Regional sinks of bromoform in the Southern Ocean

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[1] Bromoform in surface water and air was measured in the Pacific sector of the Southern Ocean during the austral summer 2007/2008 onboard research vessel icebreaker Oden. Highest concentrations and oversaturation in water were found over the continental shelves and close to the sea-ice edge in the Bellingshausen Sea. In open ocean areas, concentrations were comparably low, and the water was undersaturated. Air mixing ratios in these regions were influenced by surrounding areas as revealed by wind back trajectories. For wind that had travelled over coastal regions, thawing sea-ice, or areas with elevated chlorophyll concentrations, increased bromoform levels in air were found in the downwind direction. The results show the importance of high spatial and temporal resolution in measurements for assessments of air-sea exchange of short-lived compounds with strong local sources. As surrounding waters can act as a sink, the atmospheric load of such sources may be overestimated. Citation: Mattsson, E., A. Karlsson, and K. Abrahamsson (2013), Regional sinks of bromoform in the Southern Ocean, Geophys. Res. Lett., 40, 3991-3996, doi:10.1002/grl.50783.

1. Introduction

[2] Bromoform is the major biogenic volatile halogenated organic compound (VHOC) produced in the ocean by macro and micro algae [Gribble, 2003; Quack and Wallace, 2003]. It contributes to the pool of atmospheric inorganic bromine involved in the degradation of tropospheric and stratospheric ozone [Solomon, 1999; WMO, 1999]. Polar regions are of special concern because of their vulnerability to climate change [Anisimov et al., 2007], and this will most likely affect the air-sea gas exchange of VHOCs through changes in production rates and solubility. Even if bromoform has its strongest source in the ocean, the direction of the flux is not necessarily from water to air in these regions, which is mainly due to high solubility due to the low sea surface temperature. Studies have shown that Antarctic surface waters can act both as a source and a sink [Butler et al., 2007; Chuck et al., 2005; Hughes et al., 2009; Mattson et al., 2012; Quack and Wallace, 2003].

[3] Concentrations of bromoform in air and water show high spatial and temporal variability, since it is short lived in the atmosphere, biologically produced, and degraded in the water column. Therefore, high-spatial-resolution measurements are necessary to establish the air-sea exchange. Due to this high variability, the use of averaged bromoform concentrations over time and space will induce large errors. Carpenter et al. [2007] used monthly averaged air concentrations for the estimation of bromoform fluxes, which eliminated the diurnal variations, as have been described in other studies [Abrahamsson et al., 2004; Ekdahl et al., 1998; Karlsson et al., 2008; Yokouchi et al., 2011]. Hughes et al. [2009] also used averaged air concentrations for parts of their flux calculations, although they acknowledged the spatial and temporal variability. The variability in phytoplankton community is also a factor to consider. Smith et al. [1999] measured daily variations in phytoplankton growth rates in the Ross Sea. The finding of a coupling between increased production rates of bromoform in connection to an exponential growth phase of phytoplankton algae [Tokarczyk and Moore, 1994], together with the diurnal variation in phytoplankton growth rates, also emphasizes the importance of high-temporal-resolution data. Coastal macro algae may also contribute to spatial heterogeneity in the distribution of CHBr₃, as they are known to produce substantial amounts of CHBr₃ [Laturnus et al., 1996; 1997].

[4] Air-sea flux can be estimated from the deviation from saturation and the wind-dependent gas transfer velocity. Uncertainties in the latter depend on a number of factors such as turbulence, bubble effects [*Woolf*, 1997], and surfactants [*Nightingale et al.*, 2000; *Smith et al.*, 2011; *Wanninkhof et al.*, 2004]. Errors in the estimates can also be introduced when averaged wind speeds are used. Gas transfer velocity parameterizations usually rely on a quadratic or cubic relationship on wind speed, and the use of monthly averaged values of wind speed therefore induces large biases in models as has been seen in studies of CO₂ uptake [*Kettle and Merchant*, 2005; *Lüger et al.*, 2006].

