

## Contribution of sea ice in the Southern Ocean to the cycling of volatile halogenated organic compounds

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Received 15 April 2013; revised 18 July 2013; accepted 19 July 2013; published 15 August 2013.

[1] The contribution of sea ice to the flux of biogenic volatile halogenated organic compounds to the atmosphere in the Southern Ocean is currently not known. To approach this question, we measured halocarbons in sea ice, sea ice brine, and surface water of the Amundsen and Ross Seas. Concentrations in sea ice of these compounds, normalized to seawater salinity, ranged from 0.2 to 810 pmol L<sup>-1</sup>. Salinity-normalized chlorophyll *a* concentrations in the ice ranged from 3.5 to 190 μg L<sup>-1</sup>. Our results suggest biological production of halocarbons in sea ice, with maxima of halogenated organics and chlorophyll *a* commonly found in the interior of the ice cores. Iodinated VHOCs were found to be more enriched in sea ice than brominated ones. Furthermore, depth distributions indicated a transport of halocarbons from sea ice to air and underlying water.

**Citation:** Granfors, A., A. Karlsson, E. Mattsson, W. O. Smith Jr., and K. Abrahamsson (2013), Contribution of sea ice in the Southern Ocean to the cycling of volatile halogenated organic compounds, *Geophys. Res. Lett.*, 40, 3950–3955, doi:10.1002/grl.50777.

### 1. Introduction

[2] Volatile halogenated organic compounds (VHOCs) are known to be produced by marine phytoplankton and ice algae [Cota and Sturges, 1997; Tokarczyk and Moore, 1994]. The mechanism behind the formation of VHOC has been shown to be linked to photosynthesis through the enzymatic removal of hydrogen peroxide by haloperoxidases [Theiler *et al.*, 1978; Collén *et al.*, 1994; Tokarczyk and Moore, 1994]. These compounds are highly reactive, and because of the concentration gradient from the ocean to the atmosphere, the ocean and sea ice are sources of volatile organics to the atmosphere. After entering the atmosphere, they play an important role in atmospheric processes, as they catalyze ozone destruction and change the oxidizing conditions of the boundary layer, with significant consequences for climate and ecosystems [Abbatt *et al.*, 2012].

[3] Recently, it has been shown that variability in ozone is correlated with changing sea-ice concentrations [Gilman *et al.*, 2010; Jacobi *et al.*, 2010], which suggests that the catalytic loss of ozone by halogens may be related to sea-ice processes. Research on the role of sea ice in the formation of reactive halogens has in recent years focused on the inorganic chemistry of saline surfaces, where sea-salt halides are oxidized to more reactive forms [Simpson *et al.*, 2007]. VHOCs in sea ice of the Southern Ocean, originating from biogenic production by ice algae, have been studied to a lesser extent, and the magnitude of this biogenic source of halogens is poorly known. An indication of the importance of sea ice as a halocarbon source was given by Mattsson *et al.* [2012], who studied saturation anomalies of CHBr<sub>3</sub> and CH<sub>2</sub>ClI in Antarctic waters and concluded that sea ice was a source of naturally produced halocarbons to the atmosphere. In the Weddell Sea, Atkinson *et al.* [2012] found concentrations of iodocarbons in sea ice that were strongly enhanced relative to seawater, suggesting a significant local source within the sea ice.

[4] Although VHOCs are produced within the Antarctic sea ice, the question remains whether this source is significant in supplying halocarbons to the atmosphere relative to the flux from surface waters in leads and the open ocean. Measurements of gas diffusion rates through land-fast annual ice and pack ice near Barrow, Alaska in April and May were 30 cm h<sup>-1</sup> for halogenated gases at -15°C, and 60 cm h<sup>-1</sup> for CO<sub>2</sub> at -7°C, indicating the importance of gas migration within ice for ocean-atmosphere exchange [Gosink *et al.*, 1976]. Loose *et al.* [2011] studied diffusion of SF<sub>6</sub> and O<sub>2</sub> through laboratory sea ice, and concluded that gas ventilation of the mixed layer takes place primarily through fractures in the ice; however, during the transition from spring to summer, when warming conditions dominate, the permeability of gases in sea ice is expected to increase substantially.

