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Biogenic Halocarbons in Polar Sea Ice

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Ph.D. thesis
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UNIVERSITY OF GOTHENBURG



GÖTEBORGS UNIVERSITET

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AKADEMISK AVHANDLING

för avläggande av filosofie doktorsexamen i Naturvetenskap, inriktning kemi, som med tillstånd från Naturvetenskapliga fakulteten kommer att offentligt försvaras fredagen den 16 maj 2014 kl. 10:00 i sal KB, Institutionen för kemi och molekylärbiologi, Kemigården 4, Göteborg. Avhandlingen kommer att försvaras på engelska.

Institutionen för kemi och molekylärbiologi
Naturvetenskapliga fakulteten

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Cover picture: Ice work in Antarctica

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Abstract

Sea ice is to date a rather poorly investigated part of the cycling of volatile halogenated organic compounds, halocarbons. These compounds are natural sources of reactive iodine and bromine to the atmosphere, and are produced in the marine environment. The aim of this study was to determine the role of sea ice in terms of production and release of halocarbons to the atmosphere. Iodinated and brominated halocarbons were measured in polar sea ice as well as in snow, air, and seawater under the ice. Multiple samples were collected from the same location in order to cover variability. Studies were performed both in winter and summer, and seasonal variations were observed.

Sea ice acted as a source of halocarbons both in winter and in summer. Biotic production was observed during summer, and depth distributions of halocarbons in the ice were related to ice algal biomass. Unexpectedly high concentrations of halocarbons were found at the surface of Antarctic winter sea ice. For bromoform (CHBr_3) the concentration range was 0.2 - 20 nM in the top 10 cm of the ice. High concentrations were also found in the snow closest to the snow-ice interface. Our results suggest that an abiotic formation occurs in seasonal sea ice during polar night. This may lead to a winter accumulation of halocarbons in the marine boundary layer and enhance tropospheric ozone depletion in the polar spring.

Keywords: Volatile biogenic halocarbons | Sea ice| Antarctica|Southern Ocean | Arctic|gases|ice-air flux|ice algae|

Populärvetenskaplig sammanfattning

Att industriellt framställda ämnen som t.ex. freoner bryter ner ozon är välkänt. Det som är mindre känt är att det finns naturliga ämnen som bidrar till ozonnedbrytning. Den största källan till naturligt producerade ozonnedbrytande ämnen finns i havet. Flyktiga halogenerade kolväten, halokarboner är naturligt producerade ämnen som bildas av alger och mikroorganismer i havet och i havsisen. När de bryts ner av solljus i atmosfären bildar de reaktiva halogener (brom och jod) som deltar i en mängd reaktioner, varav den viktigaste är nedbrytning av ozon. På våren, när ljuset återvänder till polarområdena sker en så kallad "bromexplosion" där nedbrytning av ozon går oerhört fort. Undersökningar har visat att denna snabba ozonnedbrytning ofta sker ovanför havsisen.

Dagens globala klimatmodeller visar att vår planet förändras och det förutspås att förändringarna kommer att stå sig åtminstone i några hundra år framöver. De direkta konsekvenserna är ett flertal, och bland annat kommer polarisarna att minska i både utbredning och tjocklek. I Arktis har andelen tunnare is ökat med 20 % de senaste 30 åren på bekostnad av den fleråriga tjockare isen.

Det har gjorts mycket få undersökningar som behandlar halokarboner och havsisen och målet för det här arbetet var att studera hur stor betydelse halokarboner i havsisen har för nedbrytning av ozon i polarområden. Studierna har utförts under en fältstudie i Arktis och tre expeditioner till Antarktis med den svenska isbrytaren Oden och det tyska forskningsfartyget Polarstern. Halokarboner mättes i is, snö, havsvatten och luft.

Resultaten visar att havsisen är en signifikant källa av halokarboner till atmosfären. På sommaren produceras de av islevande mikroorganismer och via transport genom kanaler i isen kunde de avgå till atmosfären. Mest förvånande var de höga halter som uppmättes på vintern i ytskiktet på den nybildade isen. Eftersom det under expeditionen var mörkt dygnet runt, kunde inte dessa halter förklaras av en biologisk produktion. Istället bildas de genom kemiska reaktioner på isens yta, en bildningsmekanism som inte rapporterats tidigare.

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Part B: List of publications

This thesis is based in the following studies, referred to in the text by their Roman numerals.

- I. Granfors A., Andersson M., Chierici M., Fransson A., Gårdfeldt K., Torstensson A., Wulff A. and Abrahamsson K. (2013) Biogenic Halocarbons in Young Arctic Sea Ice and Frost Flowers, *Marine Chemistry*, 155, 124-134.
- II. Granfors A., Karlsson A., Mattsson E., Smith W. and Abrahamsson K. (2013). Contribution of Sea Ice in the Southern Ocean to the Cycling of Volatile Halogenated Organic Compounds, *GRL*, 40, 15, 3950-3955.
- III. Abrahamsson K., Granfors A., Ahnoff M. Seasonal Sea Ice – a Source of Organo-Bromine during Polar Night . *Manuscript*
- IV. Granfors A., Ahnoff M., Mills M. and Abrahamsson K. Seasonal Study of Organic Iodine in Antarctic Sea Ice. *Manuscript*

Contribution report

- I. Responsible for planning, conducting experiments, interpretation of results and writing.
- II. Responsible for interpretation of results and writing.
- III. Participated in planning, conducting experiments, interpretation of results and writing.
- IV. Responsible for planning, conducting experiments, interpretation of results and writing.

Abbreviations

VHOC	Volatile halogenated organic compounds
VSLs	Very short-lived species
ODE	Ozone depletion event
Br _y	Inorganic bromine
chl <i>a</i>	Chlorophyll <i>a</i>
GC-ECD	Gas-chromatography with electron capture detection
pptv	Parts per trillion by volume
LOQ	Limit of quantification

1. Introduction and objective

Volatile halogenated organic compounds, halocarbons, contribute to the atmospheric load of halogens. They are short-lived in the atmosphere, readily photolyzed to form reactive halogen species that influence atmospheric chemistry. Reactive halogens are known to cause ozone destruction in the stratosphere through efficient catalytic cycles, but they also play an important role for tropospheric chemistry.

The halocarbons studied in this work are of natural origin and their main sources are found in the marine environment. They are volatile compounds that consist of one to four carbon atoms and at least one halogen atom: chlorine, bromine or iodine (Table 1). They are produced by marine organisms, and can be found in high concentrations, for example in coastal areas, where they are produced by macroalgae (Carpenter *et al.*, 2003; Quack and Wallace, 2003). Phytoplankton are efficient producers in the open ocean (Moore *et al.*, 1995; Abrahamsson *et al.*, 2004), and halocarbons are also produced by sea-ice algae inhabiting the liquid brine channels of sea ice (Sturges *et al.*, 1992, Hill and Manley, 2009).

Table 1. List of studied compounds

Formula	name	Lifetime ^a (days)
CH ₃ I	Iodomethane (methyl iodide)	7
C ₂ H ₅ I	Iodoethane (ethyl iodide)	4
CH ₂ Br ₂	Dibromomethane	123
CHBrCl ₂	Bromodichloromethane	78
CH ₂ ClI	Chloriodomethane	0.1
CHBr ₂ Cl	Dibromochloromethane	59
1-C ₃ H ₇ I	1-Iodopropane (propyl iodide)	0.5
CH ₂ BrI	Bromoiodomethane	0.04
CHBr ₃	Bromoform	24
CH ₂ I ₂	Diiodomethane	0.003

^aAtmospheric lifetimes (OH+photolysis) listed in Montzka *et al.* (2011)

An important reason to study halocarbon production and emissions in polar areas is the stratospheric and tropospheric ozone destruction observed during polar spring (Barrie *et al.*, 1988; Solomon, 1990; Simpson *et al.*, 2007). In the late 1990s, production of volatile halocarbons by Arctic and Antarctic macroalgae was observed, and it was speculated that this could be of importance to stratospheric ozone destruction in the polar regions (Laturus 1996; 1998). Moreover, biogenic bromoform was suggested as the source of bromine, when a strongly negative correlation was found between ozone and bromine during ground-level ozone destruction in the Arctic (Barrie *et al.*, 1988). Recently, observations of enhanced concentrations of reactive iodine monoxide (IO) and bromine monoxide (BrO) were made in the Antarctic troposphere, over and

close to sea ice. Biologically produced iodinated halocarbons (iodocarbons) were proposed to act as precursors to IO (Saiz-Lopez *et al.*, 2007; Schönhardt *et al.*, 2008, 2012.).