[5] In this article, we present spatial variations of CHBr₃ in air and surface waters in the Pacific sector of the Southern Ocean—Drake Passage and Bellingshausen Sea, from the Oden Southern Ocean 2007 (OSO07) expedition. The effect of wind direction on the air-sea exchange was investigated by the use of wind back trajectories. This was shown to be a key parameter in order to understand the variation in the air-sea flux.

2. Experimental

[6] The expedition Oden Southern Ocean 2007 (OSO07) was conducted with the research vessel icebreaker (RVIB) *Oden* from December 2007 to January 2008, starting in Punta Arenas, Chile, and ending in McMurdo Sound, Ross Sea. A total of 96 pairwise measurements of surface water and air covering the most southerly parts of the South American coast, Drake Passage, Antarctic Peninsula, and the Bellingshausen Sea were performed (Figure 1). Real-time meteorological data and measurements of sea ice coverage, surface water temperature, and salinity were collected.

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Figure 1. Cruise track of the OSO07 expedition. The division of the cruise track into five geographical regions is made with respect to geographical similarity and water depth. Diamonds represents measurements on the continental shelf of the Coastal South America (CSA, n = 7, cruise time ~7 h). Crosses represent samples in the Drake Passage (DrP, n = 20, ~26 h). Black circles represents Coastal Antarctica (CA, n = 23, ~30 h). White triangles represent Antarctic Open Ocean (AOO, n = 26, ~34 h), and black squares represent Antarctic Sea Ice Edge (ASE, n = 19, ~44 h).

Alternating water and air measurements were performed every 40 min with a custom-made purge and trap system connected to a gas chromatograph with an electron capture detector. The system used, analyzing methods including calibration procedures, detection limits, and drift are described in *Mattson et al.* [2012].

[7] Saturation anomalies were derived from concentrations in water (C_w) and air (C_a) and calculated with the temperature-dependent Henry's law constants (*H*) given by *Moore et al.* [1995]. Air-sea flux (*F*, equation (1)) was calculated with the *Nightingale et al.* [2000] parameterization of transfer velocity (*k*, equation (2)).

$$F = k \times \left(C_w - \frac{C_a}{H} \right) \tag{1}$$

$$k = \left(0.222 \times U_{10m}^2 + 0.333 \times U_{10m}\right) \times \sqrt{\frac{600}{Sc}}$$
(2)

[8] Schmidt (*Sc*) numbers were calculated from seawater density, dynamic viscosity, and the compound-specific diffusion coefficient [*Hayduk and Minhas*, 1982], with molar volume at normal boiling temperature estimated according to *Sastri et al.* [1997]. Actual wind (1 min average) (U_d) was measured at 40 m (= d), and the 10 m wind (U_{10m}) was calculated according to

$$U_{10m} = U_d \times \frac{\ln(10/z_0)}{\ln(d/z_0)}$$
(3)

with a roughness length (z_0) of 2.5 × 10⁻⁴ m [*Högström et al.*, 2006]. Wind back trajectories were estimated with HYSPLIT 4 (Hybrid Single Particle Lagrangian Integrated Trajectory

Model) software [*Draxier and Hess*, 1997; 1998], with Global Data Assimilation System meteorological data, provided by the NOAA-Air Resources Laboratory (ARL), ftp://arlftp.arlhq.noaa.gov/pub/archives/gdas1.

3. Results and Discussion

[9] We investigated the distribution of CHBr₃ in five different geographical regions in the Pacific sector of the Southern Ocean: Coastal South America (CSA), Drake Passage (DrP), Coastal Antarctica (CA), Antarctic Open Ocean (AOO), and the Antarctic Sea Ice Edge (ASE) (Figure 1). Mean air and surface water concentrations, saturation anomalies, and fluxes were compared for the different areas (Table 1). Measured water and air concentrations varied between 6.7 to 81 pmol L⁻¹ and 0.55 to 11 parts per trillion by volume (pptv), respectively (Table 1 and Figure 2). Both under- and oversaturated regions were identified (Figure 2 and Table 1), with saturation anomalies ranging from, at most, -79% to 130%. The calculated momentary flux of CHBr₃ to the atmosphere varied between -3 and 4 nmol m⁻² h⁻¹.