[5] The sea ice in the Southern Ocean has a substantial annual biological production [Arrigo *et al.*, 1997; Lizotte, 2001], most of which occurs during austral spring. To understand of the role of Antarctic sea ice as a source of reactive halogen species, production and transport of VHOCs in and through the ice must be established. Few studies have focused on VHOCs in sea ice of the Southern Ocean, but this study provides the concentrations and distributions of nine biogenic volatile halogenated organic species produced in Antarctic summer sea ice in the Amundsen and Ross Seas. Chlorophyll *a* is used as a measure of the biomass of ice algae, and the relationship of the distribution of VHOCs to the distribution of chlorophyll *a* suggests biological production in sea ice. Furthermore, this relationship indicates that the production within the sea ice is nonuniform vertically.

Additional supporting information may be found in the online version of this article.

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0094-8276/13/10.1002/grl.50777

**Table 1.** VHOC and Chlorophyll *a* Concentrations<sup>a</sup>

Compound	Bulk Sea Ice <sup>b</sup> ( <i>n</i> = 199)	Sea Ice Normalized to Seawater Salinity <sup>c</sup> ( <i>n</i> = 198)	Brine <sup>d</sup> ( <i>n</i> = 14)	Brine Adjusted to Seawater Salinity ( <i>n</i> = 14)	Surface Water <sup>e</sup> ( <i>n</i> = 31)
CH <sub>3</sub> I	2.5 (0.34–46)	21 (1.9–260)	18 (7.9–35)	16 (7.2–32)	1.8 (0.56–4.8)
C <sub>2</sub> H <sub>5</sub> I	0.95 (0.16–132)	6.8 (1.3–570)	6.4 (1.1–19)	5.8 (1.0–17)	0.64 (0.11–3.0)
CH <sub>2</sub> Br <sub>2</sub>	1.8 (0.49–88)	15 (5.0–810)	88 (12–190)	80 (11–170)	5.1 (1.4–7.0)
1-C <sub>3</sub> H <sub>7</sub> I	1.5 (0.35–22) ( <i>n</i> = 146)	11 (2.0–230) ( <i>n</i> = 146)	18 (1.7–65) ( <i>n</i> = 13)	16 (1.6–59)	nd
CHBrCl <sub>2</sub>	0.51 (0.14–19)	3.6 (0.85–170)	7.3 (2.0–14)	6.7 (1.8–13)	1.4 (0.92–3.8)
CH <sub>2</sub> ClI	2.8 (0.047–62)	22 (0.61–410)	49 (1.1–99)	45 (1.0–90)	1.1 (0.26–2.9)
CHBr <sub>2</sub> Cl	0.68 (0.20–25)	4.4 (1.5–240)	15 (4.4–42)	14 (4.0–38)	1.6 (1.2–3.4)
CH <sub>2</sub> BrI	0.22 (0.023–21) ( <i>n</i> = 185)	1.6 (0.16–200) ( <i>n</i> = 184)	0.54 (0.052–1.8)	0.49 (0.047–1.6)	0.059 (0.013–0.21)
CHBr <sub>3</sub>	1.0 (0.12–30)	7.1 (1.1–270)	160 (23–420)	150 (21–380)	12 (7.9–22)
Chl <i>a</i>	4.3 (0.46–27) ( <i>n</i> = 111)	31 (3.5–190) ( <i>n</i> = 111)	1.90 (0.01–13) ( <i>n</i> = 16)	1.7 (0.009–12)	1.5 (0.12–9.7) ( <i>n</i> = 28)

<sup>a</sup>Units for VHOCs are in pmol L<sup>-1</sup>, and chlorophyll *a* concentrations are in μg L<sup>-1</sup>. Ranges indicated in parenthesis. *n* = number of observations; nd = no data.

<sup>b</sup>Median bulk ice concentration, where one sample represents one 10 cm ice core section.

<sup>c</sup>Median bulk ice concentration normalized for salinity (i.e., divided by bulk ice salinity and multiplied by seawater salinity). One sample represents one 10 cm ice core section.

<sup>d</sup>Mean concentrations from brine samples collected on stations 2, 13, 16, 18, 39, 40, and 41 at 40–60 cm depth.

<sup>e</sup>Mean surface seawater concentrations (10 m depth) from stations 1–41.