It has been shown that variability in ozone is correlated to 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). Snow and sea ice have also gained attention as media for multi-phase chemical reactions and formation of reactive halogens (Abbatt *et al.*, 2012). However, if organic halogens, originating from sea ice, are a significant source of halogens to the polar atmosphere is not known.

Sea ice is to date a rather poorly investigated part of halocarbon cycling. The most important issue is of course if halocarbons are released from sea ice in such quantities that they have an effect on the chemical composition of the atmosphere. Halocarbons can be produced by ice-living organisms, but how they are transported and distributed in sea ice has not been clarified. However it has been highlighted in recent studies that sea ice plays an important role for fluxes of other climate gases in the marine environment, such as CO₂ and dimethyl sulfide (DMS) (Nomura *et al.*, 2006; Zimmelink *et al.*, 2008; Loose *et al.*, 2011).

Global models have been made for halocarbon concentrations in seawater and air (Ziska *et al.*, 2013), but data from polar areas are limited, and sea ice has not been included as a source. Sea ice is not only a barrier for gas exchange between ocean and atmosphere, it is also a source that needs to be considered when halocarbon cycling is modelled. In addition, data from the winter season in polar regions are rare, and seasonal variations of halocarbons need to be further investigated.

The effect of climate change on biogenic halocarbon emission from the polar areas has been highlighted in recent studies (Atkinson *et al.*, 2012; Hughes, *et al.* 2012). These areas are warming rapidly, and temperature changes lead to changes in sea ice coverage. Sea ice plays an important role for marine phytoplankton by seeding surface waters with diatoms and essential nutrients (Garibotti *et al.*, 2003). The decline in seasonal sea ice that is seen in some parts of Antarctica may lead to reduced diatom blooms and reduced production of biogenic halocarbons in the spring (Hughes *et al.*, 2012). In the Arctic, the warming climate results in a larger fraction of seasonal sea ice. It is not known how this will affect halocarbon production and emissions in this area. The objective of this work was to clarify the role of sea ice for halocarbons in the polar marine environment. The following issues were addressed:

- Distributions of halocarbons in sea ice in relation to formation pathways and physical parameters
- Sea ice as a source of atmospheric bromine and iodine
- Impact of season and age of ice on halocarbon distributions and ice-air fluxes

Biogenic Halocarbons in Polar Sea Ice

Development of halocarbon concentration in freezing sea ice was studied in an ice freezing experiment in Arctic sea ice, in which it was proposed that an outgassing of halocarbons from sea ice occurred during freezing (Paper I). In the Southern Ocean, the role of melting summer sea ice was demonstrated, where sea ice acted as a source of volatile halogenated organic compounds to air and water. A correlation between halocarbon concentrations and ice algal biomass was found, indicating that the algae were producing these compounds. Occurrence of production in the ice was further supported by incubation studies of sea ice brine, where halocarbon production rates were estimated (Paper II). In a study of winter sea ice in the Antarctic, high concentrations of brominated halocarbons were found in the interface between sea ice and snow. An abiotic production mechanism for brominated halocarbons during winter was proposed, and this strong source of bromine to the Antarctic atmosphere was highlighted (Paper III). Seasonality in production and concentrations of iodinated halocarbons in Antarctic sea ice was studied, and resulted in a characterization of ice of different age in terms of content and distribution of iodinated halocarbons. Formation mechanisms of the iodinated compounds were discussed (Paper IV).

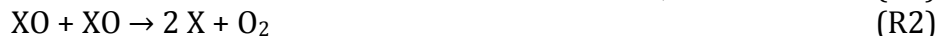
2. Halocarbons and atmospheric reactions

The main motive to study short-lived halocarbons is their impact on the chemistry of the atmosphere. Reactive bromine and iodine is involved in several atmospheric reactions. Contribution to these reactive halogens from naturally-emitted halocarbons may be significant for the reactions described below.

2.1. Stratospheric ozone destruction

Halocarbons are short-lived in the atmosphere, mainly due to photolysis. Their lifetimes range from 7 minutes for diiodomethane, CH₂I₂, to 145 days for bromochloromethane, CH₂BrCl (Ordóñez *et al.*, 2012). Iodinated compounds are considered too short-lived to reach the stratosphere, and their effects on the atmosphere are limited to the troposphere (Montzka *et al.*, 2011).

More long-lived brominated compounds such as dibromomethane (CH₂Br₂), and bromoform (CHBr₃) can be transported to the stratosphere and participate in stratospheric ozone destruction (Sturges *et al.*, 2000). Degradation of bromocarbons in the atmosphere starts with homolytic cleavage of the C-Br bond. The radical species, Br·, then reacts with oxygen to form inorganic bromine species, Br_y, mainly hydrogen bromide (HBr), hypobromous acid (HOBr) and bromine monoxide (BrO) (Hossaini *et al.*, 2010 ;Montzka *et al.*, 2011). Inorganic bromine species cause stratospheric ozone destruction in a catalytic cycle, where Br is regenerated (Reactions 1 and 2). Equivalent reactions occur with iodine and chlorine.



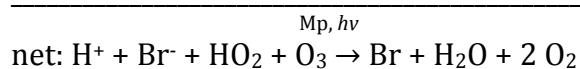
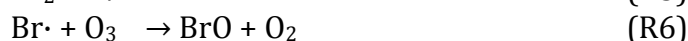
In addition to the long-lived halons and methyl bromide (CH₃Br), a contribution from very short-lived substances (VSLS), of which bromine-containing halocarbons are the most abundant, is needed to account for the observed concentrations of inorganic bromine in the stratosphere (Liang *et al.*, 2010; Montzka *et al.*, 2011). According to a 3-D model study, CHBr₃ and CH₂Br₂ contribute significantly to stratospheric reactive bromine: 0.72 pptv and 1.69 pptv respectively (Hossaini *et al.*, 2010). In the latest report from World Meteorological Organisation, (WMO), the estimated contribution of bromine to the stratosphere is 3-8 pptv from VSLS, and ~16pptv Br_y from halons and CH₃Br (Montzka *et al.*, 2011). BrO-measurements from April 2008 resulted in estimated contributions of 7 ± 6 ppt bromine from VSLS and total stratospheric bromine of 23.5 ± 6 ppt (Parella *et al.* 2013).

The impact of brominated halocarbons to reactive bromine in the stratosphere is dependent on source strength, loss, and upward transport. The most efficient mass transport from the troposphere to the stratosphere is found in the tropics. Here, events of deep convection transport air from the marine boundary layer to the upper troposphere, and troposphere-stratosphere exchange may deliver compounds to the stratosphere (Mote *et al.*, 1996). In the stratosphere, air is transported from tropical areas towards the poles in a slow circulation called the Brewer-Dobson circulation (Brewer, 1949). However, observations of CHBr₃ in the lower stratosphere in mid- and Arctic latitudes may indicate an existing

extratropical troposphere-stratosphere exchange of this substance (Sturges, 2000). Loss of bromine can occur before it reaches the stratosphere by washout of water-soluble inorganic bromine species (HOBr and HBr) (Sinnhuber and Folkins, 2006).