[10] The five geographical regions were found to be different in the distribution of bromoform. The largest source of bromoform, which corresponded to an average flux of 1.3 nmol m⁻² h⁻¹ to the atmosphere, was found in CSA (Table 1 and Figure 2). The regions DrP and AOO were found to be undersaturated to a large extent, with an average uptake of 0.66 and 0.45 nmol m⁻² h⁻¹, respectively. CA and ASE showed both regional fluxes of CHBr₃ to the atmosphere (0.2 and 1 nmol m⁻² h⁻¹, respectively) and areas that acted as sinks (-2 and -3 nmol m⁻² h⁻¹). In an earlier publication by *Mattson et al.* [2012], saturation anomalies of

| Region | | CHBr ₃ Air (pptv) | CHBr ₃ Water (pmol L ⁴) | Saturation Anomaly (%) | Flux (nmol m ⁻ h ⁻) | Water Temperature (°C) |
|------------------------|------------------|------------------------------|--|------------------------|--|------------------------|
| Coastal South America | Average Range | 7.4 1.8 to 11 | 43 12 to 81 | 35 -59 to 130 | 1.3 -0.6 to 4 | 6.7 6.3 to 7.1 |
| n = 7 | RSD (%) | 42 | 54 | | | |
| Drake Passage | Average Range | 3.1 1.8 to 6.6 | 9.9 6.9 to 13 | -42 -63 to 6 | -0.66 -2 to 0.07 | 2.9 -0.5 to 6.1 |
| n = 20 | RSD (%) | 7 | 13 | | | |
| Antarctic Coast | Average | 3.2 | 17 | -25 | -0.32 | -0.6 |
| <i>n</i> = 23 | Range RSD (%) | 2.1 to 4.9 23 | 9.8 to 29 26 | -62 to 26 | -2 to 0.2 | -0.8 to -0.3 |
| Antarctic Open Ocean | Average | 2.3 | 11 | -31 | -0.45 | -1 |
| n=26 | Range RSD (%) | 1.9 to 3.9 17 | 8.2 to 18 18 | -49 to -13 | -2 to -0.05 | -1.4 to -0.8 |
| Antarctic Sea Ice Edge | Average Range | 2.2 0.55 to 7.2 | 14 6.7 to 30 | -15 -79 to 100 | -0.42 -3 to 1 | -1.6 -1.8 to -1.2 |
| n = 20 | RSD (%) | 64 | 48 | | | |

Table 1. Comparison of Saturation Anomalies, Fluxes, and Concentrations in Water and Air for the Different Geographical Regions

CHBr₃ in the Amundsen and Ross polynyas have been presented. These two regions had an average uptake of 0.53 and 0.18 nmol m⁻² h⁻¹, respectively, which showed that the polynyas during this part of the Antarctic summer acted as sinks.

[11] Only a few studies on air-sea exchange of bromoform have been performed in waters south of 60°S [Butler et al., 2007; Carpenter et al., 2007; Chuck et al., 2005; Hughes et al., 2009]. Of these expeditions, BLAST III [Butler et al., 2007] is the most comparable one, since it was performed in the Pacific sector of the Southern Ocean (Table 2). The measured surface water concentrations were in the same range, $5.3-11 \text{ pmol } \text{L}^{-1}$, as in the present study $(6.4-15 \text{ pmol } \text{L}^{-1})$. The air concentrations from OSO07 were approximately two times higher (1.1–3.3 pptv), compared to BLAST III (0.5–1.4 pptv), which alters the saturation anomaly to more undersaturated surface waters in the present study. The major differences between the expeditions are the earlier onset and the more southerly cruise track of OSO07. Thereby, the cruise track brought us closer to the Antarctic coast, as well as the sea ice edge. This could explain the relatively higher concentrations measured in air, since coastal areas [Hughes et al., 2009] and areas covered by sea ice have been shown [Mattson et al., 2012] to have elevated concentrations of CHBr₃ in both water and air. The earlier onset of the expedition may also affect the distribution of CHBr₃, since the spring bloom takes place in November to December.