## 2. Materials and Methods

### 2.1. Study Area

[6] The 2008 Southern Ocean expedition (OSO08/09) was conducted from the *R.V.I.B. Oden* from 12 December 2008 to 7 January 2009. A total of 17 stations were occupied in the Amundsen and Ross Seas where sea ice distributions of VHOCs and ice-associated biota were assessed (Figure S1 in the supporting information). Samples of the brine within ice, as well as seawater from below the ice, were also collected.

### 2.2. Sampling and Analysis

[7] Ice samples for halocarbon analyses were collected using a stainless steel ice corer with a diameter of 0.12 m. All ice cores were divided into 10 cm sections and individually packed in gas-tight Tedlar<sup>®</sup> bags. After emptying the bags of surrounding air, the ice samples were thawed in darkness at room temperature for approximately 24 h. Sea-ice temperature was measured immediately after the ice core was recovered at 10 cm intervals using a digital thermistor (Amadigit) that had an accuracy of 0.1°C. At 7 of the 17 stations, brine was collected in “sackholes” at different depths between 40 and 60 cm from the surface of the ice. At the 10 other stations, brine sampling was impossible due to flooding and negative freeboard of the ice. Brine was incubated in Tedlar<sup>®</sup> bags at 0°C at an irradiance of 120 μmol photons m<sup>-2</sup> s<sup>-1</sup> for up to 19 h. The irradiance in the incubation bags was saturating for photosynthesis and autotrophic growth (W. O. Smith, unpublished data, 2008). All air was removed from the bags before the start of the incubations. Seawater samples were collected from 10 m using a SeaBird 911+ conductivity-temperature-depth profiler attached to a 24 Niskin bottle (10 L) rosette.

[8] Nine halocarbon compounds (CH<sub>3</sub>I, C<sub>2</sub>H<sub>5</sub>I, 1-C<sub>3</sub>H<sub>7</sub>I, CH<sub>2</sub>Br<sub>2</sub>, CH<sub>2</sub>BrCl<sub>2</sub>, CH<sub>2</sub>ClI, CH<sub>2</sub>Br<sub>2</sub>Cl, CH<sub>2</sub>BrI, and CHBr<sub>3</sub>) were quantified. They were preconcentrated with two purge-and-trap systems: Velocity XPT (Teledyne Tekmar) connected to an autosampler (AQUATEk70, Teledyne Tekmar) and a 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.* [2012].

[9] Chlorophyll *a* was measured in ice cores from stations 16, 21-1, 21-2, 27, 36, 39, 40, and 41. Water samples were collected and chlorophyll *a* determinations were assessed by fluorometry. Sea-ice algal chlorophyll was determined on 10 cm cores that were placed in clean plastic bags, melted in dim light at cool temperatures (0°C) in the laboratory, and filtered immediately upon complete melting. All samples were filtered through 25 mm Whatman GF/F filters using low (1/3 atm) vacuum. Filters were placed in 7 mL 90% acetone, extracted for at least 24 h in cold (~ -10°C), dark conditions, the filters removed, and the extracts read before and after acidification on a Turner Designs Model 700 fluorometer [Joint Global Ocean Flux Study, 1996]. The fluorometer was calibrated before and after the cruise using commercial standard solutions of purified chlorophyll *a* (Sigma), which in turn was quantified using high-performance liquid chromatography.

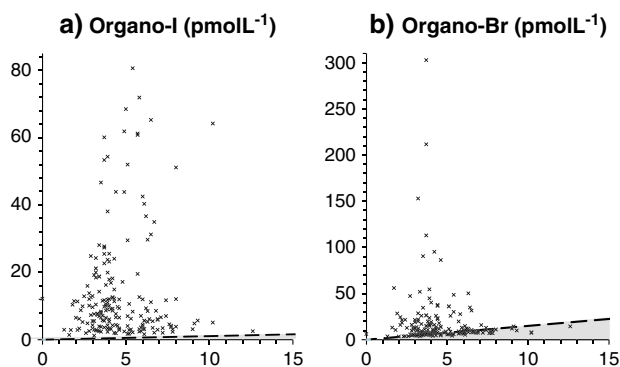
[10] Brine volume for ice temperatures between -22.9 and -0.5°C (*v<sub>b</sub>*) was derived from ice temperature (*T<sub>i</sub>*) and bulk salinity (*S<sub>i</sub>*) according to the equation of Frankenstein and Garner [1967] (equation (1)).