2.2. Tropospheric reactions

In the troposphere, reactive halogens are involved in ozone destruction by the same catalytic cycle as described for the stratosphere (R1-R2). Episodes of near total depletion of surface ozone, called ozone depletion events (ODE: s), occur in the polar spring. They were first discovered in the Arctic (Barrie, *et al.*, 1988; Oltmans *et al.*, 1989) and later in the Antarctic boundary layer (Kreher *et al.*, 1996). The fast ozone destruction by halogen radicals is explained by recycling of reactive bromine the “bromine explosion” mechanism, first proposed by Fan and Jacob (1992). These photochemical and heterogeneous reactions occur on sea salt aerosols and ice surfaces. The key is uptake from the gas phase to the aqueous phase of hypohalous acids (HOX, where X = Br, Cl, I, R3). It is followed by release of Br₂ that is rapidly photolysed according to reactions 4-7 (Simpson *et al.*, 2007).



In this reaction sequence, Br⁻ may be exchanged by Cl⁻ and the product in reaction 4 is then BrCl. Evidence has been found for formation of both Br₂ and BrCl in the snowpack (Foster *et al.*, 2001). Similarly, input of iodine-containing compounds in computer models of tropospheric halogen chemistry, enhances ozone destruction (von Glasow and Sander, 2002; Calvert and Lindberg, 2004).

Organic iodine compounds play an important role as sources of iodine to the troposphere (Vogt *et al.*, 1999; Law and Sturges, 2007). However, it is questioned if known organo-iodine sources can account for observed tropospheric IO-concentrations (Jones *et al.*, 2010). Studies of iodocarbons in the coastal Atlantic marine boundary layer proposed that iodocarbons such as CH₃I, CH₂I₂, CH₂ClI, CH₂BrI, C₂H₅I, C₃H₇I, or C₄H₉I formed by macroalgae were an important source of high IO concentrations (Carpenter *et al.*, 1999). In addition to the impact iodine on atmospheric chemistry, a correlation between particle formation and presence of IO was found (McFiggans *et al.*, 2010) However, later field studies showed that molecular I₂, also released by macroalgae, probably was the dominant source of iodine, (Huang *et al.*, 2010; Jones *et al.*, 2009). In addition, hypoiodous acid (HOI), originating from reaction of gaseous ozone with aqueous I⁻, has been proposed as an oceanic source of iodine to the marine boundary layer.

In addition to ozone destruction, reactive halogens cause oxidation of mercury and dimethyl sulphide (DMS). Oxidation of elemental mercury (Hg^0) to reactive gaseous mercury (Hg^{II}) is seen in atmospheric depletion events in the polar spring which coincide with ozone depletion. This causes deposition and accumulation of (Hg^{II}) in the snowpack and is a pathway for introducing mercury into the biosphere in polar areas (Schroeder *et al.*, 1998; Lindberg *et al.*, 2002). DMS has a potential effect on climate by forming cloud condensation nuclei. Oxidation of DMS by reactive halogens leads to reduction of DMS in the marine boundary layer, and reduces its cooling effect on climate (Boucher *et al.*, 2003; von Glasow, 2004). Furthermore, reactive halogens affect the oxidizing capacity of the troposphere by their influence on ratios of the oxidizing species HO_2/OH and NO/NO_2 (Saiz-Lopez *et al.*, 2007).

3. Sampling and analytical technique

3.1. Study sites

Samples were collected from four field campaigns, one in the Arctic (Svalbard) and three in the Southern Ocean. In Svalbard, the experimental site was near-shore in an ice-covered bay located 500 m from Ny-Ålesund (Paper I). Data from the Southern Ocean was collected during three expeditions: the OS008/09 and OS010/11 expeditions conducted during austral summer aboard the R.V.I.B. *Oden* in the Amundsen and Ross seas (Papers II and IV), and the ANTXXIX/6 expedition conducted during austral winter aboard the R.V *Polarstern* in the Weddell Sea (Papers III and IV). By sampling sea ice air and seawater at the same site, the aim was to determine if sea ice was a source of halocarbons, and to estimate the magnitude of potential fluxes from sea ice to air and water.

3.2. Sample handling

One of the challenges in sea ice sampling is to collect undisturbed samples. The bottom part of sea ice is often very porous and brine may be lost during sampling. This can lead to underestimation of gases dissolved in brine. The technique where sea ice cores are melted for analysis is the most often used method for measurement of chemical and biological parameters in sea ice (Thomas *et al.*, 2010) Other options are centrifugation of the ice core to collect brine, and brine sampling in sack holes (section 3.5).



Figure 1. Ice core samples in Tedlar bags. Photo Agneta Fransson

During sampling and handling of samples it is important to avoid degassing as well as photolytic breakdown of halocarbons. There is a risk for biological production during storage, and contamination from surrounding air and sample containers may also occur. This was kept in mind when samples were handled in the field and in the laboratory (Papers I-IV). To prevent biological halocarbon production and/or photolytic degradation before analysis, samples were placed in black plastic bags immediately after retrieval. Ice cores for halocarbon analysis were divided into sections and rapidly placed in gas tight Tedlar™ bags (Figure 1). Surrounding air was removed before samples were thawed in darkness at room temperature, and analyzed as soon as possible. The approximate time between sampling and analysis was 24 h for ice samples and 12 h for snow samples. Tedlar™ bags had advantages such as easy sample withdrawal and compactness, and were used for all ice and snow samples. No

contamination or loss of analytes was observed. Water samples were collected in Screw-capped glass vials with teflon-lined septa. It was ensured that the sample containers did not contain any headspace. An investigation of the effect of storage-time showed that water samples could be stored in glass vials in darkness and cold temperatures (approximately 4°C) for at least 100 h (Hagman, 2013).

3.3. Brine volume normalization

Analysis of melted samples gave a bulk concentration of halocarbons in the ice. However, we assumed that the halocarbons were dissolved in the liquid brine part of the ice (Section 5.1). Therefore the part of the sample that consisted of brine was estimated. Bulk concentrations of halocarbons in melted ice were divided by brine volume to obtain the estimated concentration in brine. Brine volume can be calculated from ice temperature and bulk salinity of ice, by equations based on phase relationships in ice in thermodynamic equilibrium (Assur, 1960). Cox and Weeks (1983) presented equations for calculation of brine volume, gas volume and total ice porosity based on these phase relations. In Papers I-IV the empirical expression for estimation of brine volume developed by Frankenstein and Garner (1967) was used (Equation 1).

$$v_b/v = S_i(0.0532 - 4.919/T_i) \quad -22.9^\circ\text{C} \leq T_i \leq -0.5^\circ\text{C} \quad (\text{Eq 1})$$

Where v_b/v is the brine volume (%), T_i = ice temperature (°C) and S_i = bulk salinity (parts per thousand).

In this simple equation, only ice temperature and bulk salinity are needed as input, while the Cox and Weeks equations require an estimated ice density. A disadvantage of using the relationship by Frankenstein and Garner in comparison to by Cox and Week's equation, is that gas volume is not estimated and that the expression is not valid for temperatures below -23°C. It was also noted that this expression was not valid for ice warmer than -0.5°C, which was the case for a few ice stations during the summer expeditions (Paper II).

3.4. Brine sampling

Another approach for sampling of compounds dissolved in sea ice brine is collecting brine in sack holes. The ice is partially cored to leave a core-hole in its surface (Figure 2).



*Figure 2. Brine Sampling in Sack holes.
Photo: Agneta Fransson*

Brine that drains from the surrounding ice into the hole is sampled with a syringe. This method allows sampling of sufficient brine volumes for analysis and gives an integrated sample representing brine in the ice surrounding the hole. A disadvantage is that the ice volume feeding the collected sample is unknown. Another consideration in sack hole sampling is that gas exchange with the atmosphere may occur during brine seeping. This can be minimized by covering the sack hole with a lid. A possible limitation of sack hole sampling is that it is not suitable for very cold ice, where little brine drainage can occur. In warm, very porous ice, there is also a risk for contamination with seawater.

A good agreement between halocarbon concentrations in sampled brine and sea ice concentrations normalized by brine volume can be used as a verification of the brine volume normalization. The two were often in good agreement (Paper I and II). However, it was noted that for compounds with a high concentration in the ice surface, sack-hole sampling was not representative for the whole depth of the ice (Paper IV).

