Organic bromine compounds produced in sea ice in Antarctic winter

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During polar springtime, active bromine drives ozone, a greenhouse gas, to near-zero levels. Bromine production and emission in the polar regions have so far been assumed to require sunlight. Here, we report measurements of bromocarbons in sea ice, snow, and air during the Antarctic winter that reveal an unexpected new source of organic bromine to the atmosphere during periods of no sunlight. The results show that Antarctic winter sea ice provides 10 times more bromocarbons to the atmosphere than Southern Ocean waters, and substantially more than summer sea ice. The inclusion of these measurements in a global climate model indicates that the emitted bromocarbons will disperse throughout the troposphere in the southern hemisphere and through photochemical degradation to bromine atoms, contribute ~10% to the tropospheric reactive bromine budget. Combined together, our results suggest that winter sea ice could potentially be an important source of atmospheric bromine with implications for atmospheric chemistry and climate at a hemispheric scale.
Bromine-containing organic compounds (bromocarbons) are ubiquitous in the oceans, and they are mainly formed by macro- and microalgae1. Of these naturally produced substances, bromoform (CHBr₃) is the best known, since it is the most abundant brominated organic. It is formed in enzymatic processes developed to protect algal cells of reactive oxygen species, such as hydrogen peroxide, formed during photosynthesis1,2. In addition, several other bromocarbons are formed, such as dibromomethane (CH₂Br₂), dibromochloromethane (CHBr₂Cl), and bromodichloromethane (CHBrCl₂), either directly through the same enzymatic pathway, or by nucleophilic substitution of CHBr₃. In the atmosphere, bromocarbons are photochemically degraded to reactive bromine which initiate the depletion of ozone and mercury, a contaminant of global concern3,4. BrO, formed by the reaction of atmospheric Br atoms with O₃, has an impact on the sulfur cycle through the oxidation of dimethyl sulfide (DMS), leading to a 18% reduction in the DMS burden and lifetime5. The Br atom is the dominant oxidizer in mercury depletion events in the polar atmosphere6. Reactive bromine from the decomposition of bromocarbons also contributes to the depletion of ozone in the lower stratosphere7. The interplay between the oceanic sources of bromocarbons and their atmospheric impacts has led to the suggestion that these compounds are a link between climate change and atmospheric ozone8.

Recently, it has been shown that variability in polar tropospheric bromine oxide (BrO) levels is correlated with first year sea ice concentrations, through the production of halogens in sea ice regions9. Reactive bromine is anti-correlated with ozone, which suggests that the efficiency of halogen-driven polar tropospheric ozone depletion is related to sea ice dynamics and biogeochemical processes. Research on the role of sea ice in the formation of reactive halogens has in recent years mainly focused on the inorganic chemistry of saline surfaces, where sea-salt halides are oxidized to more reactive forms10,11. Similarly, inorganic bromine has also been shown to form in saline snow12. Arctic and Antarctic sea ice algae have been estimated to emit organo-bromine with ~70–80 × 10⁸ g yr⁻¹, suggesting that the produced compounds are released into seawater and then reach the atmosphere13. Other investigations have pointed out the possibility of sea ice as a source of atmospheric CHBr₃ in the Amundsen Sea (Antarctica) during the sunlit period14. In coastal Antarctica, concentrations of iodo-carbons in sea ice were found to be strongly enhanced relative to seawater, suggesting a significant local source within the sea ice15,16,17. Therefore, although halocarbons are thought to be produced within sea ice, two key questions remain unknown: (i) whether this source is significant in supplying bromocarbons to the atmosphere relative to the flux from the surface waters in leads and the open ocean, and (ii) the role of biogeochemical cycles of bromocarbons during polar winter, as their production, and thereby emissions, have so far been assumed to require sunlight.

In this work, we report profile measurements of bromocarbons in snow, sea ice, and air during Antarctic winter that represent a new source of atmospheric bromine during the polar night. We combine the observations with a state-of-the-art global chemistry-climate model. The results provide strong evidence that Antarctic winter sea ice is a significant source of bromocarbons, which spread and contribute to the burden of atmospheric bromine throughout the southern hemisphere.

Results

Bromocarbon concentrations in Antarctic winter. A field campaign was performed from 8 June to 12 August 2013 in the Weddell Sea, Antarctica (Supplementary Figure 1). Here we report data from the dark period of the cruise 17 June to the 15 July. The concentrations of bromocarbons (CHBr₃, CH₂Br₂, CHBr₂Cl, and CHBrCl₂) were measured in snow, sea ice, and air to estimate their source strength of seasonal sea ice in the absence of sunlight (Fig. 1). These measurements were made at nine stations where 23 ice cores were collected. The thickness of the first year sea ice over which measurements were made varied between 43 and 118 cm, whereas the snow thickness varied between zero and 5–40 cm (Supplementary Table 1).