[12] The finding that the waters of the Antarctica act as sinks for bromoform contradicts the general view that seawater is most often oversaturated. For instance, Carpenter et al. [2007] estimated an average saturation anomaly of 783% in the Weddell Sea, and Hughes et al. [2009] found saturation anomalies between -50% and 637%. Our results showed that the direction of the fluxes mostly were negative, i.e., surface waters generally were taking up CHBr₃, and that the downward fluxes in these areas to a large degree were determined by the variation of CHBr3 in air rather than in water. An indication of the influence of air on undersaturated samples could be seen in the larger spread in air compared to water (relative standard deviation (RSD) of 46% and 26%, respectively) for these samples. Also, a linear trend was shown between air concentrations and negative saturation anomalies ($R^2 = 0.78$, n = 71). The corresponding trend for CHBr₃ in water was much weaker ($R^2 = 0.09$, n = 71).

Positive saturation anomalies were only found in 24 out of 95 of the pairwise measurements, and no similar relationship could be found. The spread in concentrations for these measurements was similar for air and water (RSD of 77% and 69%).

[13] To further investigate where the elevated air concentrations may have had their sources, back trajectories calculated for a period of 24 h were used (Figure 2, middle panel). In the CSA region, the highest concentrations in air and water were found (Table 1), which led to an oversaturation of up to 130%. The back trajectories in the area marked as A and B (Figure 2) showed that the wind traveled from this region out over the Drake Passage with relatively high concentrations of CHBr₃, which led to an undersaturation across the DrP. The elevated surface water concentrations of CHBr₃ in the CSA region may be related to a macro algae production [Ekdahl et al., 1998; Manley et al., 1992; Nightingale et al., 1995; Pedersén et al., 1996]. The satellite image of chlorophyll a concentrations (Figure 2, lower panel) indicated high primary production in these coastal areas, which may contribute to the elevated CHBr₃ concentrations.

[14] In the CA region, the distribution of CHBr₃ was influenced by shifts in the wind direction, which caused either over- or undersaturated waters. Back trajectories revealed two major wind directions: the air was coming either from the open ocean (C, Figure 2) or from the coastal parts of the Bellingshausen Sea (D, Figure 2). Lower mixing ratios (in average 2.8 pptv (n=11)) were observed for air that came from the open ocean, compared to the coastal air (in average 3.5 pptv (n=13)). The lower mixing ratios in air transported over the open ocean have also been acknowledged by Quack and Wallace [2003], who concluded that "clean marine air" contains ~1 pptv of CHBr₃. The elevated concentrations in coastal air may have originated from both micro and macro algae production in the coastal Bellingshausen Sea, which is supported by the findings of Hughes et al. [2009], Laturnus et al. [1996], and Reifenhäuser and Heumann [1992].

[15] At the sea ice edge (ASE) in the western part of the Bellingshausen Sea, the flux direction was influenced by winds of a more complex nature (E and F, Figure 2). Also, rather dramatic changes in both air and water concentrations were found, which lead to a variable situation with rapid shifts between over- and undersaturated states. The air concentration, when the wind was coming from over the ice



Figure 2. Measured bromoform concentrations in (bottom) the surface water (pmol L^{-1}) and (middle) air (pptv). (top) The bromoform saturation anomaly as percentage. Yellow bars represent oversaturation, where slightly whiter color illustrates higher oversaturations. Red bars show the undersaturation, where slightly whiter color illustrates a more negative undersaturation. In addition, the onboard measured wind directions/speed is shown as white arrows in the top panel. In the middle panel, 24 h back trajectories are shown as black lines. Major wind-field directions are shown as transparent red arrows, marked as A, B, C, D, E, and F. The white polygon in the middle panel represents the median sea ice extent for December 2007. In the lower panel, the color of the ocean surface illustrates the monthly mean of chlorophyll concentrations for December 2007 (Aqua/MODIS, http://neo.sci.gsfc.nasa.gov/).