3.5. Homogeneity of sea ice

Halocarbon content in sea ice can be influenced by both physical and biological processes in sea ice. The fact that these compounds are produced by ice-living organisms leads to an uneven distribution in sea ice, since biological production has high spatial variability, even within small areas. It is, thus, questionable to extrapolate results from one ice sample to be valid for a larger area.

During the Antarctic expeditions (Paper II, III and IV), multiple ice core samples were collected at the same station, when possible. The aim was to estimate spatial variability of halocarbons in sea ice, and obtain results that could represent Antarctic sea ice at that time of year. With this approach, we found that depth profiles of halocarbons in sea ice from the same station generally had maximum concentrations at the same depth. However, the magnitude of that maximum concentration was a variable (Figure 3).

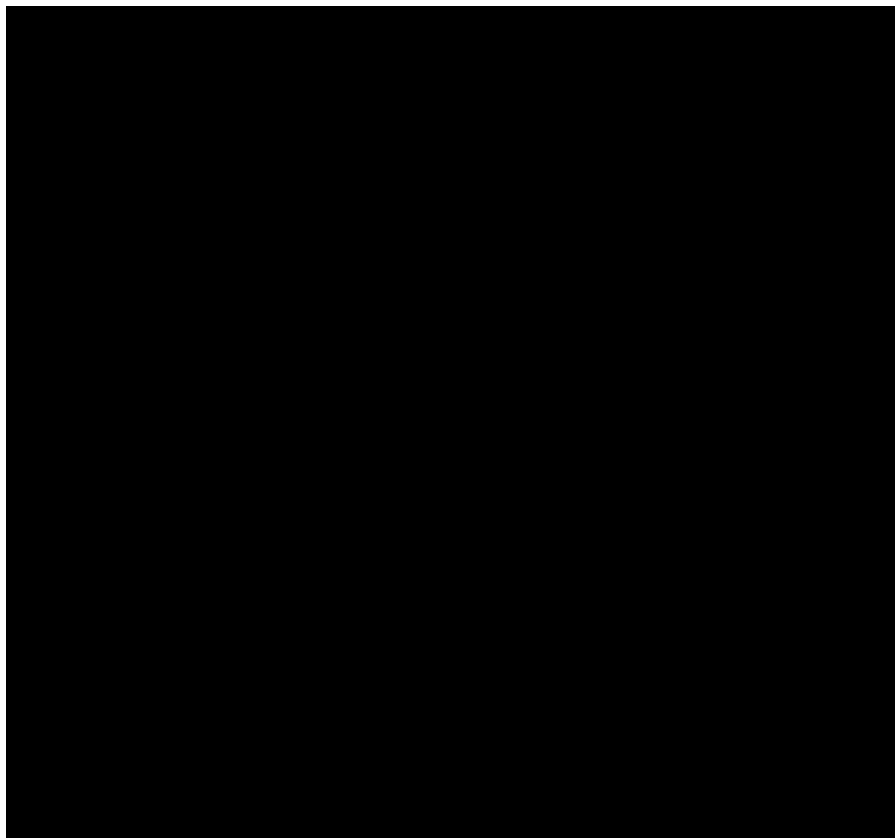


Figure 3 Depth profiles of iodinated halocarbons from two ice stations in summer and winter (Paper IV). Halocarbon concentrations are bulk ice concentrations divided by the estimated brine volume. Mean concentrations of the compounds from several ice cores sampled at the same location are presented at each depth. The error bars represent one standard deviation. Summer ice concentrations for CH_2ClI , CH_2BrI are data from five ice cores, while CH_3I was measured in three cores. Ice thickness at station 31 varied between 179 and 192 cm. Concentrations of CH_2ClI and CH_2BrI at the winter station 506 are mean concentrations of the compounds in nine ice cores while CH_3I concentrations are from seven cores. Ice thickness varied between 47 and 67 cm.

In the freezing experiment performed in Svalbard, we relied on homogeneity of the ice within our sampling site. A time series experiment was performed, where sea ice was studied during freezing in core holes, and a newly frozen ice core as well as an ice core from the surrounding ice was sampled every day (Paper I). A duplicate sample was analyzed from surrounding ice and the variation between the inventory concentrations (mean bulk concentration) of the two cores was 17 % (of average mean bulk concentration) for CH_2ClI , 2.7 % for CH_2BrI and 7.4 % for CHBr_3 , which was found to be an acceptable variation for our study.

3.6. Halocarbon analysis

Pre-concentration and separation

In halocarbon analysis, a pre-concentration step is needed due to the low concentrations present in the marine environment. The most frequently used method is purge-and-trap. The water sample is purged with clean gas and volatile compounds are trapped on an adsorbent. The trap is then heated to release the trapped compounds that can be separated and detected. Another option for trapping is a cold trap, which is also widely used. A disadvantage of this technique is that it requires liquid nitrogen, which may be difficult to handle during field campaigns.

In this work (Paper I-IV), halocarbons were pre-concentrated with a modified version of the custom-made purge-and-trap instrument described by Ekdahl and Abrahamsson (1997). In Paper II, III and IV, a commercial system, Velocity XPT, was also used for halocarbon pre-concentration. The main difference between the two systems is that in the commercial system, the compounds are trapped at ambient temperatures, while the trap is cooled to about 0°C in the custom-made system. The Velocity XPT has a rinsing step, where the system is rinsed with MilliQ-water.

One of the custom-made purge-and-trap instruments was equipped for air sample analysis in addition water sample analysis. Air was continuously drawn through a 100-m 4 mm i.d. Teflon tubing by an air pump located downstream the sampling loop. At start, the air sample loop was switched into the purge line and carried by the purge gas to the trap. Desorption and GC-ECD analysis was as for aqueous samples. This instrument was also fed with a continuous stream of water from the ship's surface water inlet. The instrument could be set up for automated sampling, continuously alternating between water and air.

Separation and detection were carried out by GC-ECD (gas-chromatography with electron capture detection). The advantage of EC detection is the high sensitivity for halogenated compounds. Another detector that is widely used for halocarbon analysis is mass spectrometry (MS). The advantage of MS is the high selectivity, although it is not as sensitive. The disadvantage of GC-ECD is that the peaks need to be well separated to get a good quantification. This can be a challenge, since a typical seawater sample contains a large number of compounds that can be detected. A good separation requires long analysis times, which is a disadvantage when samples are analyzed in the field.

In order to overcome the problem of long analysis times and achieve high sample throughput, two or three instruments were used for simultaneous analysis. Inter-calibration of instruments (Figure 4) has shown that, in most cases, the variability between instruments has been acceptable. On occasions, the commercial system has had a background signal that influenced concentrations of chlorinated compounds, probably due to contamination from rinsing water.

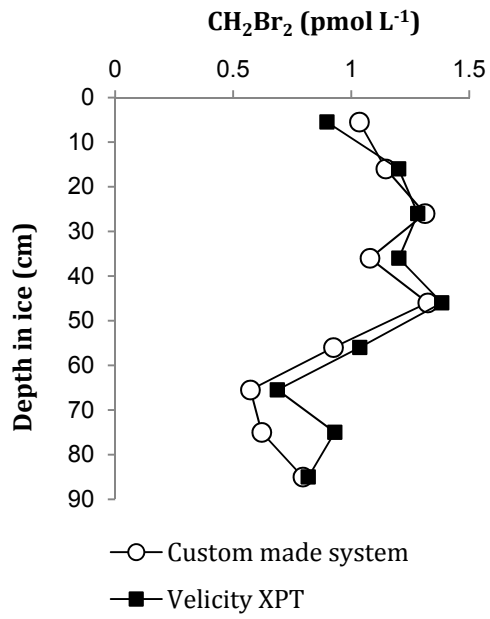


Figure 4. Bulk concentrations of CH_2Br_2 in a sea ice core from the OSO10/11 expedition. Comparison of custom-made and commercial system in determination of

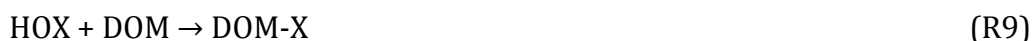
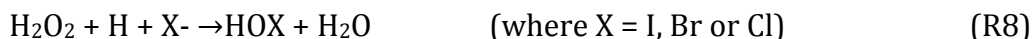
4. Halocarbon formation

The halocarbons in this study are predominantly of marine origin and are naturally produced. Some terrestrial sources exist such as wood-rotting fungi (Harper, 1985), biomass-burning (Andreae *et al.*, 1996) and volcanic eruptions (Rasmussen *et al.*, 1980), but are not discussed here. An anthropogenic source of bromoform is disinfection of seawater by chlorination and ozonation. Coastal nuclear power plants can be strong local sources of organic bromine, but globally they are not significant compared to natural sources (Quack and Wallace, 2003).