The air measurements (located at 20 m above sea ice level) revealed unexpectedly high concentrations of bromocarbons under conditions of solar zenith angle (SZA) larger than 90° (i.e., full darkness), with average values of 9.5 pptv (CHBr₃), 0.53 pptv (CHBr₂Cl), 0.91 pptv (CHBrCl₂), and 1.2 pptv for CH₂Br₂ (Fig. 1). As a comparison, studies of bromocarbons in air in the Arctic region before polar sunrise measured concentrations of CHBr₃, CHBr₂Cl, CHBrCl₂, and CH₂Br₂ to be 2.6, not detected, 0.3 and 0.8 pptv, respectively. After sunrise, the concentrations dropped by half for CHBr₃, whereas the concentrations remained fairly constant for the other compounds18. Compared with observations made in the summertime in the Southern Ocean19, the average winter air concentration of bromoform was ca. 10 times higher. Similarly, the maximum concentration of CH₂Br₂ found in winter was 2.9 pptv compared with 1.4 during summer and that of CHBrCl₂ was 2.5 pptv in summer19. The boundary layer in Antarctica during winter is much lower than over open ocean20, therefore these bromocarbon fluxes could lead to lower air concentrations under higher boundary layer height conditions. The variations in concentration were not related to wind direction. Backward air mass trajectories revealed that the dominant wind direction was from West and South (Supplementary Figure 1). We note that the highest air concentrations occurred at low wind speeds (< 6 m s⁻¹) (Fig. 1) associated with stable shallow boundary layer20.

In addition to the air observations, sharp concentration gradients in the vertical profiles of bromocarbons in sea ice and snow were observed, with highest values at the ice–snow interface (Fig. 2, Supplementary Figure 2). This implies that the observed bromocarbons were formed at the interface and diffused out of the snow. Sharp concentration gradients have previously been observed in Arctic sea ice during spring with similar distribution patterns in sea ice21 and snow22. Note that on one location (Station 500) one of the coring sites was flooded, which led to slightly different profiles, as indicated by the high salinity found close to the sea ice interface (Supplementary Figure 2, Supplementary Table 2–3). The highest concentrations found at the interface during the Antarctic winter were 1200, 1100, 270, and 18000 pM for CH₂Br₂, CHBr₂Cl, CHBrCl₂, and CHBr₃, respectively (Fig. 1), which can be compared with summer sea ice maximum values of 90, 14, 42, and 420 pM, respectively23. During summer, the depth profiles differed with bromocarbon concentrations varying to a large extent with chlorophyll-a23. The complete set of air, snow, and sea ice concentrations for all stations, salinity, temperature, and brine volume data are given in Supplementary Tables 2–4. Together with the air observations, the measured profiles across snow and sea ice show that bromocarbons are produced locally in the Antarctic winter sea ice.

Discussion

We now turn to the mechanism behind the observed production of bromocarbons in winter sea ice. The natural formation of bromocarbons has previously been demonstrated to be light dependent2, and include enzymatic pathways that rid cells of reactive oxygen species formed mainly during photosynthesis.
The reduction of hydrogen peroxide by haloperoxidases results in the formation of hypohalous acids, such as HOBr, which subsequently reacts with dissolved organic matter, forming bromocarbons. Laboratory experiments have shown that there is an abiotic pathway for HOBr production through the reaction of ozone with bromide that occurs in darkness. This proceeds via ozone deposition to the ice surface followed by oxidation of bromide. On ice surfaces, a disordered layer of molecules exist, which has been shown to favor halogen interactions. Also, the freezing of seawater enhances the ionic strength that leads to enhanced rates of chemical reactions. Recent investigations have shown that the oxidation of bromide by ozone involves the formation of the intermediate ozonide Br-OOO⁻ in aqueous bulk solution with a preference for the liquid–gas interface, and the authors conclude that the oxidation of bromide on surfaces plays a more important role than previously thought.

Subsequently, a number of different organic compounds such as ketones, phenols, alkenes etc., can react with HOBr to form bromocarbons. Therefore, the differences in organo-bromine concentrations found in our ice cores can be due to differences in composition of the organic compounds being brominated. The similarities in depth profiles within the sea ice between the individual bromocarbons indicate similar formation mechanisms for all four investigated bromocarbons.

