved organic material to investigate previously hypothesized sources of halogenated volatile organic compounds (HVOCs) in the southern high latitudes. Our results are consistent with a biogenic regional source of CHBr$_3$, and both non-biological and biological sources of CH$_3$I over these regions, but do not corroborate a regional sea-ice source of HVOCs in January and February. Based on these relationships, we estimate the average two-month (Jan.-Feb.) emissions poleward of 60° S between 180° W and 55° W of CHBr$_3$, CH$_2$Br$_2$, CH$_3$I, and CHClBr$_2$ to be 91 ± 8, 31 ± 17, 35 ± 29, and 11 ± 4 pmol m$^{-2}$ hr$^{-1}$, and regional emissions of these gases over the Patagonian Shelf to be 329 ± 23, 69 ± 5, 392 ± 32, 24 ± 4 pmol m$^{-2}$ hr$^{-1}$ respectively.

1 Introduction

Emissions of halogenated volatile organic compounds (HVOCs) influence regional atmospheric chemistry and global climate. Through the production of reactive halogen radicals at high latitudes, HVOCs contribute to tropospheric and stratospheric ozone destruction, and alter the sulfur, mercury, nitrogen oxide and hydrogen oxide cycles (e.g. WMO, 2011; von Glasow and Crutzen; 2007, Saiz-Lopez et al., 2007; Bloss et al., 2005; Boucher et al., 2003; Schroeder et al., 1998; Obrist et al., 2011). 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 and insufficient to affect the bromine budget in the middle and upper troposphere (Murphy et al., in review).

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$_2$Br$_2$), dibromochloromethane (CHClBr$_2$), and bromodichloromethane (CHBrCl$_2$) (Moore et al., 1996; Carpenter et al. 2003; Butler et al., 2007; Raimund et al., 2011). Other HVOCs, such as methyl iodide (CH$_3$I), and methyl bromide (CH$_3$Br) have many natural sources, such as coastal macroalgae, phytoplankton, the temperate forest soil and litter, and biomass burning (e.g., Bell et
CH$_3$I is also formed through non-biological reactions in surface seawater, and CH$_3$Br is emitted as a result of anthropogenic crop fumigation (e.g., Moore and Zafiriou; 1994, WMO 2014). 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., Manley and Dastoor 1998; Moore and Zafiriou 1994; Richter and Wallace 2004; Williams et al., 2007; Moore et al., 1996; Tokarczyk and Moore 1994; Sturges et al., 1992).

We owe our current understanding of marine HVOCs at high latitudes in the Southern Hemisphere largely 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; Hughes et al., 2013). These studies have demonstrated that the marine boundary layer (MBL) contains elevated levels of several HVOCs, and that numerous biological and non-biological sources of HVOCs exist. These studies indicate moderate ocean sources of CHBr$_3$ and CH$_3$Br$_2$ at high latitudes in the Southern Hemisphere, which 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. Yet ship-based measurements onboard these slow moving platforms also have drawbacks: they under sample the spatial variability of HVOCs (e.g., Butler et al., 2007) and require assumptions about gas-exchange rates to estimate fluxes.

Large-scale atmospheric observations of HVOCs are needed to understand the influence of atmospheric transport as well as the spatial variability of ocean sources on their distributions. At low latitudes, large-scale convection at the intertropical convergence zone carries bromocarbons and other HVOCs into the free troposphere and lower stratosphere (e.g., Liang et al., 2014; Navarro et al., 2015). In polar regions, however, vertical transport is more limited in scale. Small, convective plumes may form over the marginal sea ice zone, related to sea ice leads as well as winds from ice to open-waters (e.g. Schnell et al. 1989). To a large extent, however, polar regions are characterized by stable boundary layers in summer. Although vertical transport within and across a stable boundary layer remains poorly understood, wind shear, internal gravity waves, and frontal systems create turbulence that contributes to vertical mixing (e.g. Anderson et al. 2008). Given their extended photochemical lifetimes at high latitudes (see Sect. 2.5 for a brief discussion), zonal transport as well as vertical transport could have a large impact on vertical gradients of HVOCs.

Aircraft observations can rapidly map basin-wide vertical distributions, support quantitative air-sea flux estimates, and provide spatial constraints to atmospheric models, but rarely address the temporal variability in mixing ratios or emissions. Few constraints on HVOC mixing ratios or emissions based on airborne data exist at high latitudes in the Southern Hemisphere. Two earlier aircraft campaigns that have measured summertime HVOCs 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$_3$I in the MBL indicate a strong ocean source between 40° S and 50° S in austral summer, with mixing ratios above 1.2 nmol mol$^{-1}$ below ~1 km (Blake et al., 1999).

HVOCs are frequently incorporated into earth system climate models, using either climatologies or parameterizations based on satellite observations of chlorophyll and geographical region. This study uses airborne observations, geophysical datasets, and a Lagrangian atmospheric transport model to investigate HVOC distributions at high southern latitudes, evaluate existing parameterizations of HVOC emissions in a global atmospheric chemistry transport model, assess contributions from previously hypothesized regional sources for the Southern Ocean, and provide new means of estimating HVOC emissions based on relationships between airborne observations and modeled or remotely sensed surface parameters.

2 Observations

2.1 Overview

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 (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 NASA DC-8 aircraft passed over the eastern Pacific sector poleward of 60° S (defined here as Region 1) on the sixth research flight and over the Patagonian Shelf between 40° S and 55° S and between 70° W and 55° W (defined here as Region 2) on the seventh research flight of ATom-2 from Christchurch, New Zealand to Punta Arenas and from Punta Arenas to Ascension Island, 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.
2.2 Halogenated VOCs

During ORCAS and ATom-2 TOGA provided mixing ratios of over 60 organic compounds, including HVOCS, at background levels. The instrument, described in Apel et al. (2015), continuously collects and analyzes samples with a 35-second sampling period and repeats the cycle every two-minutes using online fast gas chromatography and mass spectrometry. HVOCs reported here have an overall ±15% relative accuracy and ±3% relative precision, and detection limits of ≤0.2 ppt for CHBr₃, CH₂Br₂, CHClBr₂, CHBrCl₂, and CH₂I. This study also leverages measurements of CH₄Br with a detection limit of 0.2 ppt 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. 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 CHBr₃, CH₂Br₂, CH₂I, and CHClBr₂, 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).

2.3 δ(O₂/N₂) and CO₂

The AO2 instrument measures variations in atmospheric O₂, which are reported as relative deviations in the oxygen to nitrogen ratio (δ(O₂/N₂)), following a dilution correction for CO₂ (Keeling et al., 1998; Stephens et al. 2018). The instrument’s precision is ±2 per meg units (one 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 O₂ perturbations that are superimposed on the background concentrations of O₂ in air (XO₂, in dry air = 0.2093). O₂ is consumed when fossil fuels are burned and produced during terrestrial photosynthesis. Seasonal changes in the ocean heat content lead to small changes in atmospheric N₂. As others have done (Keeling et al., 1998; Garcia and Keeling, 2001; Stephens et al., 2018), we isolated the air-sea O₂ signal by subtracting model estimates of the terrestrial photosynthesis, fossil-fuel combustion, and air-sea N₂ flux influences from the δ(O₂/N₂) measurement (Equation 1). The difference of the δ(O₂/N₂) measurement and these modeled values is multiplied by XO₂ to convert to ppm equivalents as needed (ppm eq; Keeling et al., 1998; Equation 1).

\[ \text{O}_2\text{-ppm-equiv} = [\delta(O_2/N_2) - \delta(O_2/N_2)_{\text{Land}} - \delta(O_2/N_2)_{\text{Fossil Fuel}} - \delta(O_2/N_2)_{\text{N}_2}] \times \text{XO}_2 \]  

We obtained the modeled δ(O₂/N₂) signal land influences from the land model component of the Community Earth System (CESM), the fossil fuel combustion influences from the Carbon Dioxide Information Analysis Center (CDIAC; Boden et al. 2017), and the air-sea N₂ influences from the oceanic component of CESM. These fluxes were all advected through the specified dynamics version of CAM, as described below in Sect. 3.1 and in Stephens et al. (2018). The XO₂ in 2016 is the Tohjima et al. (2005) value from the year 2000 adjusted for the 4 ppm yr⁻¹ or ~20 per meg yr⁻¹ decrease in O₂ between 2000 and 2016.
CO2 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., in prep., 2019). Dry-air mole fractions were calculated using empirical corrections to account for dilution and broadening effects in the laboratory before and after the campaign deployments, and in-flight calibrations were used to determine an offset correction for each flight. Corrected CO2 data have a total average uncertainty of 0.07 ppm (McKain et al. in prep., 2019). To merge them with the TOGA data, these faster O2 and CO2 measurements were arithmetically averaged over TOGA’s 35-s sampling periods (Stephens et al., 2017 and https://espo.nasa.gov/atom/content/ATom).