4.1. Enzymatic formation of halocarbons by marine algae and diatoms - biosynthetic pathway

The biosynthetic pathway for halocarbon formation consists of an oxidation of halides by hydrogen peroxide, H₂O₂, in the presence of a haloperoxidase enzyme. The first proposed mechanism for formation of CHBr₃ and CH₂Br₂ by bromoperoxidase was based on studies of the red seaweed *Bonnemaisonia hamifera*, where ketones present in the seaweed were brominated by peroxidase. The ketones are unstable and decay to form volatile brominated compounds (Theiler *et al.*, 1978).

According to later studies (Wever *et al.*, 1991; 1993) it is more likely that the algae release HOBr into the surrounding seawater, where fast reaction with dissolved organic matter (DOM) takes place. The decay of the brominated DOM leads to formation of halocarbons, of which CHBr₃ and CH₂Br₂ are the most abundant brominated compounds (Reactions 8-10).



Haloperoxidases are grouped according to which halide ion they are able to utilize for the halogenation. Chloroperoxidases use Cl⁻, Br⁻ and I⁻; bromoperoxidases utilize Br⁻ and I⁻; while iodoperoxidases use I⁻ as the halogen source. The mechanism where halocarbons are formed from the reaction of HOX with organic matter is of the same type as the haloform-reaction (R11), known from the disinfection of water by chlorination (Helz and Hsu, 1978).

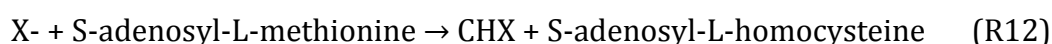


The haloperoxidase reacts with an activated CH-bond in the α-position to a carbonyl or carboxyl group to form the C-X bond. It is followed by hydrolysis of the X_nC-(C=O)-bond and leads to formation of dihalo- and trihalomethanes (Ballschmiter, 2003).

The above reactions require that the haloperoxidase enzyme is located at or near the cell surface and this has been shown for several species of macroalgae (Wever and van Horst, 2013 and references therein). Extracellular release of HOI and HOBr has been observed for diatoms and ice algae (Hill and Manley, 2009).

H₂O₂, involved in halocarbon formation, is generated in the plant cell during photosynthesis and respiration. Increased release of H₂O₂ in macroalgae (seaweeds) is caused by environmental conditions such as light stress (Pedersén *et al.*, 1996; Manley and Barbero 2001). It has been proposed that formation of halocarbons is a result of oxidative stress and that the reaction is due to scavenging of H₂O₂ and other oxidants that may be harmful to the cell (Collén, 1994; Pedersén *et al.*, 1996). An increased release of halocarbons from the brown algae *Laminaria digitata* was reported as a response to oxidative stress (Palmer *et al.*, 2006). Another purpose of halocarbon production might be a chemical defense against fungi, bacteria and grazers (Wever *et al.*, 1991). A release of HOBr at the algal surface is both directly bactericidal and disturbs bacterial signaling systems (Hansen *et al.*, 2003; Borchardt, 2001).

The methyl halides, such as CH₃I, are formed in a different mechanism aided by methyltransferase (R12, Wousmaa and Hager 1990, Manley 2002).



4.2. Marine algae as halocarbon producers

Macroalgae are large producers of halocarbons, and high concentrations are found along coastlines with beds of macroalgae (Shi *et al.*, 2014). Bromoform concentrations of up to 3 nmol l⁻¹ have been observed in shore-regions (Quack and Wallace 2003 and references therein). While macroalgae are the main halocarbon-producers in coastal areas, diatoms dominate the oceanic production. Marine phytoplankton and sea ice algae, especially diatoms are known halocarbon producers (Moore, 1996; Sturges *et al.*, 1997, Hill and Manley, 2009, Section 5.2). For diatoms, a higher production rate of HOI and HOBr was found for polar than for temperate species (Hill and Manley, 2009).

The importance of ice algae as halocarbon producers was indicated by Carpenter *et al.* (2007), who related high surface water concentrations of CH₂I₂ in the Weddell Sea to melt water from sea ice and sea ice algal blooms. In the Amundsen Sea, higher surface water concentrations of CHBr₃ and CH₂ClI were found in sea ice-covered areas than in open water, suggesting sea ice as a source (Mattsson *et al.*, 2012). Sturges *et al.*, (1997) reported elevated concentrations of bromoform in sea ice and snow from the Canadian Arctic, and in the Weddell Sea, Atkinson *et al.* (2012) observed concentrations of iodocarbons in sea ice that were strongly enhanced relative to seawater.

Nine halocarbon compounds were measured in sea ice samples from the Amundsen and Ross Seas (Paper II). Enhanced halocarbon concentrations relative to seawater were observed, even when concentrations were related to salinity of the samples. This showed that the elevated concentrations were not only a result of physical concentration in the ice, and that production occurred in the ice. Chlorophyll *a* (chl *a*) was used as a measure of biomass of ice algae, and biological production of halocarbons in the ice by ice algae was supported by correlating vertical distributions of chl *a* and several of the measured halocarbons (Figure 5).

Biogenic Halocarbons in Polar Sea Ice

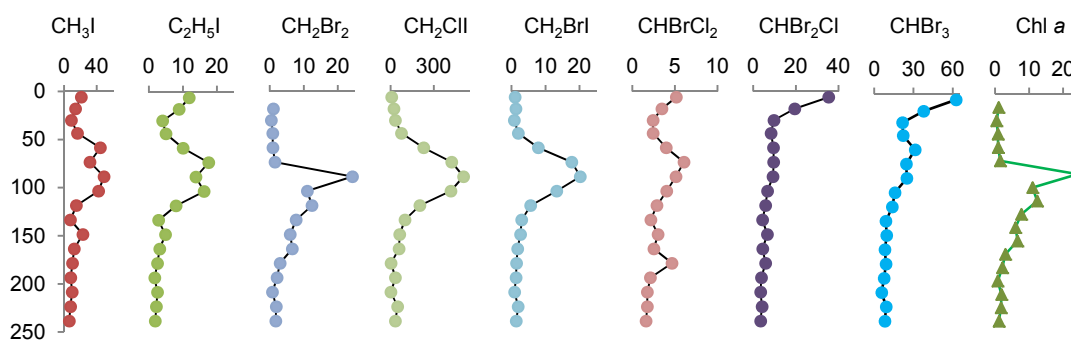


Figure 5. Vertical distribution of halocarbons and chlorophyll *a* in annual Antarctic sea ice in summer. Concentrations of halocarbons are the estimated concentrations in sea ice brine in pmol l^{-1} . Concentrations of chl *a* are in $\mu\text{g l}^{-1}$.

Correlations in vertical distributions were found between chl *a* and the halocarbons CH_3I , $\text{C}_2\text{H}_5\text{I}$, CHBrCl_2 , CH_2ClI , $1\text{-C}_3\text{H}_7\text{I}$ and CH_2BrI , which suggested that maximum concentrations were a result of biological production at that depth (Table 2, Paper II).

