On Biogenic Halocarbons in Antarctic Waters

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Cover illustration: Bromoform concentration in the surface waters of the Southern Ocean

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Abstract

Little is known regarding the distribution of naturally produced volatile halogenated organic compounds, halocarbons, in Antarctic waters and the contribution of these waters to the global atmospheric load of halogens. In the atmosphere, halocarbons are degraded by photolysis, and form reactive halogen radicals. These radicals are thereafter involved in the catalytic degradation of ozone and formation of aerosols. Ozone degradation mainly occurs over the poles, and the process is most prominent during the springtime in the stratosphere at the South Pole.

Biogenic halocarbons are formed by algae during photosynthesis. As such, the formation of halocarbons takes place in all oceans, but with large spatial and temporal variations. To determine the source strength of the oceans, it is essential to establish reliable estimates of the air-sea exchange, as well as production and degradation rates of halocarbons in the assessment of the role the oceans play in the destruction of ozone.

In this work, the major aim has been to broaden the knowledge of the distribution of biogenic halocarbons in the Pacific sector of the Southern. Studies of the relationship between halocarbon distributions and biophysical variables indicated sea ice as the main regulating factor. The production and degradation rates in sea ice were therefore established, and the net production was found to be able to sustain concentration gradients in the ice. High resolution measurements of halocarbons in surface water and air were conducted to establish the air-sea exchange of halocarbons, and the results showed that the cold waters acted as a sink (100 days of minimum sea ice extent), with an uptake of 0.04 Gmol Br for bromoform, in contrast to earlier findings. A three year study during the austral summer in the Amundsen Sea was conducted, and the distributions and fluxes of halocarbons were found to be consistent. A novel approach utilising transposed- orthogonal projections to latent structures T-OPLS, indicated that biogenic halocarbons could be used to study the circulation of water masses on the shelf in the Amundsen Sea.

Keywords: Volatile biogenic halocarbons, Antarctica, Southern Ocean, Sea ice, snow, air-sea exchange

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Populärvetenskaplig sammanfattning

Flyktiga halogenerade kolväten, även kallade halokarboner, återfinns i både haven och atmosfären. De vanligaste naturligt bildade halokarbonerna innehåller brom eller jod medan de antropogena oftast innehåller fluor eller klor. De största naturliga källorna av dessa ämnen är haven. Här bildas halokarboner av tång och växtplankton när de försöker göra sig av med överskott av väteperoxid som bildas under fotosyntesen. Vad som påverkar produktionen av halokarboner är fortfarande oklart. Den högsta produktionen av halokarboner återfinns i kustnära områden där tång frodas, men eftersom det öppna havet är så mycket större till ytan är även detta en betydelsefull källa. Halokarboner som uppehåller sig i ytan kan övergå till atmosfären, eftersom de är flyktiga. Väl där kan de delta i ozonnedbrytande processer, när de utsatta för solljus bildar reaktiva radikaler. Dessa processer är mest påtagliga över polerna, där ozonhalten på sommarhalvåret minskar drastiskt i halt. Polarområdena är också viktiga att studera ur ett klimatologiskt perspektiv, eftersom de är känsliga för den globala uppvärmningen som sker på jorden, exempelvis har en ökad avsmältning av glaciärerna i Antarktis observerats. Halokarboner är förhållandevis lite undersökt i Antarktis jämfört med de tempererade haven.

Under tre år med den svenska isbrytaren Oden genomfördes mätningar av halokarboner i havsis, atmosfär och hav i Amundsen och Ross haven. Resultaten från mätningarna i havsisen visade att isen är en betydelsefull källa av halokarboner till atmosfären och denna borde inkluderas i framtida globala budgetar av halokarboner. Luft och havsvattenmätningar i de olika regionerna visade att dessa vatten kan agera som en sänka för halokarboner i atmosfären, vilket var en viktig upptäckt då dessa vatten tidigare har ansetts endast vara en källa av halokarboner till atmosfären..