$$v_b = S_i(0.0532 - 4.919/T_i) \quad (1)$$

[11] Salinity and conductivity of the melted sea ice were measured using a conductivity meter (WTW Cond 330i, Germany) with a precision and accuracy of ±0.05. VHOC and chlorophyll *a* concentrations in bulk ice and brine were normalized to seawater salinity using equation (2)

$$C_s = (C_{\text{bulk}}/S_{\text{bulk}}) \times S_{\text{sw}} \quad (2)$$

where *C<sub>s</sub>* is the salinity-normalized concentration, *C<sub>bulk</sub>* the bulk ice VHOC or chlorophyll *a* concentration measured in the melted ice, *S<sub>bulk</sub>* the bulk ice salinity, and *S<sub>sw</sub>* the mean surface seawater salinity.



**Figure 1.** Total organic iodine and organic bromine in ice samples. Compounds included in calculation of total iodine and bromine are  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}_2$ ,  $\text{CH}_2\text{CII}$ ,  $\text{CH}_2\text{Br}_2\text{Cl}$ ,  $\text{CH}_2\text{BrI}$ , and  $\text{CHBr}_3$ .  $1\text{-C}_3\text{H}_7\text{I}$  was not included since it was not measured in surface seawater. Dashed line is the dilution line of (a) total organic iodine and (b) total organic bromine derived from the mean concentrations in seawater of the same compounds and represents a conservative dilution from seawater. The dilution line describes the theoretical dilution of VHOC concentration from saline seawater to the fresher melted bulk ice, and compounds with a conservative behavior would lie on the dilution line. Samples above the dilution line are enriched in iodine or bromine compared to seawater and below the dilution line demonstrates degradation in the ice.

### 3. Results and Discussion

[12] In total, 22 ice cores were analyzed for halocarbon content and 9 for chlorophyll *a*. At station 6, halocarbon concentrations were above the upper limit of detection. This core is, therefore, not included in the results. At station 35, concentrations of iodinated compounds were 10–50 times higher here than at the other stations. The ice may have been newly formed, and the differences in concentrations may have resulted from a highly favorable growth environment for the ice algae (e.g., no nutrient limitation).