2.4 Observed HVOC patterns and relationships

Zonal cross-sections of HVOC 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 CHI, CHBr3, and CHClBr2, typically remain confined to the lower ~2-4 km of the atmosphere (Fig. 2a, b, and 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 CH2Br2 and CHBrCl2 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 CHBrCl2 preclude the identification of strong regional sources at this time. Meridional distributions also indicate lower latitude sources of CHI and CH2Br (≥ -50°), potentially resulting from terrestrial and anthropogenic contributions, and higher latitude sources (≤ -60°) of CHBr3, CH2Br2, and CHClBr2 (Fig. 2a-d,f).

Across our study area in both 2016 and 2017, we found that CHBr3 and CH2Br2 exhibit a consistent enhancement ratio with each other in the MBL both in Region 1 and Region 2 (Fig. 3a, c), which suggests these species may be co-emitted. Previous studies have documented co-located source regions of CHBr3 and CH2Br2 in the Southern Ocean (e.g. Hughes et al., 2009; Sturges et al., 1993), and laboratory studies indicate that phytoplankton and their associated bacteria, including a diatom species isolated from coastal waters along the Antarctic Peninsula and common to the Southern Ocean, are capable of emitting both CHBr3 and CH2Br2 (Hughes et al., 2013; Tokarczyk and Moore 1994). 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. For instance, Hughes et al. (2013) also report distinct seawater slopes between CH2Br2 to CHBr3, when chl a was increasing. Mixing ratios of CHBr3 and CHClBr2 were also correlated (Fig. 3d) in Region 2, and, a similar, weaker relationship was observed in Region 1 (Fig. 3b). CHClBr2 is a less well-studied compound than CH2Br2. Yet these consistent relationships suggest that CHBr3 and CHClBr2 may either share some of the same sources or have sources that co-vary.

2.5 Observed HVOC relationships to δ(O2/N2) and CO2
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. S4). In
Fig. 4 we present type II major axis regression fits to data between the ocean surface and the
lowest 7 km for bromocarbons with photochemical lifetimes of $\geq$ 1 month and from the lowest 2
km for CH$_4$, I with a photochemical lifetime of $\sim$ 1 week. We used a type II major axis regression
model (bivariate) to balance the influence of measurement uncertainty in HVOCs (on the y-axis)
and the 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$_3$Br$_2$ with $\delta$(O/N)$_2$, in both 2016 and 2017 and in
Region 1 and Region 2, provides support for a regional biogenic source of these two HVOCs
(Fig. 4a, b and Fig. 4d, e). The air-sea exchange of oxygen 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/N)$_2$ from thermal N$_2$ fluxes (see Equation 1, Sect. 2.3 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 $\sim$ 1 week.
CHBr$_3$ (and CH$_3$Br$_2$) is 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 HVOCs is also similar to O$_2$, although the photochemical loss of HOVCs will alter
their ratio over time.

Our observations suggest a biological source for CHBr$_3$ and CH$_3$Br$_2$ in Region 1 (Fig. 4a and Fig.
4b). In contrast to CHBr$_3$ and CH$_3$Br$_2$, we observe a weaker relationship between CH$_4$ and O$_2$ in
Region 1 (Fig. 4c), consistent with the existence of other, non-biological sources of CH$_4$ in this
region. Figure 4d-f illustrates strong relationships between all three HVOCs and O$_2$ in Region 2.
This implies that the dominant source of CH$_4$ emissions over the Patagonian shelf is biological.
The slope of the regression between CHBr$_3$ and O$_2$ also changes noticeably between Region 1
and Region 2. Molar enrichment ratios are 0.20 $\pm$ 0.01, and 0.07 $\pm$ 0.004 nmol : mol for CHBr$_3$
and CH$_3$Br$_2$ to O$_2$ in Region 1, and 0.32 $\pm$ 0.02, 0.07 $\pm$ 0.004 pmol : mol in Region 2. In Region
2, we also report enrichment ratios of CH$_4$ to O$_2$ of 0.38 $\pm$ 0.03 pmol : mol, based on the

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$_3$Br$_2$ in the lowest
7 km were negatively correlated with CO$_2$ in both years in Region 1 and Region 2 (Fig. S3a, b, d,
Interestingly, CH$_3$I 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$_3$I (see Supplement for details on calculations of bulk sea air equilibration times). For longer lived species, correlations for HVOCs to CO$_2$ have similar $r^2$-values as those for HVOCs 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 HVOC flux estimates (see Sect. 5.1 for details).

3 CAM-Chem Evaluation

3.1 CAM-Chem Model Configuration

The Community Earth System Model version 1 (CESM1), Community Atmosphere Model 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 CAM4 (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 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 FINN and MEGAN 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$_3$Br, CHBrCl, 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. The model used an existing CH$_3$I flux climatology (Bell et al., 2002), and CH$_3$Br 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.

3.2 Model-Observation comparisons
The ORCAS dataset provides an exceptional opportunity to evaluate the CAM-Chem HVOC emission scheme (Ordoñez et al., 2012) at high latitudes in the Southern Hemisphere. We compared modeled HVOC emissions 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\textsubscript{3}I remain confined to the MBL (Fig. 5a and Fig. 6a), presumably due to its relatively short photochemical lifetime. Modeled and observed CH\textsubscript{3}I 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 under predicts CH\textsubscript{3}I above the MBL, which may indicate slower observed photochemical loss than the model predicts. We found strong correlations and agreement to within a factor of ~2 between modeled and observed CHBr\textsubscript{3} and CH\textsubscript{2}Br\textsubscript{2} (Fig. 5c-f and Fig. 6c-f). Relatively long lifetimes ($\geq 1$ month) in Region 1 likely enable vertical and zonal transport of CHBr\textsubscript{3} and CH\textsubscript{2}Br\textsubscript{2} to the mid and upper troposphere (Fig. 5c and e). The model was biased low with respect to measurements of CH\textsubscript{2}Br 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 CHCIBr\textsubscript{2}, although it did a reasonable job of representing the mean vertical gradient in CHBrCl\textsubscript{2}, in both Region 1 and Region 2. In both cases, however, the model failed to capture the spatial variability in both CHCIBr\textsubscript{2} and CHBrCl\textsubscript{2} observations (Fig. 5i-l and Fig. 6i-l). Region 2 contains stronger sources of HVOCs 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.

4 Geophysical Surface Influences

4.1 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 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 functions (ppt m$^2$ s pmol$^{-1}$) at a spatial resolution of 0.25° x 0.25° for each sample point.

Uncertainty in the surface influence functions is strongly influenced by the accuracy of the underlying meteorological transport. 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 functions. 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 wind speed error will correlate with surface influence error, and thus we take 19% as an approximation of the surface influence strength uncertainty. We consider the wind direction error to evaluate the possible size of spatial errors in footprint location. We find a 1-sigma error of 14 degrees in wind speed. Given median wind speeds in this domain, this corresponds to a possible error of 260 km/day possible error.