Part A. Table of contents

Part B. List of Publications

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

I. Mattson, E., Karlsson, A. Smith, W.O., and Abrahamsson, K. (2012) The relationship between biophysical variables and halocarbon distribution in the waters of the Amundsen and Ross seas, Antarctica, *Marine Chemistry*, 141-142, 1-9, doi:10.1016/j.marchem.2012.07.002

II. Mattsson, E., Karlsson, A., and Abrahamsson, K. (2013) Regional sinks of bromoform in the Southern Ocean, *Geophysical Research Letters*, Vol. 40, 1-6, doi:10.1002/grl.50783

III. Mattsson, E., Karlsson, A. Granfors, A. M. Josefson and Abrahamsson, K. Inter-annual variation of halocarbons in the Amundsen and Ross Sea, *Manuscript*

IV. Granfors, A., Karlsson, A. Mattsson, E., Smith, W.O., and Abrahamsson, K. (2013) Contribution of sea ice in the Southern Ocean to the cycling of volatile halogenated organic compounds, *Geophysical Research Letters*, Vol. 40, 1-6, doi:10.1002/grl.50777

Contribution Report

Paper I:	Responsible for planning, conducting experiments, interpretation and writing
Paper II:	Responsible for planning, conducting experiments, interpretation and writing
Paper III:	Participated in planning, conducting experiments, interpretation and writing No participation on experimental part of OSO2010.
Paper IV:	Participated in planning and interpretation

Abbreviations

AASW	Antarctic Surface Water
CDW	Circumpolar Deep Water
mCDW	modified Circumpolar Deep Water
AABW	Antarctic Bottom Water
SW	Shelf Water
ISW	Ice Shelf Water
ACC	Antarctic circumpolar current
NADW	North Atlantic Deep Water
AIW	Antarctic Intermediate Water
RIS	Ross Ice Shelf
ECD	Electron capture detector
GC	Gas chromatograph
MS	Mass spectrometer

1 Rationale

Volatile halogenated organic compounds, VHOCs, or more commonly, halocarbons, have two independent sources; human industrial activities and biogenic processes in the oceans. Halocarbons are defined as hydrocarbons with one or several covalently bonded halogens, e.g. fluorine, chlorine, bromine or iodine. When halocarbons are released into the atmosphere, they are subjected to photolysis, producing reactive halogen radicals, which produces reactive halogen free radicals. These free radicals are involved in ozone depletion both in the troposphere and in the stratosphere.

The largest source of biogenic halocarbons on Earth is the oceans. The role of these compounds in the degradation of ozone has been investigated ever since Lovelock [1973] found that marine algae could produce CH_3I. The biogenic compounds include a number of chlorinated, brominated, and iodinated compounds, where bromoform is the single largest contributor to organo-bromine in the atmosphere [*WMO*, 2010]. There are still uncertainties regarding the global circulation of these compounds even if the mechanisms behind the biological production of halocarbons have been extensively studied, and algal production rates have been established. For instance, the oceanic source of $CHBr_3$ based on algal production has been estimated to be ~ 3 Gmol yr^{-1}, and the emission of $CHBr_3$ to the atmosphere ~10 Gmol yr^{-1}, which indicates a discrepancy of ~ 7 Gmol yr^{-1}[*Quack and Wallace*, 2003]. Parameters that control the biological production, geographical distribution, seasonal variation, the air-sea flux, and the degradation of halocarbons are all factors that need to be further investigated to minimize the discrepancies in the global models of source strengths and fluxes. Uncertainties can also be found in the models due to the under-sampling of the oceans, with respect to geographical, temporal and seasonal coverage. Data from tropical regions are abundant and covers all seasons, whereas investigations of Polar regions are scarce, and usually conducted during the summer.

The aim of this work has been to broaden the knowledge of biogenic halocarbons (Table 1) in the waters surrounding the Antarctica, with special emphasis on the Bellingshausen, Amundsen, and Ross Seas. To understand the driving forces of the halocarbon distribution, the coupling to biogeophysical parameters and sea ice have been investigated (Papers I and IV). The removal of halocarbons from the mixed layer due to degradation and downward mixing was investigated through studies of the water column (Paper III).