| Table 2. | Comparison of Measured CHBr ₃ | Concentrations in Southern | Ocean (65°W-165°E | e, 55°S–74°S), Satu | ration Anomaly, and | l Flux |
|----------|--|----------------------------|-------------------|---------------------|---------------------|--------|
| (OSO07, | n = 275) | | | | | |

| Expedition | | CHBr ₃ Air (pptv) | CHBr ₃ Water (pmol L ⁻¹) | Saturation Anomaly (%) | Flux (nmol $m^{-2} d^{-1}$) |
|------------------------|-------------|------------------------------|---|------------------------|------------------------------|
| OSO07a | Mean | 2.2 | 10 | -31 | -8 |
| | Median | 1.9 | 8.1 | -31 | -4 |
| | Range (90%) | 1.1 to 3.3 | 6.4 to 15 | -56 to 7 | -20 to 1 |
| Blast III ^b | Mean | 0.9 | 8.1 ^c | 48 ^d | 5.4 ^e |
| | Median | 0.9 | 7.8° | 27 ^d | 4.4 ^e |
| | Range (90%) | 0.5 to 1.4 | $5.3^{\rm c}$ to $11^{\rm c}$ | 12 ^f to 140 | -7.6 to 32^{e} |

^aData excluded CSA and data included from *Mattson et al.* [2012].

^bData retrieved from Blast III expedition 1996 [*Butler et al.*, 2007].

^cRecalculated from mixing ratios (pptv) given in *Butler et al.* [2007].

^dSaturation anomaly values were calculated by *Butler et al.* [2007] by comparing mean values in air and water for the whole cruise, not by the pairwise method of deriving saturation anomaly.

^eFlux calculations made with different transfer velocity parameterization.

^fBlast III data set indicates possible wrong sign.

(F, Figure 2), reached levels of 7.2 pptv, with undersaturation as a result. As can be seen from Figure 2, these high values were followed by mixing ratios of under 1 pptv, which shifted the system to an oversaturated state. Sea ice algae are known to produce substantial amounts of CHBr₃ [*Schall et al.*, 1996; *Sturges et al.*, 1993]. Therefore, high mixing ratios in air as well as increased concentrations in surface waters could be attributed to processes related to algal activity in the surface water or in the sea ice.

[16] The rapid changes in saturation anomalies observed during the cruise took place on time scales of a few hours, which indicates that rapid changes in the wind direction can shift an area from being a source of atmospheric CHBr₃ to acting as a sink or vice versa. This also has implications on the use of average mixing ratios for flux calculations, as such features may be lost.

4. Conclusions

[17] At the onset of the expedition, our hypothesis was, as concluded in other studies, that waters around the Antarctica act mainly as a source for bromoform. From the data shown, we can infer that the waters of the Pacific sector more often served as a sink. This was mainly due to the high variability of bromoform air concentrations. The rapid changes in wind directions, and thereby the source of air concentrations, could be discerned due to the simultaneous measurements of air and water. The water concentrations were shown to be fairly constant in the different areas, but differences of 0.5–1 pptv in air could change the direction of the air-sea exchange dramatically. It is therefore essential to collect high spatial and temporal resolution air measurements in order to make accurate estimates of the fluxes.

[18] We do not dispute the fact that the oceans are a source of bromoform, but we emphasize that expeditions only give a snapshot in time and space. Bromoform is produced in surface waters, coastal areas, and sea ice as described by many studies, but this may not be reflected in calculations for a given site. Also, a local high production could be carried with the air to other regions, and the low temperatures of the surrounding waters can then act as local sinks. This fact could lead to wrong assumptions when estimating the magnitude of the source strength to the atmosphere from regionally constrained areas of high halocarbon production.

[19] We can also conclude that polynyas, with high primary productivity, did not act to any larger extent as a source of bromoform to the atmosphere. Instead, coastal areas and sea ice seem to be of more importance.

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