4.2 Ancillary Data

For this study, remotely sensed and reanalysis data were used with STILT influence functions in linear and multi-linear regressions to explain observed mixing ratios of CHBr$_3$, CH$_2$Br$_2$, CH$_3$Br and CH$_3$I. These data included a combination of chl $a$, sea ice concentration, 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 influence functions.

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 $a$ (OCI algorithm) and absorption due to gelbstoff and detrital material at 443 nm and its uncertainty (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$_3$I (Moore et al., 1994). 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 influence functions. 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. 5.2).

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 influence functions because the photo-production of CH₂I 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 PAR or temperature.

4.3 Relationships between predicted influences and observations

We used STILT to explore the relationships between observed mixing ratios and the upstream geophysical 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 HVOCs such as marine phytoplankton, phytoplankton in sea ice brines, and decomposing organic matter in surface seawater (e.g. Moore and Zafirou 1994; Moore et al., 1996; Tokarczyk and Moore 1994; Sturges et al., 1992). These relationships can help evaluate the likelihood of particular HVOC sources, and in the case of statistically significant correlations may be used to derive an estimated flux field (See Sect. 5.2 for details).

We tested whether observed mixing ratios (Z) could be explained by a linear relationship in which the predictor variable is the product of the surface influence function (H) and a potential geophysical source distribution (s), such as chl a, as well as an intercept (b), a slope (a), and error term ξ (Equation 2; Fig S5). Moreover, this relationship can be generalized as a multiple linear regression with multiple surface influence functions (HS₁, HS₂,…) and slope coefficients (a₁, a₂; Equation 3), when HVOC mixing ratios may be related to multiple gridded geophysical influence functions (Hs). The multiple linear regression may also include an interaction term (HS₁HS₂) between predictor variables (e.g. HS₁ and HS₂) with a slope coefficient (a₃) to improve the fit. Statistical correlations between mixing ratios and geophysical influence functions are used to support or reject hypothesized sources. A flux (μmol m⁻² s⁻¹) may be then estimated for each grid cell based on the product of the slopes (a₁, a₂,…) and the potential source distributions (HS₁, HS₂, …). 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 source fields, added in quadrature, to estimate the uncertainty in these fluxes (see Fig. 7 and Sect. 5.2 for fractional uncertainties). We note that the uncertainty in STILT transport (see Sect. 4.1 for details) is inherently reflected in the relative uncertainty of the regression coefficients (a₁, a₂, …).

\[ Z = aHs + b + \xi \]  

(2)
We found statistically significant negative correlations between the upstream sea ice influence and both CHBr$_3$ and CH$_3$Br mixing ratios, and no positive relationships between upstream sea-ice influence and any measured HVOC, such as CH$_3$I in Region 1 (Fig. 7). 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. We interpret this result to mean that increased summertime sea ice acts either to reduce the production of HVOCs by blocking sunlight or as a physical barrier to oceanic emissions of HVOCs from under-ice algae. Both of these mechanisms are also consistent with a link between enhanced CHBr$_3$ and CH$_3$Br emissions due to sea-ice retreat. High concentrations of CHBr$_3$ have been linked to sea ice retreat and surface sea-ice melt water (Carpenter et al., 2007). We note that over-turned first year sea-ice, which can expose under-ice algae colonies to the air, likely still present a local source of CHBr$_3$, CH$_3$Br$_2$, or other HVOCs to the MBL.

In other studies, it has also been proposed that sea ice could be an important source for CHBr$_3$ and other HVOCs, since high mixing ratios of CHBr$_3$ have been observed at the sea-ice and ice-snow interface in the austral spring (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 HVOCs over sea-ice covered waters in summer, and our results do not indicate a need to include one. Our data, which were collected in January and February, however, cannot assess the importance of sea ice as a source of HVOCs 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 sea ice related HVOC emissions.

We observed a statistically significant positive correlation between the footprints of 8-day satellite composites of the chl $a$ concentration, which is widely used as a proxy for near-surface phytoplankton biomass, and mixing ratios of CHBr$_3$ and CH$_3$Br$_2$ in Region 1 (Fig. 8a and Fig. 8b). 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$_3$Br mixing ratios were not significantly correlated with chl $a$ footprints (Fig. 8c). Although potentially suggesting that marine phytoplankton and microalgae were not a strong regional source of CH$_3$Br during ORCAS, it is also possible that the relatively long lifetime of CH$_3$Br precludes a definitive analysis of its origin based on chl $a$ using 7-day back-trajectories. Neither CHCl Br$_2$ nor CHBrCl$_2$ were significantly correlated with chl $a$ composite footprints (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$_3$I 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$_3$I, 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$_3$I (Fig. 9c).

Although certain species of phytoplankton are capable of producing CH$_3$I (e.g. Manley and de la Cuesta 1997; Hughes et al., 2011), several studies also indicate a non-biological source for CH$_3$I in the surface ocean. This non-biological source, though not fully understood, requires light, a humic-like substance at the surface ocean, and iron availability, which is scarce in the Southern Ocean (Moore and Zarifou 1994; Richter and Wallace 2004). Iron, which is used extensively by phytoplankton in the surface ocean, can be replenished in surface waters by wintertime mixing of subsurface iron enriched waters, sea ice melt, intense recycling of organic material, and aeolian dust (McGillicuddy et al. 2015; Tagliabue et al. 2014; Williams et al. 2007). Sources of iron that may boost CH$_3$I emissions other than recycling of organic material at the sea surface are an omitted variable in our analysis.

Several previous studies have correlated mixing ratios of CH$_3$I to satellite retrievals of photosynthetically active radiation (PAR) and temperature, citing the link between temperature and PAR to the solar radiation necessary for the photo-production of CH$_3$I in surface waters (e.g. Happell et al., 1996; Yokouchi et al., 2001). We note that chl $a$, which is a proxy for living algal biomass, was correlated with CDOM in Region 1 and Region 2, ($r^2 = 0.24$; data not shown).

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 ppt, and average photochemical loss according to the TUV 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$_2$Br$_2$ has a lifetime of 270 days, CH$_3$I 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 geophysical influence function regression coefficients and estimated fluxes.

5 Flux estimation

5.1 O$_2$-based emission estimates

We make use of the robust relationships between airborne observations of O$_2$ and HVOCs combined with modeled O$_2$ fluxes to estimate HVOC fluxes over the Southern Ocean. For CHBr$_3$, CH$_2$Br$_2$, and CHClBr$_2$ we construct ocean emission inventories for January and February using a scaled version of modeled air-sea O$_2$ fluxes from simulations using a configuration of the CESM model nudged to reanalysis temperatures and winds as described in Stephens et al. (2018)
to facilitate comparisons across regions and atmospheric models (Fig. 9). An earlier free running version of CESM was one of the best evaluated for reproducing the seasonal cycle of \( O_2/N_2 \) 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 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 (2001; also adjusted down by 51% to better match observations) to the CESM model flux estimates in Region 1 and Region 2 (adjusted down by 47%). Based on the ratios of HVOC 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\(_3\)Br\(_2\) 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 (7.3% in Region 1 and 3.4% in Region 2) were added in quadrature to yield uncertainties in calculated HVOC rate estimates.