Table 2. Spearman's rank correlation coefficients (ρ) and p-values for the correlation between VHOCs and chlorophyll *a* in sea ice (bulk ice concentrations normalized for brine volume)^a

Compound	ρ	p-value	n
CH_3I	0.46	<<0.001	111
$\text{C}_2\text{H}_5\text{I}$	0.42	<<0.001	111
CH_2Br_2	ns		
CHBrCl_2	0.34	0.0002	111
CH_2ClI	0.27	0.01	111
CHBr_2Cl	ns		
$1\text{-C}_3\text{H}_7\text{I}$	0.25	0.01	99
CH_2BrI	0.23	0.02	107
CHBr_3	ns		

^aOne sample represents one 10-cm ice core section. ns = not significant ($\rho < 0.2$ and $p > 0.05$)

4.3. Abiotic formation

One possible abiotic pathway for halocarbon formation is the photochemical production of iodomethane, CH_3I , in the surface ocean (Happell and Wallace 1996, Moore and Zafiriou 1994). Similarly, photochemical production of alkyl halides, such as CH_3I and $\text{C}_2\text{H}_5\text{I}$, in the Arctic snowpack has been proposed. The alkyl halides are then formed by reaction of alkyl radicals, produced from photolysis of carbonyl compounds, with iodine atoms that origin from oxidation of iodide by OH-radicals (Swanson *et al.*, 2002).

For dihalomethanes, such as CH_2I_2 and CH_2BrI , abiotic formation via reaction of HOI and HOBr with organic material in the quasiliquid layer on sea ice and

snowpack was proposed by Carpenter *et al.* (2005). The source of HOBr was suggested to be atmospheric deposition or reactions in the liquid phase. Uptake of ozone on the ocean surface may be an abiotic formation pathway for CH₂I₂ and CH₂ClI. In laboratory experiments, performed in darkness, seawater was exposed to ambient levels of ozone and iodocarbons were monitored. It was proposed that reaction of O₃ with iodide lead to formation of HOI and that subsequent reaction with dissolved organic matter (DOM) produced halocarbons via a haloform-type reaction (Martino et al 2009).

In Paper III, abiotic formation of the brominated halocarbons CHBr₃, CH₂Br₂, CHBrCl₂ and CHBr₂Cl in the snow-ice interface during polar night is suggested. High concentrations of bromocarbons were found in the top 10 cm of the sea ice and in the snow closest to the ice surface. Sharp concentrations gradients were observed downward in the ice and upward through the snow cover. Abiotic formation was proposed through a dark reaction of ozone with halides on ice-surfaces according to Oum *et al.* (1998), where hypobromous acid is formed (R13).



A simplified overview of the reactions leading to formation and release of halocarbons from sea ice is presented in Figure 6.

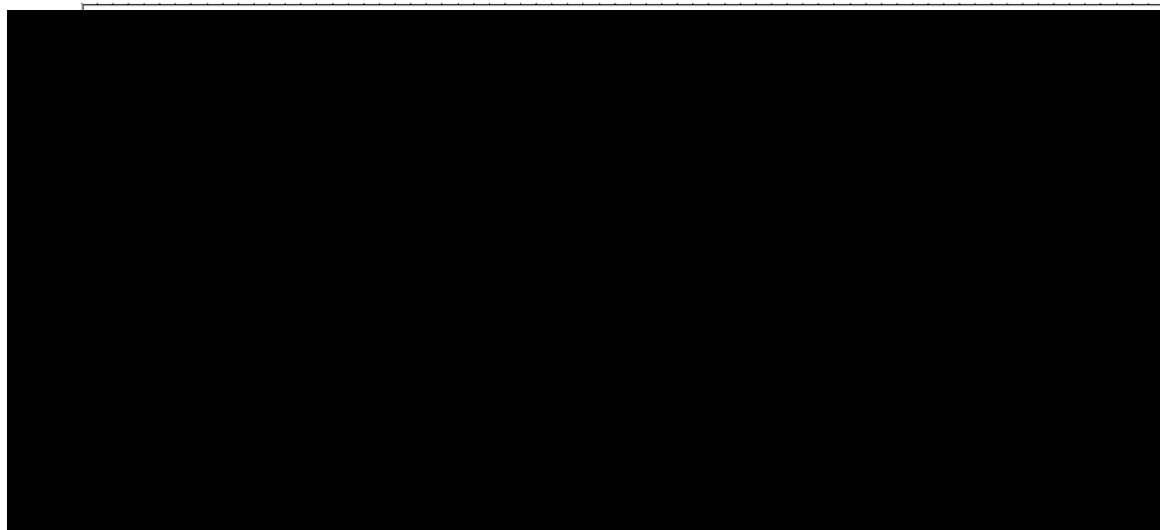


Figure 6. Abiotic formation of halocarbons at the sea ice surface (Paper III).

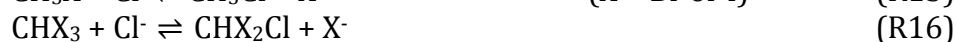
The same pathway could explain surface ice formation of iodinated compounds in winter sea ice, since HOBr will readily react with available iodide and form HOI according to R 14.



Concentrations and depth distributions of CH_2ClI , CH_2BrI and CH_2I_2 in ice sampled in summer and winter were compared (Paper IV). These compounds were distributed differently in winter ice than in summer ice. This was attributed to an abiotic formation of iodocarbons in the snow-ice interface during winter.

4.4. Halide substitution

Halocarbons can undergo nucleophilic substitution of bromine and iodine with chlorine which is present in high concentration in seawater. This occurs for both monohalogenated (R15) and polyhalogenated compounds (R16-R17).



Formation of CH_2ClI has been proposed to occur from CH_2I_2 via halogen-exchange. However, laboratory studies of the degradation of CH_2I_2 in dark incubations have shown that it does not readily undergo nucleophilic attack by chloride ions, but the reaction is induced by photolysis of CH_2I_2 (Class and Ballschmiter 1988; Martino *et al.*, 2005).

Equation R16 and R17 can form CHBr_2Cl and CHBrCl_2 from CHBr_3 , which has been confirmed by laboratory studies (Geen, 1992). Depth distributions of these compounds in Polar oceans, with relatively higher concentrations of CHBrCl_2 in deep waters may also be a result of halogen substitution (More and Tokarczyk, 1993; Karlsson, 2012). The relationship between CHBr_3 and its reaction products can help to estimate the age of a watermass, and may be utilized for tracing movements of watermasses in the deep ocean.

5. Sea ice and snow as media for halocarbon production and release

The fact that sea ice is porous makes it a possible habitat for microorganisms and enables exchange between ice and atmosphere. Sea ice is, thus, a potential source for biogenic gases. Snow cover will affect release of halocarbons to air and has also been suggested as a source of CH_3I and $\text{C}_2\text{H}_5\text{I}$ (Swanson *et al.*, 2002; Atkinson *et al.*, 2012).

5.1. Sea ice physics

Sea ice, in contrast to lake ice, contains a fluid phase, which controls biogeochemical cycles and fluxes in the ice. The major ions present in sea water (Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , and CO_3^{2-}) are not incorporated into the crystal lattice of sea ice, but are rejected during ice growth. The largest part is rejected to the underlying seawater and plays an important role in ocean circulation as it forms deep-water masses (Orsi *et al.*, 1999). Some of the solutes are retained in liquid inclusions, brine. The length of these inclusions can range from 0.1 to 10 mm (Light *et al.*, 2003). Ice porosity is also affected by gas inclusions. These constitute 1-5 % of first year ice and increase in springtime (Perovich and Gow, 1996).

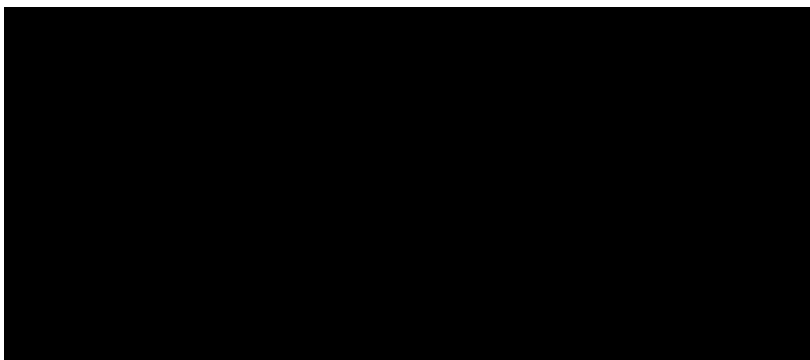


Figure 7. Calculated brine volume and measured bulk salinity and temperature in seasonal sea ice, sampled in the Weddell Sea (Paper IV).