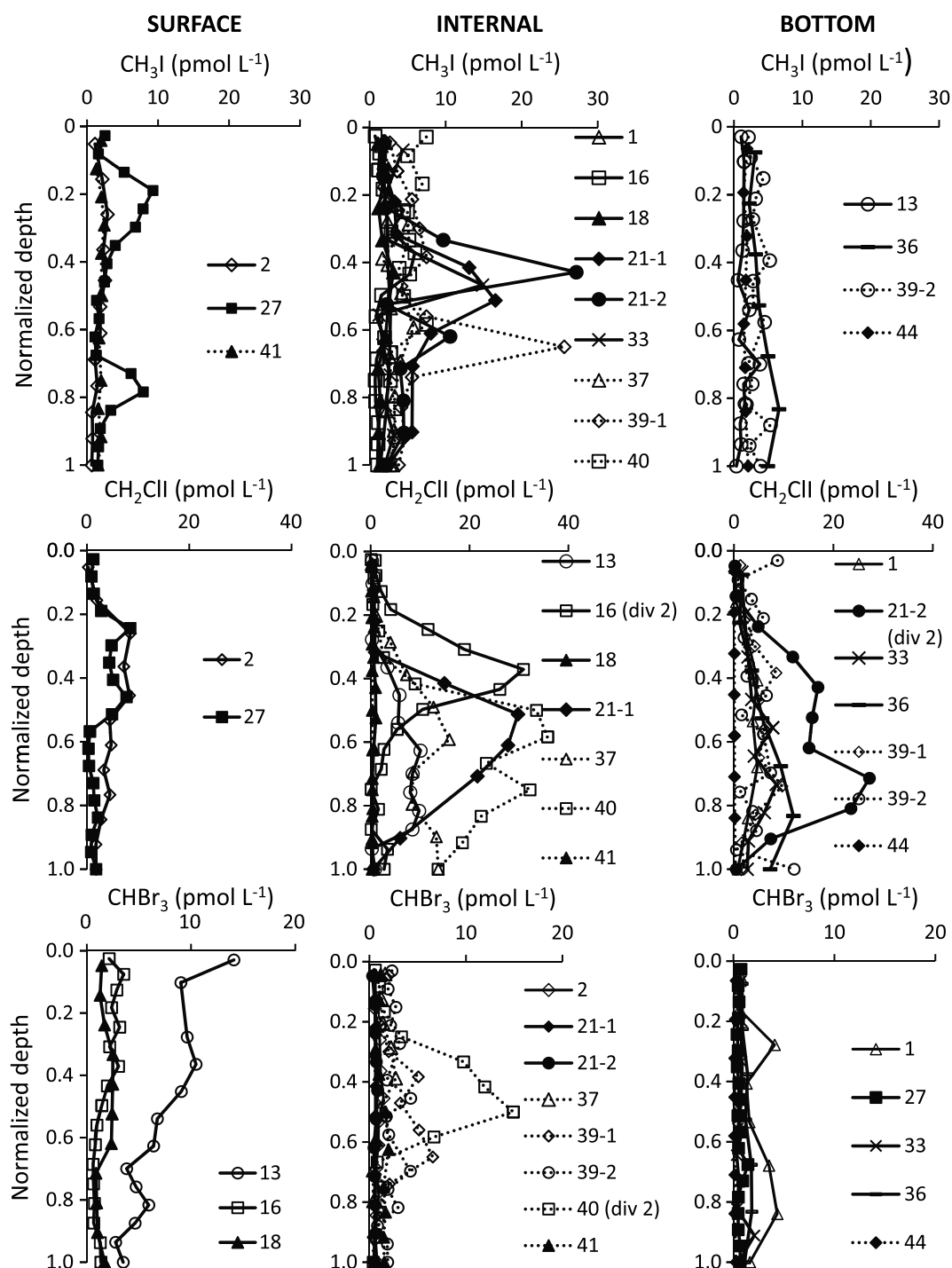
[13] Concentrations of individual VHOCs in bulk sea ice ranged from 0.023 to 88  $\text{pmol L}^{-1}$  in the melted ice cores (Table 1). To be able to compare the bulk ice concentrations of VHOCs to those of the underlying seawater, they were normalized to seawater salinity (see section 2.2). Any differences between concentrations in sea ice and concentrations in seawater should then be the result of chemical or biological processes in the sea ice. The VHOCs were found to be enriched in sea ice, and normalized concentrations ranged from 0.17 to 810  $\text{pmol L}^{-1}$ , or up to 100 times higher than surface water concentrations. The maximum salinity-normalized concentrations for the individual compounds  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $1\text{-C}_3\text{H}_7\text{I}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}_2$ ,  $\text{CH}_2\text{CII}$ ,  $\text{CH}_2\text{Br}_2\text{Cl}$ ,  $\text{CH}_2\text{BrI}$ , and  $\text{CHBr}_3$  ranged between 140 and 810  $\text{pmol L}^{-1}$  (Table 1). Only a few measurements of halocarbons in pack ice have been reported. Atkinson *et al.* [2012] measured halocarbons in sea ice of the Weddell Sea and found average concentrations of iodocarbons to be 5–30  $\text{pmol L}^{-1}$  when concentrations were normalized to salinity. This was over 10 times those found in the seawater beneath the ice. Maximum bromoform ( $\text{CHBr}_3$ ) concentrations in the same study were higher than we observed, but in general, our results are in good agreement with the previous measurements.

[14] There was a distinction between the enrichment of iodinated and brominated compounds in sea ice. Median normalized concentrations in ice of the iodinated compounds  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5\text{I}$  were about 10 times higher than in surface seawater, and the enrichment was even more pronounced for  $\text{CH}_2\text{CII}$  and  $\text{CH}_2\text{BrI}$ , where the ice concentrations were about 30 times higher than those of the underlying seawater. Brominated compounds were also enriched in sea ice, but the enhancement was less pronounced than for the iodinated species, with median ice concentrations of  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}_2$ , and  $\text{CH}_2\text{Br}_2\text{Cl}$  that were  $\sim 3$  times higher than in seawater.  $\text{CHBr}_3$ , on the other hand, had a median ice concentration that was slightly lower than that of the surface seawater (Table 1). These results are similar to what was indicated in an investigation in the Weddell Sea in January–February, where sea-ice concentrations of brominated compounds were below seawater levels, while iodinated compounds were found to be enriched in the ice [Fogelquist and Tanhua, 1995].