Figure 10 shows the mean emissions for Jan. and Feb. of CHBr\(_3\), CH\(_3\)Br\(_2\), and CHClBr\(_2\) in Region 1 and Region 2. Mean regional emissions of CHBr\(_3\) and CH\(_3\)Br\(_2\) and CHClBr\(_2\) are 91 \( \pm \) 8, 31 \( \pm \) 17, and 11 \( \pm \) 4 pmol m\(^{-2}\) hr\(^{-1}\) in Region 1 and 329 \( \pm \) 23, 69 \( \pm \) 5, and 24 \( \pm \) 5 pmol m\(^{-2}\) hr\(^{-1}\) in Region 2 (Table 1). The mean flux of CH\(_3\)I in Region 2 is 392 \( \pm \) 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 Antarctic polar 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 significantly lower than our observationally derived values in Region 1, with the exception of CH\(_3\)I. Conversely, CAM-Chem emissions are significantly higher than our estimated biological emissions in Region 2, with the exception of CHClBr\(_2\) in Region 1, which remains under predicted by the model (Table 1). We note that in Region 2, CAM-Chem fluxes of CHBr\(_3\) and CH\(_3\)Br\(_2\), although still significantly different, are more similar to our estimated fluxes.

**5.2 STILT-based emission estimates**

Similar to our \( O_2 \)-based emission estimates, we used the relationship between geostatistical influence functions and CH\(_3\)I mixing ratios to predict a flux field in Region 1. The shortwave
radiation and detrital material influence function coefficients and an interaction term from a
multi-linear regression (Fig. 9) were used to estimate an average non-biological flux of CH$_3$I
(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$_3$I in future versions of CAM-Chem.
Our estimated regional mean 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, our observations of
CH$_3$I are also much lower than the modeled mixing ratios. As discussed above, the strong
correlations between CH$_3$I and O$_3$ in Region 2 also suggest a dominant biological source for this
compound. As a result, we have not used this relationship to parameterize a flux for CH$_3$I in
Region 2 (see Sect. 2.5 and 5.1 for details).

6 Conclusions

Our work combined TOGA and AWAS HVOC airborne observations from the ORCAS and
ATom-2 campaigns, with coincident measurements of O$_3$ and CO$_2$, geophysical datasets and
numerical models, including the global climate model CAM-Chem, and the Lagrangian transport
model, STILT. We evaluated model predictions, calculated biogenic enrichment ratios, inferred
regional sources, and provided novel means of parameterizing ocean fluxes. We found that the
Southern Ocean MBL is enriched in HVOCs, and these MBL enhancements are less pronounced
in Region 1 (at higher latitudes) than in Region 2 over the productive Patagonian shelf. Our
results indicated that the Southern Ocean poleward of 60°S (Region 1) and Patagonian Shelf
(Region 2) are moderate regional sources of CHBr$_3$, CHBr$_2$, and CH$_3$I, and weak sources of
CHClBr$_3$ and CHBrCl$_3$ in January and February. CAM-Chem provided a good foundation for
parameterizing HVOC emissions, particularly for CHBr$_3$ and CH$_3$I in Region 1 and Region 2.
Conversely, CHClBr$_3$ and CHBrCl$_3$ emissions were underestimated by a factor of two or three in
the model, while CH$_3$I emissions were overestimated by a factor of more than three, and airborne
observations indicated that the CAM-Chem CH$_3$I surface boundary condition may be too low
by ~25%.

Our results suggested that summertime biological HVOC fluxes may be parameterized with
some success based on airborne observations of enrichment ratios, as well the influence of
remotely sensed parameters. CHBr$_3$ and CH$_2$Br$_2$ exhibited strong and robust correlations with O$_3$
as well as weaker correlations with the influence of chl a, which is a proxy for phytoplankton
biomass. CHClBr$_3$ and CHBr$_2$ were well correlated with one another. Together, these
correlations suggested a biological source for these gases over the Southern Ocean. We found
that CH$_3$I mixing ratios in Region 1 were best correlated with a non-biological geophysical
influence function, although biogenic CH$_3$I emissions appear important in Region 2.

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
models and ship-based studies (Table 1). Our emission estimates of CHBr$_3$, CH$_2$Br$_2$,
CH$_3$I, and CHClBr$_3$ were lower than most prior estimates from the Antarctic polar region in
summer, although they were significantly higher than CAM-Chem’s prescribed emissions in
Region 1, where HVOC mixing ratios are under predicted (Table 1; Fig. 5). In the case of CH$_3$I,
our estimated emissions suggest that the prescribed emissions in CAM-Chem may be too high.
Our parameterization of the flux in Region 1 and Region 2 could be used to explore inter-annual variability in emissions, which is not captured by the Bell et al. (2002) 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. Nevertheless, these methods may facilitate parameterizing emissions of new species or improving existing emissions. 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.

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 HVOC data curation for this project. BBS, EJM, and RFK were responsible for the data curation of 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 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 HVOC emissions and conducting CAM runs. MCL was responsible 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 HVOC data.

Acknowledgements. We would like to thank the ORCAS and ATom-2 science teams and the NCAR Research Aviation Facility and NASA DC-8 pilots, technicians and mechanics for their support during the field campaigns. In addition, we appreciate the NCAR EOL staff who have facilitated computing and data archival. In particular, we thank Tim Newberger for his help in supporting the NOAA Picarro CO$_2$ observations and Andrew Watt for his help in supporting the AO2 O$_2$ observations. This work was made possible by grants from NSF Polar Programs (1501993, 1501997, 1501292, 1502301, 1543457), NSF Atmospheric Chemistry Grants 1535364, 1623745, and 1623748 and NASA funding of the EVS2 Atmospheric Tomography (ATom) project, as well as the support of the NCAR Advanced Study Program (ASP) Postdoctoral Fellowship Program and computing support from Yellowstone, provided by NCAR’s Computational and Information Systems Laboratory. The National Center for Atmospheric Research is sponsored by the National Science Foundation.
References

Abrahamsson, K., Lorén, A., Wulff, A. and Wängberg, S.-Å.: Air–sea exchange of halocarbons: the influence of diurnal and regional variations and distribution of pigments, Deep Sea Research Part II: Topical Studies in Oceanography, 51(22-24), 2789–2805, doi:10.1016/j.dsr2.2004.09.005, 2004a.

Abrahamsson, K., Bertilsson, S., Chierici, M., Fransson, A., Froneman, P. W., Lorén, A. and Pakhomov, E. A.: Variations of biochemical parameters along a transect in the Southern Ocean, with special emphasis on volatile halogenated organic compounds, Deep Sea Research Part II: Topical Studies in Oceanography, 51(22-24), 2745–2756, doi:10.1016/j.dsr2.2004.09.004, 2004b.

Abrahamsson, K., Granfors, A., Ahnoff, M., Cuevas, C. A. and Saiz-Lopez, A.: Organic bromine compounds produced in sea ice in Antarctic winter, Nature Communications, 9(1), doi:10.1038/s41467-018-07062-8, 2018.

Anav, A., Friedlingstein, P., Beer, C., Ciais, P., Harper, A., Jones, C., Murray-Tortarolo, G., Papale, D., Parazoo, N. C., Peylin, P., Piao, S., Stich, S., Viyov, N., Wiltshire, A. and Zhao, M.: Spatiotemporal patterns of terrestrial gross primary production: A review: GPP Spatiotemporal Patterns, Reviews of Geophysics, 53(3), 785–818, doi:10.1002/2015RG000483, 2015.

Apel, E.: ORCAS Trace Organic Gas Analyzer (TOGA) VOC Data. Version 1.0, [online] Available from: https://data.eol.ucar.edu/dataset/490.018 (Accessed 29 January 2019), 2017.

Apel, E. C., Hornbrook, R. S., Hills, A. J., Blake, N. J., Barth, M. C., Weinheimer, A., Cantrell, C., Rutledge, S. A., Basarab, B., Crawford, J., Diskin, G., Homeyer, C. R., Campos, T., Flocke, F., Fried, A., Blake, D. R., Brune, W., Pollack, I., Peischl, J., Ryerson, T., Wennberg, P. O., Crounse, J. D., Wisthaler, A., Mikoviny, T., Huey, G., Heikes, B., O’Sullivan, D. and Riemer, D. D.: Upper tropospheric ozone production from lightning NOx, convection: Smoke ingestion case study from the DC3 campaign, Journal of Geophysical Research: Atmospheres, 120(6), 2505–2523, doi:10.1002/2014JD022121, 2015.