Changes in brine volume and salinity during cooling and warming are controlled by ice temperature, and physical properties of sea ice can be described if temperature or salinity is known (Assur, 1960). This approach assumes thermodynamic equilibrium between the phases (liquid brine, solid ice and precipitated solid salts). The thermodynamic model may not be sufficient for describing strongly desalinated ice (Thomas *et al.*, 2010). An example of the vertical distribution of brine volume and salinity in sea ice is given in Figure 7.

5.2. Sea ice algae and bacteria

Sea ice ecosystems are one of the largest on earth, and sea ice algae are significant primary producers both in the Arctic Ocean (Gosselin *et al.*, 1997) and in the Southern Ocean (Thomas and Dieckmann, 2002; Arrigo and Thomas, 2004). Sea ice algae are an important energy and nutritional source to juvenile krill, and during winter, when phytoplankton biomass in the water column is extremely low, they are a crucial food source for overwintering species (Gleitz and Thomas, 1993; Arrigo and Thomas, 2004).

Diatoms are the dominating group of ice algae, both in the Arctic and Antarctica (Figure 8). During seawater freezing, algae and bacteria are incorporated from the water into the forming ice (Garrison *et al.*, 1989), during the entire period of freezing (Werner *et al.*, 2007). Gradually, during aging of the ice, there is a change in species composition. Large centric diatoms become less common, while small pennate species such as *Fragilariopsis cylindrus* and *Nitzschia frigida* become more dominating (Gleitz and Thomas, 1993). Similarly, a transition is seen in the bacterial population to species that are better adapted to growth and reproduction in cold environments (Thomas and Dieckmann, 2002).



Figure 8. Pennate, ice-living diatom *Nitzschia* spp. Photo Pauline Snoeys

Vertical distributions of sea ice microalgal communities are a result of physical processes, such as light, temperature and space but also of nutrient supply. Ackley and Sullivan (1994) described four major regions for biomass maxima in Antarctic sea ice: flooded surfaces, at the freeboard layer, in interior ice and in the bottom layer. Importance of interior communities in contrast to previously studied under-ice blooms in both polar areas was suggested after observation of a microalgal autumn bloom in the interior multi-year-ice in Weddell Sea (Fritsen *et al.*, 1994).

Interior sea ice algal communities were observed in Antarctic sea ice and associated to halocarbon production (Paper II). Concentrations of halocarbons and chlorophyll *a* (chl *a*), were compared in order to confirm production of halocarbons by ice algae. Large variation in the vertical distribution of chl *a*, was observed in ice cores and maxima often appeared in the upper and interior part. This was compared to vertical distributions of nine halocarbon compounds (Table 3.) Five of the nine halocarbon compounds studied: CH₃I, CH₂Br₂, CH₂BrCl₂, CH₂Br₂Cl, and CHBr₃, most often had a maximum concentration in the internal ice.

Table 3. Percentages of all samples in which the specified compounds have a maximum concentration in the surface (upper third), internal region (middle third) or in the bottom (bottom third) of the ice core.

Compound	Surface ice	Internal ice	Bottom ice
CH ₃ I	19	56	25
C ₂ H ₅ I	44	25	31
CH ₂ Br ₂	19	44	38
1-C ₃ H ₇ I	54	9	36
CHBrCl ₂	6	56	38
CH ₂ ClI	13	44	44
CHBr ₂ Cl	25	44	31
CH ₂ BrI	27	33	40
CHBr ₃	19	50	31
Chl <i>a</i>	56	44	0

Sympagic (ice-associated) species are exposed to large seasonal variations in temperature, salinity and light conditions. Ice algae have several strategies for survival in winter conditions, such as secreting macromolecules and exopolymeric substances (EPS) that form gels and function as cryoprotectors. They can also use osmolytes such as DMSP as protection against the high salinities in the brine channels (Arrigo *et al.*, 2010). Sea ice algae survive the harsh winter conditions, although their growth is inhibited in the dark. Nutrient availability may be a limiting factor to ice algal growth (Arrigo *et al.*, 2010). However, nutrients may also be enriched in the ice as a result of microbial regeneration of nitrogen compounds (Werner *et al.*, 2007). In one of few studies in winter sea ice, it was observed that the diversity of species of Arctic sea ice algae was similar as in other seasons. However, their abundance was several orders of magnitude lower than peak levels (Werner *et al.*, 2007). Sea ice bacteria can be active even at temperatures as low as -20°C (Junge *et al.*, 2004).

Concentrations of organo-iodine compounds in the interior of winter sea ice were, with the exception of CH₃I, lower than in ice sampled in the summer (paper IV). The vertical distributions were also clearly different in winter, which suggested a different formation mechanism in summer. For CH₃I, both concentrations and depth distributions were similar in ice from both seasons, which implied that this compound had a biotic formation through the enzymatic methyltransferase pathway in both summer and winter.

5.3. Trace gases in ice

Diffusion through brine channels may be a pathway for the exchange of trace gases between the sea ice and atmosphere. This transport depends on a number of factors such as, ice thickness, brine volume, gas bubbles (Loose *et al.*, 2011) and biofilms and gels (section 5.2). Only a few attempts have been made to estimate gas diffusivities in cold first-year sea ice, and they differ between gases: 18 - 90 * 10⁻⁵ cm² s⁻¹ for CO₂ (Gosink *et al.*, 1976, Nomura *et al.*, 2006); 3-6*10⁻⁵ for O₂ (Loose *et al.*, 2011), and 0.4-20 * 10⁻⁵ for SF₆ (Gosink *et al.*, 1976; Loose *et al.*, 2010). No estimate of gas diffusion has been reported for warmer, more porous ice, but it is likely that diffusion rates are larger due to its more porous structure. Vertical profiles of halocarbons in in summer sea ice often had maximum concentrations in the interior ice (Paper II, Paper IV). This may indicate that there was a production in the ice and that a diffusive flux was present.

Halocarbons and biological parameters were studied simultaneously during freezing of sea ice in a natural environment (Paper I). The aim was to find factors that controlled halocarbon concentrations in the ice, focusing on a potential flux to the atmosphere during freezing. Concentrations of CH₂BrI linearly decreased with time in the ice during freezing, and a diffusion coefficient of 7.5 x 10⁻⁵ cm² s⁻¹ was estimated (Figure 9). This value corresponds well to coefficients determined for CH₃I, CH₂H₆I, 2-C₃H₇I and 1-C₃H₇I of 1-3 10⁻⁵ cm² s⁻¹ in tank experiments (Shaw *et al.*, 2011).

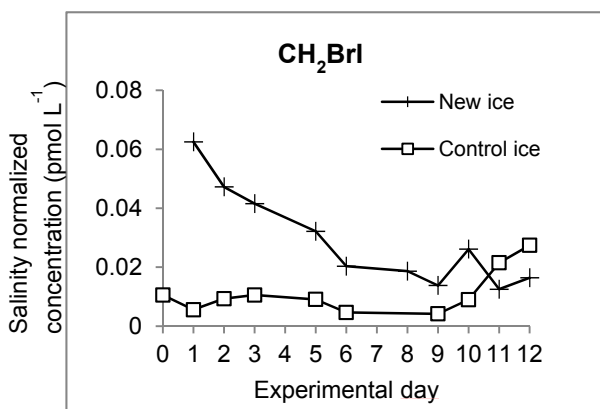


Figure 9. Temporal variation of mean CH_2BrI^- concentration, normalized to salinity, in surface ice (0 - 10 cm depth) compared to old ice (control).