[15] We have summed the Br and I content of the eight halocarbons  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $1\text{-C}_3\text{H}_7\text{I}$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{BrCl}_2$ ,  $\text{CH}_2\text{CII}$ ,  $\text{CH}_2\text{Br}_2\text{Cl}$ ,  $\text{CH}_2\text{BrI}$ , and  $\text{CHBr}_3$  to illustrate the bromine and iodine enrichment of the sampled sea ice. Dilution lines were drawn from seawater concentrations of organo-I and organo-Br, based on the mean measured seawater concentrations of the halocarbon compounds (Figure 1). The concentrations of the iodinated compounds were in all cases above the dilution line, which indicated that they were produced in the ice. For the brominated compounds, the results were more complicated, since the concentrations were both above and below the dilution line. This indicates that both production and degradation occurred. It was observed, when dilution lines were drawn for the individual compounds (data not shown), that at some stations where  $\text{CHBr}_3$  was depleted in the ice (below the dilution curve) its degradation products by chloride substitution,  $\text{CHBr}_2\text{Cl}$  and  $\text{CHBrCl}_2$  [Class and Ballschmitter, 1988], were enriched (above the dilution curve). This indicates an earlier production of  $\text{CHBr}_3$  followed by partial degradation and suggests that these brominated compounds originated from biological production earlier in the spring. Similar results for bromocarbons have been found in the Arctic Ocean [Karlsson, 2012].

[16] The Weddell Sea had earlier been identified as an “iodine hotspot,” with large amounts of IO released to the atmosphere [Saiz-Lopez *et al.*, 2007], and iodocarbons have been studied as a possible enhancement mechanism of iodine release from sea ice and a source of IO in the atmosphere [Atkinson *et al.*, 2012]. Although the iodocarbon flux calculated by Atkinson was too small to explain atmospheric IO levels, it is interesting that our study of the Amundsen and Ross Seas indicated an extreme enrichment of iodinated compounds in the sea ice compared to brominated ones.

[17] Our ice and brine samples were collected during summer, often under conditions when the ice was melting and the sea-ice brine had a relatively low salinity. Brine sampled in sack holes had a salinity of  $37 \pm 0.4$  [Fransson *et al.*, 2011]. This salinity was higher than the mean surface seawater salinity of 33.8, but not radically different; therefore, salinity normalization had only a minor influence on the brine concentrations. Maximum halocarbon concentrations measured directly in brine were generally not as high as the maximum salinity-normalized ice concentrations but were substantially

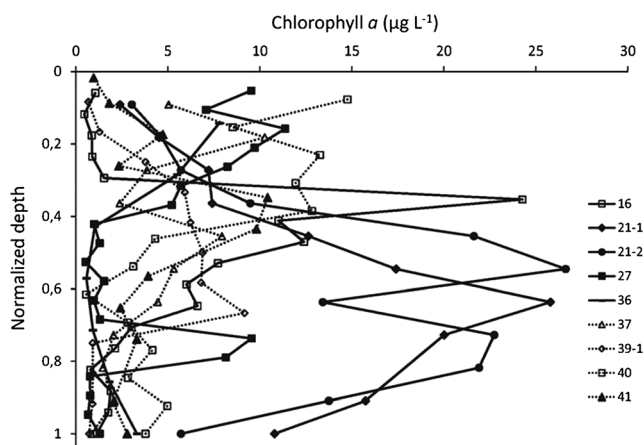


**Figure 2.** Three types of depth distributions in sea ice for  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{ClI}$ , and  $\text{CHBr}_3$ : surface, internal, and bottom, which denotes the vertical position of maximum halocarbon concentration (upper third, middle third, or bottom third of core). div 2: concentration divided by 2. Normalized depth is the fraction of total depth of the ice, where 0 is air/ice interface and 1 is ice/water interface. Station numbers are noted in the figure legend and station locations are shown in Figure S1.

higher than those found in seawater (Table 1). In the same area a year earlier, concentrations in brine were, on average, slightly lower than we observed but exceeded those in seawater [Mattsson *et al.*, 2012], again suggesting the linkage between biological processes and their temporal variability.