Atkinson, H. M., Huang, R.-J., Chance, R., Roscoe, H. K., Hughes, C., Davison, B., Schönhardt, A., Mahajan, A. S., Saiz-Lopez, A., Hoffmann, T. and Liss, P. S.: Iodine emissions from the sea ice of the Weddell Sea, Atmospheric Chemistry and Physics, 12(22), 11229–11244, doi:10.5194/acp-12-11229-2012, 2012.

Atlas, E.: ORCAS Advanced Whole Air Sampler (AWAS) Data. Version 1.0, [online] Available from: https://data.eol.ucar.edu/dataset/490.027 (Accessed 29 January 2019), 2017.

Ayers, G. P.: Comment on regression analysis of air quality data, Atmospheric Environment, 35(13), 2423–2425, doi:10.1016/S1352-2310(00)00527-6, 2001.

Bates, T. S.: Preface [to special section on First Aerosol Characterization Experiment (AGE 1)], Journal of Geophysical Research: Atmospheres, 104(D17), 21645–21647, doi:10.1029/1999JD900365, 1999.

Bell, N., Hsu, I., Jacob, D. J., Schultz, M. G., Blake, D. R., Butler, J. H., King, D. B., Lober, J. M. and Maier-Reimer, E.: Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models: GLOBAL ATMOSPHERIC METHYL IODIDE, Journal of Geophysical Research: Atmospheres, 107(D17), ACH 8–1–ACH 8–12, doi:10.1029/2001JD001151, 2002.

Blake, N. J., Blake, D. R., Wingenter, O. W., Sive, B. C., Kang, C. H., Thornton, D. C., Bandy, A. R., Atlas, E., Flocke, F., Harris, J. M. and Rowland, F. S.: Aircraft measurements of the latitudinal, vertical, and seasonal variations of NMHCs, methyl nitrate, methyl halides, and DMS during the First Aerosol Characterization Experiment (ACE 1), Journal of Geophysical Research: Atmospheres, 104(D17), 21803–21817, doi:10.1029/1999JD900238, 1999.

Blei, E. and Heal, M. R.: Methyl bromide and methyl chloride fluxes from temperate forest litter, Atmospheric Environment, 45(8), 1543–1547, doi:10.1016/j.atmosenv.2010.12.044, 2011.

Bloss, W. J.: Impact of halogen monoxide chemistry upon boundary layer OH and HOX concentrations at a coastal site, Geophysical Research Letters, 32(6), doi:10.1029/2004GL02084, 2005.
Glover, D. M., Jenkins, W. J. and Doney, S. C.: Modeling Methods for Marine Science, Cambridge University Press., 2011.

Guenther, A. B., Jiang, X., Heald, C. L., Sakulanyonvittayta, T., Duhl, T., Emmons, L. K. and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geoscientific Model Development, 5(6), 1471–1492, doi:10.5194/gmd-5-1471-2012, 2012.

Happell, J. D., Wallace, D. W. R., Wills, K. D., Wilke, R. J. and Neill, C. C.: A purge-and-trap capillary column gas chromatographic method for the measurement of halocarbons in water and air. [online] Available from: http://www.osti.gov/servlets/purl/366493-84sOy/webviewable/ (Accessed 26 July 2018), 1996.

Hossaini, R., Mantle, H., Chipperfield, M. P., Montzka, S. A., Hamer, P., Ziska, F., Quack, B., Krüger, K., Tegtmeier, S., Atlas, E., Sala, S., Engel, A., Bönisch, H., Keber, T., Oram, D., Mills, G., Ordóñez, C., Saiz-Lopez, A., Warwick, N., Liang, Q., Fung, W., Moore, F., Miller, B. R., Marécal, V., Richards, N. A. D., Dorf, M. and Pfeilsticker, K.: Evaluating global emission inventories of biogenic bromocarbons, Atmospheric Chemistry and Physics, 13(23), 11819–11838, doi:10.5194/acp-13-11819-2013, 2013.

Hughes, C., Chuck, A. L., Rossetti, H., Mann, P. J., Turner, S. M., Clarke, A., Chance, R. and Liss, P. S.: Seasonal cycle of seawater bromoform and dibromomethane concentrations in a coastal bay on the western Antarctic Peninsula: BROMOCARBON SEASONALITY ANTARCTICA, Global Biogeochemical Cycles, 23(2), n/a–n/a, doi:10.1029/2008GB003268, 2009.

Hughes, C., Johnson, M., Utting, R., Turner, S., Malin, G., Clarke, A. and Liss, P. S.: Microbial control of bromocarbon concentrations in coastal waters of the western Antarctic Peninsula, Marine Chemistry, 151, 35–46, doi:10.1016/j.marchem.2013.01.007, 2013.

Hurrell, J. W., Hack, J. J., Shea, D., Caron, J. M. and Rosinski, J.: A New Sea Surface Temperature and Sea Ice Boundary Dataset for the Community Atmosphere Model, Journal of Climate, 21(19), 5145–5153, doi:10.1175/2008JCLI2292.1, 2008.

Keeling, R. F., Manning, A. C., McEvoy, E. M. and Shertz, S. R.: Methods for measuring changes in atmospheric O3 concentration and their application in southern hemisphere air, Journal of Geophysical Research: Atmospheres, 103(D3), 3381–3397, doi:10.1029/97JD02537, 1998.

Lai, S. C., Williams, J., Arnold, S. R., Atlas, E. L., Gebhardt, S. and Hoffmann, T.: Iodine containing species in the remote marine boundary layer: A link to oceanic phytoplankton: IODINE SPECIES AND PHYTOPLANKTON, Geophysical Research Letters, 38(20), n/a–n/a, doi:10.1029/2011GL049035, 2011.

Lamarque, J.-F.: Response of a coupled chemistry-climate model to changes in aerosol emissions: Global impact on the hydrological cycle and the tropospheric burdens of OH, ozone, and NOx., Geophysical Research Letters, 32(16), doi:10.1029/2005GL023419, 2005.

Lamarque, J.-F., Emmons, L. K., Hess, P. G., Kinnison, D. E., Tilmes, S., Vitt, F., Heald, C. L., Holland, E. A., Lauritzen, P. H., Neu, J., Orlando, J. J., Rasch, P. J. and Tyndall, G. K.: CAM-chem: description and evaluation of interactive atmospheric chemistry in the Community Earth System Model, Geoscientific Model Development, 5(2), 369–411, doi:10.5194/gmd-5-369-2012, 2012.

Liang, Q., Atlas, E., Blake, D., Dorf, M., Pfeilsticker, K. and Schaufler, S.: Convective transport of very short lived bromocarbons to the stratosphere, Atmospheric Chemistry and Physics, 14(11), 5781–5792, doi:10.5194/acp-14-5781-2014, 2014.

Lin, J. C.: A near-field tool for simulating the upstream influence of atmospheric observations: The Stochastic Time-Inverted Lagrangian Transport (STILT) model, Journal of Geophysical Research, 108(D16), ACH 2–1–ACH 2–17, doi:10.1029/2002JD003161, 2003.

Liu, X., Easter, R. C., Ghan, S. J., Zaveri, R., Rasch, P., Shi, X., Lamarque, J.-F., Gettelman, A., Morrison, H., Vitt, F., Conley, A., Park, S., Neale, R., Hannay, C., Ekmann, A. M. L., Hess, P., Mahowald, N., Collins, W., Iacono, M. J., Bretherton, C. S., Flanner, M. G. and Mitchell, D.: Toward a minimal representation of aerosols in climate dynamics...
models: description and evaluation in the Community Atmosphere Model CAM5, Geoscientific Model Development, 5(3), 709–739, doi:10.5194/gmd-5-709-2012, 2012.