An additional focus area has been to determine the air-sea exchange of halocarbons and investigate possible factors which affect the magnitude and direction of the flux. (Paper I and II and III). The validity of the results was tested by repeating the investigations during three almost consecutive years (Paper III).

2 Background

The occurrence of ozone in the stratosphere is essential for all living organisms, since it blocks harmful ultraviolet radiation (UVB) from penetrating down to the Earth surface. The involvement of halocarbons in atmospheric ozone degradation was established by *Molina and Rowland* [1974]. They concluded that chlorofluorocarbons (CFCs) emitted to the atmosphere where degraded by photolysis, which produced chlorine free radicals that could degrade stratospheric ozone. At the time of this finding, no real possibilities to monitor stratospheric ozone on a global scale were available. The research of ozone degradation caused by CFCs progressed slowly, and the possibility to monitor stratospheric ozone was not established until the launch of the satellite Nimbus-7 in 1978. The first picture of the thinning of the ozone layer published in 1985, when Pawan Bhartia at NASA´s Goddard Space Flight Center, presented the famous image of what later would be called the "ozone hole" [*Keating et al.*, 1985].

Parallel to Molina and Rowland's finding, James Lovelock found that marine algae could produce methyl iodide, a compound known mainly as an industrial chemical reagent .compound that was mostly used as a chemical reagent [*Lovelock et al.*, 1973]. In addition to monohalogenated methanes, *Burreson et al.* [1976] found that marine algae were able to produce polyhalogenated methanes, such as bromoform. Around this time, it was also suggested that bromine was more efficient than chlorine in the degradation of ozone, and $CHBr_3$ was identified to be an important carrier of bromine to the atmosphere [*Wofsy et al.*, 1975].

When halocarbons, such as $CHBr_3$, enter the atmosphere, the major removal processes are photolysis due to UV-radiation (Eqn. 2), and oxidation processes initiated by abstraction of hydrogen by OH/Cl (Eqn. 1). Photolytic cleavage of the C-Br bond in Eqn. 2 yields bromine radicals, which subsequently may react with oxygen (Eqn. 3) or ozone (Eqn. 4) in the atmosphere. This ultimately leads to the formation of inorganic bromine, Br_y (Br, BrO, HBr, HOBr, $BrONO_2$). The intermediate reactions in equation 1 and 2 that are involved in the complete degradation of $CHBr_2\cdot$ and $CBr_3\cdot$ are described in detail by *Hossaini et al.* [2009] and *McGivern et al.* [2004]. Due to the kinetics of oxidation and photolysis described in equation 1 - 5, a tropospheric lifetime of $CHBr_3$ has been estimated to ~ 15-30 days [*Hossaini et al.*, 2010; *Liang et al.*, 2010]. Equations 6 and 7 explain the formation, whereas equations 8 and 9 describe the destruction of ozone due to absorption of UV-light in the stratosphere.

Table 1. List of Compounds

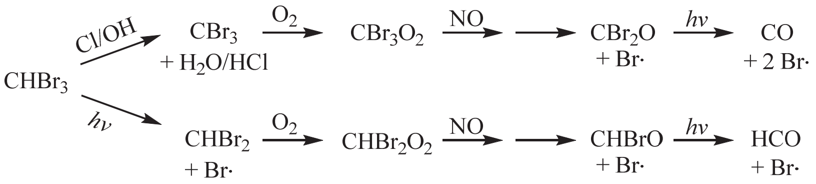
Formula	Name	Half-life atmosphere (OH + photolysis)[ii]
Biogenic Compounds[i]		*(days)*
CH_3I	Iodomethane (methyl iodide)	7
CH_3CH_2I	Iodoethane (ethyl iodide)	4
$CH_3CH_2CH_2I$	1-Iodopropane (propyl iodide)	0.5
CH_3CHICH_3	2-Iodopropane (iso-propyl iodide)	1.2
$CH_3CH_2CH_2CH_2I$	1-Iodobutane (butyl iodide)	n.d.[iii]
$CH_3CH_2CHICH_3$	2-Iodobutane (sec-butyl iodide)	n.d.[iii]
CH_2I_2	Diiodomethane	0.003
CH_2BrI	Bromoiodomethane	0.04
CH_2ClI	Chloroiodomethane	0.1
CH_3Br	Bromomethane (methyl bromide)	3.3-3.4 years
CH_2Br_2	Dibromomethane	123
$CHBr_3$	Tribromomethan (bromoform)	24
$CHBr_2Cl$	Dibromochloromethane	59
$CHBrCl_2$	Bromodichloromethane	78
CH_2BrCl	Bromochloromethane	137
Anthropogenic Compounds		*(years)*
CH_3CCl_3	1,1,1-trichloroethane (Methyl chloroform)	5
CCl_4	Tetrachloromethane (Carbon tetrachloride)	26