5.4. Snow

The net flux of halocarbons from sea ice to air is affected by diffusion in snow. Grain size, snow thickness and amount of liquid water in the snow are factors that may affect gas flux (Bartels-Rausch *et al.*, 2013). Diffusion in combination with ventilation will ultimately determine the flux through snow. Empirical studies of diffusivity of halogenated compounds in snow, showed that mass transfer coefficients could be derived from diffusion coefficients in air and the snow porosity (Herbert *et al.*, 2006).

In Paper III, the measured concentrations in snow (thickness 10-40 cm) were used to estimate net flux of bromocarbons from sea ice. From the concentration profiles in snow, the diffusion controlled region could be separated from the ventilated zone (Figure 10). Bromocarbon concentrations in interstitial air were determined from snow porosity and concentrations in melted snow, assuming that partition of bromocarbons to the solid snow was negligible. Fluxes were calculated using the species specific diffusion coefficients in air, snow depth and the linear concentration decrease. Their magnitude was compared to flux calculations according to Wanninkhof and McGillis (1999), using Equation 2.

$$F = K_w(C_a/H - C_w) \quad (\text{Eq 2})$$

where K_w is the transfer velocity, C_a is the concentration in the atmosphere and H is the Henry's law constant. Surface ice concentrations were used as C_w . This approach assumes that flux is not influenced by snow cover, and that a brine layer is present on the ice surface. The flux from the ice surface is calculated equivalent to that from a sea surface, although the higher viscosity of the brine due to salinity is taken into account.

There is to date no generally accepted equation for calculating fluxes of halocarbons from snow covered sea ice. Most likely the presence of snow will affect fluxes from sea ice, and when flux was calculated based on snow concentrations gave a smaller bromocarbons flux than when Equation 2 was used (Paper III). However, both approaches result in large fluxes that would lead to accumulation of organo-bromine in the troposphere, which can form reactive bromine species in polar spring.

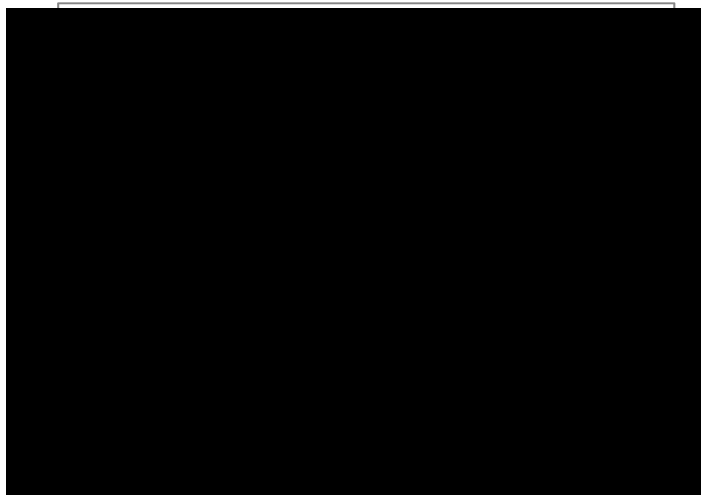


Figure 10. Depth profile of bromoform and chlorodibromomethane in sea ice (brine normalized concentration) and snow from the Weddell Sea in winter (Paper III).

5.5. Frost flowers

Frost flowers are an additional pathway for transport of brine, and thereby halocarbons, to the ice surface. These crystalline structures are formed on new sea ice when air, which is supersaturated with water vapor, condenses on the ice surface. Sea ice brine is wicked up on the frost flowers by surface tension and concentration gradients.

Halocarbons were measured in newly formed frost flowers in the Arctic study site at Svalbard (Paper I). These contained CHBr_3 , CHBrCl_2 and CHBr_2Cl in concentrations comparable to those in brine, sampled at the same location. Iodinated halocarbons were found in lower concentrations that resembled those in seawater. After 20 h the frost flowers were sampled again, and now, concentrations of both iodinated and brominated halocarbons were lower. Approximately 95 % of the halocarbon content had disappeared, while the salinity remained unchanged. We attributed this to evaporation or photolysis of the halocarbons between the two sampling occasions, and that the frost flowers were a source of organo-halogens, although it was of short duration.

Frost flowers sampled at four of the stations during the winter expedition contained high concentrations of brominated halocarbons, compared to seawater concentrations. However, the content of iodinated halocarbons more resembled that in seawater (Paper IV). The average salinity of melted frost flowers was 67 PSU, comparable to brine salinity: 97 PSU, which might indicate that loss of iodocarbons from the frost flowers occurred before sampling due to evaporation.

6. Main results

Vertical distribution of halocarbons in sea ice varied with season. In summer a biotic formation within the sea ice governed the distribution for poly-halogenated compounds, with the highest concentrations in the interior ice. In contrast, during polar night, an abiotic production lead to extremely high concentrations, at least 10 times more than in summer, in the upper most layers of the ice. The distribution of the mono-halogenated CH_3I was governed by a biotic production in both seasons.

Physical parameters such as variation in salinity and temperature had a minor influence on vertical distributions, and the halocarbons were shown to have a non-conservative distribution. Photolysis, of especially the iodinated compounds, was observed in snow, and it could only be speculated if this process governs the distribution in the surface ice. High atmospheric concentrations of halocarbons was observed in winter, average concentration 5 times that of summer, which most probably was an effect of a flux of halocarbon in winter in combination with photolysis during summer (Figure X).

At polar night, newly formed ice was shown to be a significant source of atmospheric organo-bromine and organo-iodine. The calculated fluxes of up to $50 \text{ nmol m}^{-2} \text{ h}^{-1}$ for bromoform and $0.4 \text{ nmol m}^{-2} \text{ h}^{-1}$ for CH_2ClI highlight seasonal sea ice as foci for halocarbon production.

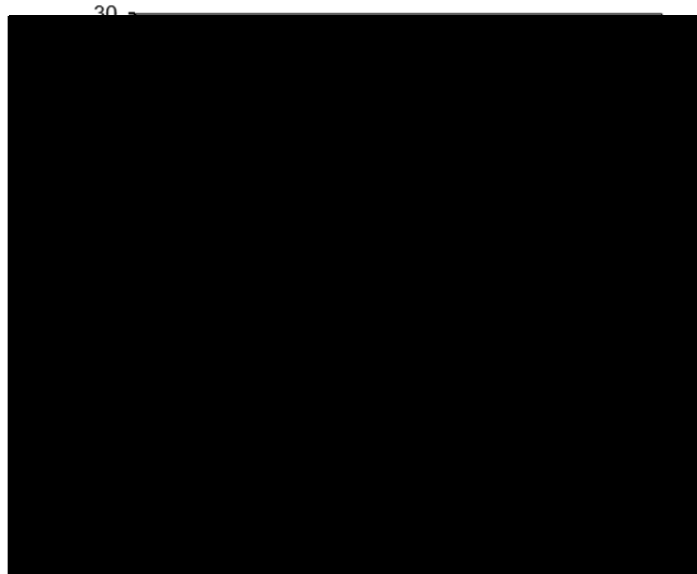


Figure 11. Air concentrations of bromoform measured during ANT XXIX/6 (Winter and OSO 10/11 (summer)).

7. Future outlook

The unexpectedly high abundances of brominated and iodinated halocarbons in winter sea ice, also reflected in snow and air, calls for further investigations, both in the field and in the laboratory. A follow up of estimated ice-air fluxes with direct flux measurements in the field would be desirable. Moreover, the abiotic formation mechanism that may occur on the surface of seasonal winter sea ice needs to be validated in laboratory experiments.

Ideally future field investigations would be performed during an extended period of time, at the same location. In order to clarify the role of halocarbons in tropospheric ozone depletion events, they should be monitored in sea ice, snow and air in the transition to polar spring.

In a future perspective, a continuation of the multi-disciplinary approach would be valuable. A relation between halocarbons in sea and biological parameters measured in the field may provide insight in what influence the changing climate will have on biogenic halocarbon production in polar oceans.

8. Acknowledgements/Tack

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Min biträdande handledare Melissa: du är en inspiration för alla isforskare!

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