[18] A substantial amount of variability of VHOCs in sea ice was found among sample sites, as well as with depth in ice. The bulk ice halocarbon concentrations were assessed as a function of depth in the ice, and these profiles commonly

showed pronounced maxima in the interior of the core, with decreased concentrations of VHOCs above and below. To illustrate variations with depth and between stations, the halocarbon depth profiles were divided into three types: surface, internal, and bottom, according to the vertical position of maximum halocarbon concentration (upper third, middle third, or bottom third of core) (Figure 2). All three types of profiles were found for all compounds. For five of the nine halocarbon compounds studied ( $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{Br}_2$ ,



**Figure 3.** Depth profiles of chlorophyll *a* in sea ice. Normalized depth is the fraction of total depth of the ice, where 0 is air/ice interface and 1 is ice/water interface. Station numbers are noted in the figure legend and station locations are shown in Figure S1.

$\text{CH}_2\text{BrCl}_2$ ,  $\text{CH}_2\text{Br}_2\text{Cl}$ , and  $\text{CHBr}_3$ ), the dominant profile was the one with an internal maximum.  $\text{C}_2\text{H}_5\text{I}$  and  $1\text{-C}_3\text{H}_7\text{I}$  most often had maxima in the upper part of the ice core, while  $\text{CH}_2\text{ClI}$  and  $\text{CH}_2\text{BrI}$  often had maxima near the bottom of the ice (Figure 2 and Table S1).

[19] Chlorophyll *a* concentrations in ice ranged from 0.46 to  $27 \mu\text{g L}^{-1}$  (Table 1), with the highest chlorophyll *a* concentrations generally found in the upper two thirds of the cores (Figure 3 and Table S1). *Meiners et al.* [2012] found that chlorophyll in cores from the Antarctic exhibited three types of distributions: those with a surface maximum, those with a maximum at intermediate depths, and those with a bottom maximum. Those with an intermediate maximum were the least common type (16% of all reported cores), and the mean maximum chlorophyll concentration for internal maxima was  $20 \mu\text{g L}^{-1}$ . In contrast, our ice cores exhibited an upper or intermediate maximum, and the mean maximum concentration was  $15 \mu\text{g L}^{-1}$ . These variations likely reflect the formation of sea ice, its patterns of flooding, and the in situ growth of ice algae.

[20] A VHOC concentration maximum in one part of the core is an indication of VHOC production in that part of the ice; furthermore, a correlation between VHOCs and chlorophyll *a*, a measure of biomass of ice algae, would further suggest biological production. For stations where both VHOCs and chlorophyll *a* were measured simultaneously, the Spearman rank correlation coefficient ( $\rho$ ) between halocarbon compounds and chlorophyll *a* was determined. Positive correlations between chlorophyll *a* and  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{CHBrCl}_2$ ,  $\text{CH}_2\text{ClI}$ ,  $1\text{-C}_3\text{H}_7\text{I}$ , and  $\text{CH}_2\text{BrI}$  were observed (Table 2). The iodinated compounds  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5\text{I}$  showed strongest correlations with chlorophyll *a* ( $\rho = 0.46$  and  $0.42$ , respectively). Our interpretation is that the vertical distribution of these VHOCs in sea ice is dependent on direct or indirect [*Hill and Manley*, 2009] biological production by ice algae inside the brine channels and that the maximum concentrations were generated by biological production at that depth. The positive relationship between chlorophyll *a* and iodinated halocarbons in sea water was also observed by *Mattsson et al.* [2012].

[21] Further support for biological VHOC production in the ice was seen in incubations studies of brine. Measurement of

VHOC production rates were conducted on sea-ice brine, sampled on the ice stations, and indicated the presence of two competing processes: production and degradation, also described by *Mattsson et al.* [2012] and *Karlsson* [2012]. Net production was observed at some of the stations: production rates were  $4.0\text{--}5.1 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $\text{CH}_3\text{I}$ ,  $1.1\text{--}1.4 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $\text{C}_2\text{H}_5\text{I}$ ,  $10\text{--}24 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $\text{CH}_2\text{Br}_2$ ,  $0.4\text{--}3.1 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $1\text{-C}_3\text{H}_7\text{I}$ ,  $0.7\text{--}4.4$  for  $\text{CHBrCl}_2$ ,  $6.0\text{--}21 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $\text{CH}_2\text{ClI}$ ,  $1.0\text{--}11 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $\text{CHBr}_2\text{Cl}$ ,  $0.07 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $\text{CH}_2\text{BrI}$ , and  $6\text{--}17 \text{ pmol L}^{-1} \text{ d}^{-1}$  for  $\text{CHBr}_3$ . Net production was observed for a majority of the compounds at three out of seven studied stations: stations 2, 16, and 39.