Manley, S. L. and Dastoor, M. N.: Methyl iodide (CH3I) production by kelp and associated microbes, Marine Biology, 98(4), 477–482, doi:10.1007/BF00391538, 1988.

Maslak, J.: Near-Real-Time DMSP SSM/I-SSMIS Daily Polar Gridded Sea Ice Concentrations, Version 1, 1999.

Mattson, E., Karlsson, A., Smith, W. O. and Abrahamsson, K.: The relationship between biophysical variables and halocarbon distributions in the waters of the Amundsen and Ross Seas, Antarctica, Marine Chemistry, 140-141, 1–9, doi:10.1016/j.marchem.2012.07.002, 2012.

McGillicuddy, D. J., Sedwick, P. N., Dinniman, M. S., Arrigo, K. R., Bibby, T. S., Greenan, B. J. W., Hofmann, E. E., Klinck, J. M., Smith, W. O., Mack, S. L., Marsay, C. M., Sohst, B. M. and van Dijken, G. L.: Iron supply and demand in an Antarctic shelf ecosystem: Ross Sea Iron Supply and Demand, Geophysical Research Letters, 42(19), 8088–8097, doi:10.1002/2015GL065727, 2015.

Moore, R. M. and Groszko, W.: Methyl iodide distribution in the ocean and fluxes to the atmosphere, Journal of Geophysical Research: Oceans, 104(C5), 11163–11171, doi:10.1029/1998JC900073, 1999.

Moore, R. M. and Zafiriou, O. C.: Photochemical production of methyl iodide in seawater, Journal of Geophysical Research, 99(D8), 16415, doi:10.1029/94JD00786, 1994.

Moore, R. M., Webb, M., Tokarczyk, R. and Weyer, R.: Bromoperoxidase and iodoperoxidase enzymes and production of halogenated methanes in marine diatom cultures, Journal of Geophysical Research: Oceans, 101(C9), 20899–20908, doi:10.1029/96JC01248, 1996.

Murphy, D. M., Froyd, K. D., Bian, H., Brock, C. A., Dibb, J. E., DiGangi, J. P., Diskin, G., Dollner, M., Kucp, A., Scheuer, E. M., Schill, G. P., Weinzierl, B., Williamson, C. J. and Yu, P.: The distribution of sea-salt aerosol in the global troposphere, Atmospheric Chemistry and Physics Discussions, 1–27, doi:10.5194/acp-2018-1013, 2018.

NASA Goddard Space Flight Center, O. E. L.: SeaWiFS Ocean Color Data, 2014.

National Centers For Environmental Prediction/National Weather Service/NOAA/U.S. Department Of Commerce: NCEP GDAS/FNL 0.25 Degree Global Tropospheric Analyses and Forecast Grids, 2015.

Navarro, M. A., Atlas, E. L., Saiz-Lopez, A., Rodriguez-Lloveras, X., Kinnison, D. E., Lamarque, J.-F., Tilmes, S., Filius, M., Harris, N. R. P., Meneguz, E., Ashfold, M. J., Manning, A. J., Cuevas, C. A., Schauffler, S. M. and Donets, V.: Airborne measurements of organic bromine compounds in the Pacific tropical tropopause layer, Proceedings of the National Academy of Sciences, 112(45), 13789–13793, doi:10.1073/pnas.1511463112, 2015.

Neale, R. B., Richter, J., Park, S., Lauritzen, P. H., Vavrus, S. J., Rasch, P. J. and Zhang, M.: The Mean Climate of the Community Atmosphere Model (CAM4) in Forced SST and Fully Coupled Experiments, Journal of Climate, 26(14), 5150–5168, doi:10.1175/JCLI-D-12-00236.1, 2013.

Nevison, C. D., Manizza, M., Keeling, R. F., Kahru, M., Bopp, L., Dunne, J., Tiptura, J., Ilyina, T. and Mitchell, B. G.: Evaluating the ocean biogeochemical components of Earth system models using atmospheric potential oxygen and ocean color data, Biogeosciences, 12(1), 193–208, doi:10.5194/bg-12-193-2015, 2015.

Nevison, C. D., Manizza, M., Keeling, R. F., Stephens, B. B., Bent, J. D., Dunne, J., Ilyina, T., Long, M., Resplandy, L., Tiptura, J. and Yokimoto, S.: Evaluating CMIP5 ocean biogeochemistry and Southern Ocean carbon uptake using atmospheric potential oxygen: Present-day performance and future projection: CMIP5 APO AND SOUTHERN OCEAN CARBON FLUX, Geophysical Research Letters, 43(5), 2077–2085, doi:10.1002/2015GL067584, 2016.

Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J. and Upstill-Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, Global Biogeochemical Cycles, 14(1), 373–387, 2000.

Obrist, D., Tas, E., Peleg, M., Matveev, V., Faïn, X., Asaf, D. and Luria, M.: Bromine-induced oxidation of mercury in the mid-latitude atmosphere, Nature Geoscience, 4, 22, 2010.
Ordóñez, C., Lamarque, J.-F., Tilmes, S., Kinnison, D. E., Atlas, E. L., Blake, D. R., Sousa Santos, G., Brasseur, G. and Saiz-Lopez, A.: Bromine and iodine chemistry in a global chemistry-climate model: description and evaluation of very short-lived oceanic sources, Atmospheric Chemistry and Physics, 12(3), 1423–1447, doi:10.5194/acp-12-1423-2012, 2012.

Quack, B. and Wallace, D. W. R.: Air-sea flux of bromoformaldehyde: Controls, rates, and implications: AIR-SEA FLUX OF Bromoformaldehyde, Global Biogeochemical Cycles, 17(1), doi:10.1029/2002GB001890, 2003.

Raimund, S., Quack, B., Bozec, Y., Vernet, M., Rossi, V., Garçon, V., Morel, Y. and Morin, P.: Sources of short-lived bromocarbons in the Iberian upwelling system, Biogeosciences, 8(6), 1551–1564, doi:10.5194/bg-8-1551-2011, 2011.

Read, K. A., Mahajan, A. S., Carpenter, L. J., Evans, M. J., Faria, B. V. E., Heard, D. E., Hopkins, J. R., Lee, J. D., Moller, S. J., Lewis, A. C., Mendes, L., McQuaid, J. B., Oetjen, H., Saiz-Lopez, A., Pilling, M. J. and Plane, J. M. C.: Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, Nature, 453(7199), 1232–1235, doi:10.1038/nature07035, 2008.

Resplandy, L., Keeling, R. F., Stephens, B. B., Bent, J. D., Jacobson, A., Rödenbeck, C. and Khatiwala, S.: Constraints on oceanic meridional heat transport from combined measurements of oxygen and carbon, Climate Dynamics, 47(9-10), 3335–3357, doi:10.1007/s00382-016-3029-3, 2016.

Reygondeau, G., Longhurst, A., Martinez, E., Beaugrand, G., Antoine, D. and Maury, O.: Dynamic biogeochemical provinces in the global ocean: DYNAMIC BIOGEOCHEMICAL PROVINCES, Global Biogeochemical Cycles, 27(4), 1046–1058, doi:10.1002/gbc.20089, 2013.

Richter, U. and Wallace, D. W. R.: Production of methyl iodide in the tropical Atlantic Ocean: PRODUCTION OF METHYL IODIDE, Geophysical Research Letters, 31(23), doi:10.1029/2004GL020779, 2004.

Rienecker, M. M., Suarez, M. J., Todling, R., Bacmeister, J., Takacs, L., Liu, H. C., Gu, W., Sienkiewicz, M., Koster, R. D., Gelaro, R., Stajner, I. and Nielsen, J. E.: The GEOS VALOR/GEOS Weather Research and Forecasting model: description and evaluation, WRF Version 3.2.1, 2008.

Saiz-Lopez, A., Mahajan, A. S., Salmon, R. A., Bauguitte, S. J.-B., Jones, A. E., Roscoe, H. K. and Plane, J. M. C.: Boundary Layer Halogens in Coastal Antarctica, Science, 317(5836), 348–351, doi:10.1126/science.1144108, 2007.