Micro-organisms could also be responsible for the bromocarbon production, as they have been shown to be active in sea ice during winter. For instance, if the enzymatic pathways are active, the stress caused by the measured high salinity at the ice interface, low temperatures, and/or inclusion in the ice lattice could increase the production, and contribute to the high concentrations of bromocarbons found at the snow/ice interface. Hence, although little is known about how bromocarbons form under darkness, our results provide a strong case, for the first time, that first year Antarctic sea ice has extremely high bromocarbon concentrations at a period with no sunlight.

Next, the magnitude of the release of individual bromocarbons from the ice surface to the atmosphere was calculated based on the assumption that the bromocarbons were formed on the
surface of sea ice and subsequently diffused through the snow to the atmosphere. The interstitial air concentrations were calculated from the concentrations found in melted snow, the fraction of water and air, respectively, and the Henry’s law constants (Methods). We found the concentration gradient in snow to decrease linearly (Fig. 2, Supplementary Table 4). Adsorption and desorption studies of halocarbons (i.e., CHCl3 and CHBr3) on ice revealed that CHBr3 is mobile at temperatures as low as 85 K, with the effective diffusivities calculated for SF6 in snow at Summit, Greenland32. The median ice show that the median concentrations are low (0.5 − 8 pptv) and required sample pre-treatment. The variations in concentrations during the above described measurements are exemplified in Supplementary Figure 3. At station 506 the concentrations of CHBr3 varied between 20 and 100 pptv with the highest values at midnight. These variations were related to wind speed. Around midnight the wind speed dropped from ca 7 m s$$^{-1}$$ to ca 1 m s$$^{-1}$$ to, later in the night, increase again to ca 9 m s$$^{-1}$$. This trend was valid for all bromocarbons (positive linear regression between bromocarbons and wind speed dropped from ca 7 m s$$^{-1}$$ to ca 1 m s$$^{-1}$$ to, later in the night, increase again to ca 9 m s$$^{-1}$$. This trend was valid for all bromocarbons (positive linear regression between bromocarbons and wind). As no earlier attempts have been made to estimate the flux of bromocarbons from sea ice surfaces through snow to the atmosphere we here performed calculations using an established

**Table 1 Estimated flux of bromocarbons from sea ice**

| Flux (nmol m$$^{-2}$$ h$$^{-1}$$) stations without snow | Flux (nmol m$$^{-2}$$ h$$^{-1}$$) stations with snow (n = 9) |
|-------------------------------------------------|-------------------------------------------------|
| CH2Br2  | Range 20; 50  | 0.5-7  |
| Median  | Median 2      | 1      |
| CHBrCl2 | Range 3; 5    | 0.1-8  |
| Median  | Median 1      | 2      |
| CHBrCl2 | Range 50; 70  | 0.5-8  |
| Median  | Median 2      | 2      |
| CHBr3   | Range 800; 1700 | 8-200  |
| Median  | Median 50     |        |

The fluxes were calculated utilizing the diffusion through snow calculations.

1 Stations 488 and 489 had no snow cover
2 Stations 493-506 had a snow cover of 5-40 cm

![Fig. 2 Profiles of brominated halocarbons (CHBr3, CH2Br2, CHBr2Cl, and CHBrCl2) in sea ice and snow. Data from station 506 include eight sea ice core profiles and four snow profiles. The line at 0 cm indicates the sea ice–snow interface. The total snow depth was 17 cm. The complete concentration data set is found in Supplementary Tables 3-5.](image-url)
method for calculating sea-air fluxes, utilizing the upper most sea ice values instead of seawater concentrations and the air concentrations measured in the snow closest to the ice surface. For stations 488 and 489 that did not have any snow cover (Table 1) we used the measured wind speed. We found that the two methods (Methods) produced median values of flux estimates in the same order of magnitude at the stations where multiple cores were sampled (Supplementary Table 5). This fact could be seen as an indirect evidence that the flux through snow could be sustained by the sea ice surface. In Fig. 1, the snow concentrations could be compared with the upper most layer of the sea ice. In general, the higher the concentration in sea ice the higher the values in snow (Supplementary Tables 2–3, Fig. 2 and Supplementary Figure 2). A principal component analysis (Supplementary Figure 4) also reveals that the highest concentrations of bromocarbons were found in the upper most part of the core and in the snow closest to the ice. The variability in sea ice is known to be one major obstacle for extrapolating physical, chemical, and biological properties. On kilometer scales, it can be concluded that the distribution pattern was consistent in the seasonal ice. However, there was a large variation in the concentrations of individual bromocarbons in snow and surface sea ice, which was reflected in the calculated fluxes which varied with one order of magnitude. The variability on meter scales showed less variation (Supplementary Table 5). The snow concentrations were clearly linked to the surface concentrations in sea ice (Fig. 1), and thereby the magnitude of the flux. At station 500, where parts of the flow were flooded, the lowest concentrations were found and also the lowest flux. Predicted global sea to air fluxes of CHBr₃ and CH₂Br₂ in the Southern Ocean are lower than our ice–snow–air fluxes by several orders of magnitude. This demonstrates that areas covered with seasonal ice are potential foci for bromocarbons to the atmosphere, even in the absence of sunlight. Figure 3 depicts a simplified schematic of the ice–snow–air interface and the suggested release mechanisms of organic bromine from Antarctic winter sea ice to the atmosphere.