[22] The possible contribution of VHOCs produced in sea ice to the atmospheric halogens is dependent on their transport in brine channels and may be mediated by air inclusions in the ice [*Loose et al.*, 2011]. In turn, the sizes of brine and air inclusions are governed by ice temperature and bulk salinity. We found the average brine volume to be 13% (Stations 41 and 44 excluded, since ice temperatures  $>0^\circ\text{C}$  made brine volume calculations impossible), with average ice temperatures of  $-1.6^\circ\text{C}$  and mean bulk salinity of 5, suggesting that the ice was highly porous and the brine channels completely interconnected. Since halocarbons were found to be enriched in the ice, it was expected that losses of halocarbons had occurred and were occurring both upwards and downwards within the ice core.

[23] The depth profiles of VHOC with concentrations in ice that, at many stations, had their maximum halocarbon concentrations in the interior (Figure 2 and Table S1), with a concentration decrease that often was linear towards the surface as well as the bottom, may indicate that VHOCs were produced in the interior and transported in both directions towards the surfaces (air and ocean) of the ice. These types of profiles were especially common for  $\text{CH}_2\text{ClI}$  and  $\text{CH}_2\text{BrI}$ , but occurred for all compounds. A diffusion-like transport of halogenated gases through sea ice has been shown by *Loose et al.* [2011] and *Gosink et al.* [1976] and will influence the distribution of our measured halocarbons as well. Although the size of the contribution of sea ice to halogen flux cannot be determined, our data strongly support the conclusion that sea ice is a significant source of halocarbons [*Mattsson et al.*, 2012].

#### 4. Conclusions

[24] A large variation with depth as well as with space in the sea ice of the Southern Ocean makes it difficult to give a

**Table 2.** Spearman's Rank Correlation Coefficients ( $\rho$ ) and *p* Values for the Correlation Between VHOCs and Chlorophyll *a* in Sea Ice (Bulk Ice Concentrations Normalized for Brine Volume)<sup>a</sup>

Compound	$\rho$	<i>p</i> Value	<i>n</i>
$\text{CH}_3\text{I}$	0.46	$<<0.001$	111
$\text{C}_2\text{H}_5\text{I}$	0.42	$<<0.001$	111
$\text{CH}_2\text{Br}_2$	ns		
$\text{CHBrCl}_2$	0.34	0.0002	111
$\text{CH}_2\text{ClI}$	0.27	0.01	111
$\text{CHBr}_2\text{Cl}$	ns		
$1\text{-C}_3\text{H}_7\text{I}$	0.25	0.01	99
$\text{CH}_2\text{BrI}$	0.23	0.02	107
$\text{CHBr}_3$	ns		

<sup>a</sup>Ice samples were collected on stations 16, 21, 27, 36, 39, 40, and 44. One sample represents one 10 cm ice core section. ns = not significant ( $\rho < 0.2$  and  $p > 0.05$ ).

univocal description of the VHOC content of this environment. In general, our results show that summer sea ice of the Southern Ocean is enriched in halocarbons compared to seawater, especially iodinated ones. We found a production of halocarbons in the interior sea ice, which was of biological origin. This was supported by the positive correlation between several iodinated halocarbons and chlorophyll *a*, as well as net production rates determined from brine incubation studies. Furthermore, depth distributions of halocarbons, with concentration gradients in sea ice, indicated a contribution of halogens from the ice to both air and underlying water. This suggests that the summer sea ice in the Southern Ocean is a source of halocarbons, especially iodocarbons, to the surrounding environment and our data provides additional input to determine the role of Antarctic sea ice as a source of reactive halogen species.

[25] **Acknowledgments.** We would like to thank Daniel Barrdahl and Johan Engelbrektsson who helped with sampling and analyses, as well as all members of the OSO expedition, officers and crew of *I/B Oden* and personnel of Raytheon Polar Services. This research was supported by the Swedish Science Foundation and NSF grant ANT-0836144. We would also like to thank the Swedish Polar Research Secretariat for logistical support.

[26] The editor thanks anonymous reviewers for their assistance in evaluating this paper.

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