Saiz-Lopez, A., Lamarque, J.-F., Kinnison, D. E., Tilmes, S., Ordóñez, C., Orlando, A. J., Plane, J. M., Mahajan, A. S., Sousa Santos, G., Atlas, E. L., Blake, D. R., Sander, S. P., Schauffler, S., Thompson, A. M. and Brasseur, G.: Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere, Atmospheric Chemistry and Physics, 12(9), 3939–3949, doi:10.5194/acp-12-3939-2012, 2012.

Saiz-Lopez, A., Fernandez, R. P., Ordóñez, C., Kinnison, D. E., Gómez Martín, J. C., Lamarque, J.-F. and Tilmes, S.: Iodine chemistry in the troposphere and its effect on ozone, Atmospheric Chemistry and Physics, 14(23), 13119–13143, doi:10.5194/acp-14-13119-2014, 2014.

Schauffler, S. M., Atlas, E. L., Blake, D. R., Flocke, F., Lueb, R. A., Lee-Taylor, J. M., Stroud, V. and Travnicek, W.: Distributions of brominated organic compounds in the troposphere and lower stratosphere, Journal of Geophysical Research: Atmospheres, 104(D17), 21513–21535, doi:10.1029/1999JD900197, 1999.

Schroeder, W. H., Anlauf, K. G., Barrie, L. A., Lu, J. Y., Steffen, A., Schneeberger, D. R. and Berg, T.: Arctic springtime depletion of mercury, Nature, 394, 331, 1998.

Sive, B. C., Varner, R. K., Mao, H., Blake, D. R., Wingenter, O. W. and Talbot, R.: A large terrestrial source of methyl iodide, Geophysical Research Letters, 34(17), doi:10.1029/2007GL030528, 2007.

Stephens, B.: ORCAS Merge Products. Version 1.0, [online] Available from: https://data.eol.ucar.edu/dataset/490.024 (Accessed 31 December 2018), 2017.

Stephens, B. B., Keeling, R. F., Heimann, M., Six, K. D., Murnane, R. and Caldeira, K.: Testing global ocean carbon cycle models using measurements of atmospheric O$_2$ and CO$_2$ concentration, Global Biogeochemical Cycles, 12(2), 213–230, doi:10.1029/97GB03500, 1998.
Stephens, B. B., Keeling, R. F. and Paplawsky, W. J.: Shipboard measurements of atmospheric oxygen using a vacuum-ultraviolet absorption technique, Tellus B, 55(4), 857–878, doi:10.1080/143554503000075x, 2003.

Stephens, B. B., Long, M. C., Keeling, R. F., Kort, E. A., Sweeney, C., Apel, E. C., Atlas, E. L., Beaton, S., Bent, J. D., Blake, N. J., Bresch, J. F., Casey, J., Daube, B. C., Diao, M., Diaz, E., Dierssen, H., Donets, V., Gao, B.-C., Gierach, M., Green, R., Haag, J., Hayman, M., Hills, A. J., Hoecker-Martínez, M. S., Honomichl, S. B., Hornbrook, R. S., Jensen, J. B., Li, R.-R., McCubbin, I., McKain, K., Morgan, E. J., Nolte, S., Powers, J. G., Rainwater, B., Randolph, K., Reeves, M., Schaufler, S. M., Smith, K., Smith, M., Stith, J., Stossmeister, G., Toohey, D. W. and Watt, A. S.: The O$_3$/N$_2$ ratio and CO$_2$ Airborne Southern Ocean Study, Bulletin of the American Meteorological Society, 99(2), 381–402, doi:10.1175/BAMS-D-16-02061.1, 2018.

Sturges, W. T., Cota, G. F. and Buckley, P. T.: Bromofrom emission from Arctic ice algae, Nature, 358, 660, 1992.

Sturges, W. T., Cota, G. F. and Buckley, P. T.: Vertical profiles of bromofrom in snow, sea ice, and seawater in the Canadian Arctic, Journal of Geophysical Research: Oceans, 102(C11), 25073–25083, doi:10.1029/97JC01860, 1997.

Tagliabue, A., Sallé, J.-B., Bowie, A. R., Lévy, M., Swart, S. and Boyd, P. W.: Surface-water iron supplies in the Southern Ocean sustained by deep winter mixing, Nature Geoscience, 7(4), 314–320, doi:10.1038/ngeo2101, 2014.

Tilmes, S., Lamarque, J.-F., Emmons, L. K., Kinnison, D. E., Marsh, D., Garcia, R. R., Smith, A. K., Neely, R. R., Conley, A., Vitt, F., Val Martin, M., Tanimoto, H., Simpson, I., Blake, D. R. and Blake, N.: Representation of the Community Earth System Model (CESM1) CAM4-chem within the Chemistry-Climate Model Initiative (CCMI), Geoscientific Model Development, 9(5), 1853–1890, doi:10.5194/gmd-9-1853-2016, 2016.

Tohjima, Y.: Preparation of gravimetric standards for measurements of atmospheric oxygen and reevaluation of atmospheric oxygen concentration, Journal of Geophysical Research, 110(D11), doi:10.1029/2004JD005595, 2005.

Tokarczyk, R. and Moore, R. M.: Production of volatile organohalogens by phytoplankton cultures, Geophysical Research Letters, 21(4), 285–288, doi:10.1029/94GL00009, 1994.

Tortell, P. D. and Long, M. C.: Spatial and temporal variability of biogenic gases during the Southern Ocean spring bloom, Geophysical Research Letters, 36(1), doi:10.1029/2008GL035819, 2009.

Tortell, P. D., Asher, E. C., Ducklow, H. W., Goldman, J. A. L., Dacey, J. W. H., Grzymski, J. J., Young, J. N., Kranz, S. A., Bernard, K. S. and Morel, F. M. M.: Metabolic balance of coastal Antarctic waters revealed by autonomous $^3$H$_2$O and $^{18}$O$_2$/Ar measurements: metabolic balance of Antarctic waters, Geophysical Research Letters, 41(19), 6803–6810, doi:10.1002/2014GL061266, 2014.

Williams, J., Gros, V., Atlas, E., Maciejczyk, K., Batsaikhan, A., Schöler, H. F., Forster, C., Quack, B., Yassaa, N., Sander, R. and Van Dingenen, R.: Possible evidence for a connection between methyl iodide emissions and Saharan dust, Journal of Geophysical Research, 112(D7), doi:10.1029/2005JD006702, 2007.

WMO (World Meteorological Organization): Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report, Geneva, Switzerland., 2011.

Wofsy, S. C.: HIAPER Pole-to-Pole Observations (HIPPO): fine-grained, global-scale measurements of climatically important atmospheric gases and aerosols, Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences, 369(1943), 2073–2086, doi:10.1098/rsta.2010.0313, 2011.