We now use a state-of-the-art global chemistry-climate model constrained with the observed bromocarbons fluxes during the period of measurements and over Antarctic first year sea ice (Methods). The results show an accumulation of brominated halocarbons in the atmosphere during the polar winter until the austral sunrise in August when photodecomposition starts to reduce the bromocarbon concentrations (Fig. 4, Supplementary Figures 5, 6, 7). Remarkably, since bromocarbons are relatively long-lived (weeks to months) the winter emissions of bromocarbons spread to lower latitudes and even to the stratosphere, adding to the global atmospheric bromine burden. Consideration of this new source of polar bromine requires re-assessment of the bromine-mediated impacts on the global tropospheric ozone budget and mercury deposition.

Methods

Halocarbon measurements. Data were collected during the ANTXXIX/6 expedition conducted during austral winter aboard the R.V Polarstern from 8 June to 12 August 2013 in the Weddell Sea (Supplementary Figure 1). Samples of ice, snow, and brine, were collected at nine different stations, during the dark period of the cruise (Supplementary Table 1). At stations 500 and 506, multiple samples were collected over two or more days. A Mark II coring system from Kovacs Enterprise with a diameter of 0.09 m made out of a light weight filament wound composite tube with plastic coiling was used. Ice cores were divided into 10 cm sections and individually packed in gas-tight Tedlar® bags. The air surrounding the sample was removed from the bags using a manual pump according to Granfors et al. The ice samples were thawed in darkness at room temperature for ~24 h. Snow samples were collected as close as possible to the ice coring site (maximum distance ca 10 m) and divided into ~10 cm sections, individually packed in gas-tight Tedlar® bags. The snow samples were thawed in darkness at room temperature for ~12 h. The halocarbon compounds CHBr₃, CH₂Br₂, CHClBr, and CHClBr₂ were quantified. They were pre-concentrated using three purge-and-trap systems: Velocity XPT (Teledyne Tekmar) connected to an autosampler (AQUAtik®, Teledyne Tekmar), and two custom-made purge-and-trap system, which were coupled to gas chromatographs with electron capture detection (Varian 3800), according to the methods described by Mattsson et al. One of the custom-made purge-and-trap instruments (custom-made system 1 Supplementary Table 6) was equipped for air sample analysis in addition to water sample analysis. Air was continuously drawn through a 100 m, 4 mm inner diameter, Teflon tube by an air pump located downstream from the sampling loop. This instrument was also fed with a continuous stream of water from the ship's surface water inlet.
system was set up to automatically alternate between water and air sampling. The systems were calibrated with external standards of CH$_2$Br$_2$ (Merck, 99%), CHBrCl$_2$ (Fluka, > 98%), CH$_2$ClI (Fluka, > 97%), CHBr$_2$Cl (Fluka, > 97%), and CHBr$_3$ (Merck, > 98%) diluted from stock solutions in methanol (Sigma-Aldrich, suitable for purge-and-trap analysis) in seawater to give final concentrations in the picomolar range in the purge chamber. The same standard solutions were used for calibration of air measurements. The detection limits of the systems are given in Supplementary Table 6. The overall repeatability for individual compounds was between 1% and 5%. The three instruments were inter-calibrated using standards as well as samples with high and low concentrations of the compounds.

Fig. 4 Modeled distribution of monthly averaged tropospheric (CHBr$_3$, CH$_2$Br$_2$, CHBr$_2$Cl, and CHBrCl$_2$) over the Southern Hemisphere. This spatial distribution is the result of sea ice emissions of bromocarbons during the Antarctic winter using the averaged fluxes of bromocarbons from Table 1 (flux in stations with snow)
Sea ice temperatures were measured immediately after the ice core was recovered at 15 cm intervals using a digital thermometer, Amadigit, resolution 0.1°C (summer expedition) and a high precision RTD thermometer with a Pt100 temperature sensor with an accuracy of ±0.1°C (winter expedition). Salinity and conductivity of the melted sea ice were measured using a conductivity meter, WTWCond30i or 3210, with a precision and accuracy of ±0.1.

Brine volume ($v_b$) was derived from ice temperature ($T_i$) and bulk salinity ($S_b$) according to the equation of Frankenstein and Garner [1967] $v_b = S_b(0.0532 - 4.919/T_i)$ (Eq. 1).

For presentation of the vertical distribution of halocarbons in sea ice, halocarbon concentrations in bulk ice were divided by the brine volume calculated for each sample. This brine normalized concentration represents the estimated concentration of halocarbons in the sea ice brine.

**Flux calculations.** Stations 493–506 had a snow cover of 5–40 cm. Vertical profiles in snow (thickness > 10 cm) indicated that the snow was ventilated above this level. The interstitial air concentrations were calculated from the measured concentrations in melted snow, the volume of air and water in the samples and the Henry’s law constant at ambient temperature. The linearly decreasing concentrations in snow along with the following air diffusion coefficients were used to calculate fluxes according to Fick’s first law (Eq. 2) for CHBr$\text{}_3$, CHBr$\text{}_2$Cl, CH$\text{}_2$Br$\text{}_2$, CHBrCl$\text{}_2$ and CHBrCl$\text{}_3$.

\[
\text{Flux} = D_{\text{air}} \times \frac{\nabla c}{z} (2)
\]

where $X$ is the individual concentration of bromocarbons, $D_{\text{air}}$ the molecular diffusivity and $z$ the snow depth.

To compare, fluxes were also derived using a sea-air flux model according to Waninkoff and McGillis. The Schmidt numbers were calculated based on brine salinities and ice surface temperatures. Henry’s law constants were calculated according to Moore et al. The air concentrations used in the calculations were those from the air measured in snow closest to the ice surface. This exercise yielded median fluxes of the bromocarbons CHBr$\text{}_3$, CHBr$\text{}_2$Cl, CH$\text{}_2$Br$\text{}_2$, CHBrCl$\text{}_2$ and CHBrCl$\text{}_3$ of 70, 15, 0.4, and 4 nmol m$^{-2}$ h$^{-1}$ respectively.

### Table 2 Measured and modeled surface air bromocarbon concentrations

| Bromocarbon species | Measured range/ Modeled range/ |
|---------------------|--------------------------------|
| CHBr$\text{}_3$     | nd−32                          |
|                     |                                |
| CHBr$\text{}_2$Cl   | 0.1−3.2                        |
| CH$\text{}_2$Br$\text{}_2$ | 0.3—3.2                 |
| CHBrCl$\text{}_2$   | 0.1—1.9                        |
| CHBrCl$\text{}_3$   |                                |

The modeled values correspond to a layer 0–200 m. Altitude for the same date and location of the measurements.

The CAM-Chem model. The model employed in this work is the global 3-D chemistry-climate model CAM-Chem (Community Atmospheric Model with chemistry, version 4.0) to assess the impact of the measured bromocarbons emissions upon the distribution of bromocarbons and reactive bromine throughout the southern hemisphere. The model includes a comprehensive chemistry scheme to simulate the evolution of trace gases and aerosols in the troposphere and the stratosphere. The model runs with the iodine and bromine chemistry schemes from previous studies, including the photochemical breakdown of bromo- and iodo-carbons emitted from the oceans and abiotic oceanic sources of HOI and I$_2$.

For this work, emissions of CHBr$\text{}_3$, CH$\text{}_2$Br$\text{}_2$, CHBrCl$\text{}_2$, and CHBrCl$\text{}_3$ from Antarctic first year sea ice at SZA higher than 90° have been implemented, according to measured fluxes. These emissions are only active during the campaign time period (18 June to 14 July), as a linear function of first year sea ice fraction. CAM-Chem has been configured in this work with a horizontal resolution of 1.9° latitude by 2.5° longitude and 26 vertical levels, from the surface to ~40 km altitude. All model runs in this study were performed in the specified dynamics mode using offline meteorological fields instead of an online calculation, to allow direct comparisons between different simulations. This offline meteorology consists of a high-frequency meteorological input from a previous free running climatic simulation. The MERRA reanalysis data is used in the model to supply the implemented sea ice fields.

Data availability

The code and data that support the findings of this study are available upon request.

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Author contributions
K.A., A.G., and M.A. conceived the experiments, participated in the cruise, and sampled and interpreted all halocarbon data. C.A.C. and A.S.L. performed the atmospheric modeling. All authors interpreted the results and contributed to writing the manuscript.

Additional information
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