Wofsy, S. C., Afshar, S., Allen, H. M., Apel, E., Asher, E. C., Barletta, B., Bent, J., Bian, H., Biggs, B. C., Blake, D., Blake, N., Bourgeois, I., Brock, C. A., Brune, W. H., Budney, J. W., Bui, T. P., Butler, A., Campuzano-Jost, P., Chang, C. S., Chin, M., Commane, R., Correa, G., Crouse, J. D., Cullis, P. D., Daube, B. C., Day, D. A., Dean-Day, J. M., Dibb, J. E., Digangi, J. P., Diskin, G. S., Dollner, M., Elkins, J. W., Erdesdy, F., Fiore, A. M., Flynn, C. M., Froyd, K., Gesler, D. W., Hall, S. R., Hanisco, T. F., Hannun, R. A., Hills, A. J., Hintsa, E. J., Hoffmann, A., Hornbrook, R. S., Huey, L. G., Hughes, S., Jimenez, J. L., Johnson, B. J., Katoch, J. M., Keeling, R., Kim, M. J., Kupc, A., Lait, L. R., Lamarque, J.-F., Liu, H. B., McKain, K., Melaughlin, R. J., Meinardi, S., Miller, D. O., Montzka, S. A., Moore, F. L., Morgan, E. J., Murphy, D. M., Murray, L. T., Nault, B. A., Neuman, J. A., Newman, P. A., Nicely, J. M., Pan, X., Paplawsky, W., Peischl, J., Prather, M. J., Price, D. J., Ray, E., Reeves, J. M., Richardson, M., Rollins, A. W., Rosenlof, K. H., Ryerson, T. B., Scheuer, E., Schill, G. P., Schroder, J. C., Schwarz,
J. P., St.Clair, J. M., Steenrod, S. D., Stephens, B. B., Strode, S. A., Sweeney, C., Tanner, D., Teng, A. P., Thames, A. B., Thompson, C. R., Ullmann, K., Veres, P. R., Vizenor, N., Wagner, N. L., Watt, A., Weber, R., Weinzierl, B., et al.: ATom: Merged Atmospheric Chemistry, Trace Gases, and Aerosols, [online] Available from: https://daac.ornl.gov/cgi-bin/dsviewer.pl?ds_id=1581 (Accessed 31 December 2018), 2018.

Yang, B., Yang, G.-P., Lu, X.-L., Li, L. and He, Z.: Distributions and sources of volatile chlorocarbons and bromocarbons in the Yellow Sea and East China Sea, Marine Pollution Bulletin, 95(1), 491–502, doi:10.1016/j.marpolbul.2015.03.009, 2015.

Yokouchi, Y., Nojiri, Y., Barrie, L. A., Toom-Sauntry, D. and Fujinuma, Y.: Atmospheric methyl iodide: High correlation with surface seawater temperature and its implications on the sea-to-air flux, Journal of Geophysical Research: Atmospheres, 106(D12), 12661–12668, doi:10.1029/2001JD900083, 2001.

Ziska, F., Quack, B., Abrahamsson, K., Archer, S. D., Atlas, E., Bell, T., Butler, J. H., Carpenter, L. J., Jones, C. E., Harris, N. R. P., Hepach, H., Heumann, K. G., Hughes, C., Kuss, J., Krüger, K., Liss, P., Moore, R. M., Orlíková, A., Raimund, S., Reeves, C. E., Reifenhäuser, W., Robinson, A. D., Schall, C., Tanhua, T., Tegtmeier, S., Turner, S., Wang, L., Wallace, D., Williams, J., Yamamoto, H., Yvon-Lewis, S. and Yokouchi, Y.: Global sea-to-air flux climatology for bromoform, dibromomethane and methyl iodide, Atmospheric Chemistry and Physics, 13(17), 8915–8934, doi:10.5194/acp-13-8915-2013, 2013.
Tables

Table 1. HVOC emission estimates (pmol m$^2$ hr$^{-1}$) in Region 1 and Region 2 calculated in this study, from CAM-Chem (Ordoñez et al. 2012) and from several other modeling and ship-based observational studies.

| Region/Months       | CHBr$_3$ | CH$_2$Br$_2$ | CH$_3$I | CHClBr$_2$ | Reference               |
|---------------------|----------|--------------|---------|------------|-------------------------|
| Region 1 (JF)       | 91 ± 8   | 31 ± 18      | 35 ± 29 | 11 ± 4     | This Study              |
| Region 2 (JF)       | 329 ± 23 | 69 ± 5       | 392 ± 32| 25 ± 5     | 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) |
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.
Figure 2. Meridional-altitudinal cross-sections of mixing ratios of a) CH$_3$I, b) CHBr$_3$, c) CH$_3$Br, d) CHClBr$_2$, and e) CHBrCl$_2$ from the TOGA and mixing ratios of f) CH$_3$Br 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, respectively.
Figure 3. Mixing ratios of CHBr₃ vs. CH₂Br₂ across the ORCAS and ATom-2 campaigns in Region 1 (Fig.3a,b) and in Region 2 (Fig.3c,d). Type II major axis regression model (bivariate least squares regressions) are based on ORCAS data below 2 km illustrates a regional enhancement ratio. Error bars represent the uncertainty in HVOC measurements.
Figure 4. Mixing ratios of CHBr$_3$, CH$_2$Br$_2$, and CH$_3$I vs. O$_2$ on ORCAS and ATom-2 in Region 1, pole ward of 60° S (a-c) and Region 2 over the Patagonian Shelf (e-f). Slopes ± standard errors from type II major axis regression model (bivariate least squares regression) fits of ORCAS data (using variables scaled to their range) are shown. To isolate the contribution of ocean O$_2$ fluxes, the ORCAS δ(O$_2$/N$_2$) values reported here represent the Δδ(O$_2$/N$_2$) to observed values between 5-7 km and are adjusted for CESM O$_2$ land and fossil fuel contributions and the influence of air-sea N$_2$ fluxes. Figure S3 shows the same plots relative to unadjusted ORCAS δ(O$_2$/N$_2$) values and illustrates that these corrections are minor. The slopes reported in the figure are converted to pmol:mol ratios prior to estimating biogenic HVOC 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.
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 HVOC measurements at that altitude, including measurements below the detection limit (DL), which 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.
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 $r^2 \geq 0.2$). The bold, black line in each vertical profile represents the binned (mean) mixing ratio of HVOC measurements at that altitude, including measurements below the detection limit (DL), which 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.
Figure 7. Linear type II regressions between influence functions convolved with sea ice distributions (not including land ice), and mixing ratios for CHBr$_3$, CH$_2$Br$_2$, and CH$_3$I in Region 1, poleward of 60° S. Surface influence functions (ppt m$^2$ s pmol$^{-1}$) in each grid cell were multiplied by predictor variables, such as fractional sea ice concentration, which is unit-less, yielding sea ice surface influence units of ppt m$^2$ s pmol$^{-1}$, as shown on the x-axis. Linear regression lines are only shown where a statistically significant relationship was found.
Figure 8. Linear type II regressions between influence functions of eight day composites of chl $a$ and mixing ratios of HVOCs (a-d) poleward of 60° S (Region 1). Surface influence functions (ppt m$^{-2}$ s pmol$^{-1}$) in each grid cell were multiplied by predictor variables, such as chl $a$ (µg m$^{-3}$), resulting units of ppt s pmol$^{-1}$ m$^{-1}$, shown on the x-axis. Linear regression lines are only shown where a statistically significant relationship was found.
Figure 9. Observed CH$_3$I plotted against geostatistical influence of downward shortwave radiation (a) and absorption due to detritus (b) and the predicted mixing ratios of CH$_3$I based on a multiple linear regressions (MLR) using these two predictors and an interaction term in Region 1, poleward of 60° S (c). Surface influence functions (ppt m$^2$ s pmol$^{-1}$) in each grid cell were multiplied by predictor variables, such as shortwave radiation (W m$^{-2}$), yielding units of ppt Ws pmol$^{-1}$, and detrital absorption (m$^{-1}$), yielding units of ppt m s pmol$^{-1}$, shown on the x-axes. Based on these relationships (a,b), we included these predictors in a multiple linear regression (± standard deviations; Equation 2), 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).
Figure 10. Mean Jan. – Feb. O$_2$-based CHBr$_3$ and CH$_2$Br$_2$ 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 O$_2$ fluxes are scaled by the slope between the oceanic contribution to δ(O$_2$/N$_2$) and CHBr$_3$ and CH$_2$Br$_2$, and and CHClBr$_2$, reported in Fig. 4. Note that these fluxes represent mean biogenic fluxes in Jan. - Feb. (see Sect. 5.1 for details).
Figure 1. Mean estimated CH$_3$I fluxed for Jan. – Feb. The multilinear regression in Fig. 9 between CH$_3$I 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.