i) *Some can have both anthropogenic and biogenic sources*
ii) *Half-lives listed in [WMO, 2010]*
iii) *n.d., no data available*

Polar sea ice has primarily been regarded as a barrier limiting the exchange of halocarbons between the ocean and the atmosphere. However, as halocarbons were shown to be produced by algae living inside sea ice, this additional source of halocarbons to the atmosphere was suggested [*Karlsson*, 2012;

Sturges et al., 1992; *Sturges et al.*, 1993] (Paper I and IV). Today, atmospheric BrO is regularly monitored by satellites, and its abundance in the stratosphere has been found to be larger than expected from solely anthropogenic sources (CH_3Br, halons), which suggests that contribution of biogenic halocarbons carrying bromine can be a significant source [*WMO*, 2010]. Estimates based on the inventory of short-lived halocarbons in the atmosphere suggest that the oceanic load of short-lived brominated compounds should be 500 Gg yr^{-1} of $CHBr_3$, and 70 Gg yr^{-1} CH_2Br_2 [*Ordóñez et al.*, 2011].

Even though iodinated halocarbons have also been suggested to be involved in degradation of stratospheric ozone [*Solomon et al.*, 1994], they are usually considered as too short-lived (Table 1) to reach such altitudes. However, it has been shown that iodine oxide radicals and reactive organic iodine compounds are formed in the troposphere [*Pechtl et al.*, 2007]. Recent theoretical studies indicate that iodine compounds emitted to the Arctic atmosphere have a significantly greater ozone and mercury depletion effect than bromine compounds. Also, iodinated compounds are involved in marine aerosol formation, and iodine-containing aerosols have been associated with ozone depletion events during the polar sunrise.



$$\mathrm{CHBr_3} \xrightarrow{\mathrm{Cl/OH}} \mathrm{CBr_3} + \mathrm{H_2O/HCl} \xrightarrow{O_2} \mathrm{CBr_3O_2} \xrightarrow{NO} \longrightarrow \mathrm{CBr_2O} + \mathrm{Br\cdot} \xrightarrow{hv} \mathrm{CO} + 2\,\mathrm{Br\cdot} \tag{1}$$

$$\mathrm{CHBr_3} \xrightarrow{h\nu} \mathrm{CHBr_2} + \mathrm{Br\cdot} \xrightarrow{O_2} \mathrm{CHBr_2O_2} \xrightarrow{NO} \longrightarrow \mathrm{CHBrO} + \mathrm{Br\cdot} \xrightarrow{hv} \mathrm{HCO} + \mathrm{Br\cdot} \tag{2}$$

$$\mathrm{Br\cdot} + O_2 \longrightarrow \mathrm{BrO} + \mathrm{O\cdot} \tag{3}$$

$$\mathrm{Br\cdot} + O_3 \longrightarrow \mathrm{BrO} + O_2 \tag{4}$$

$$\mathrm{BrO} + O_3 \longrightarrow \mathrm{Br\cdot} + 2\,O_2 \tag{5}$$

$$O_2 + hv \longrightarrow 2\,\mathrm{O\cdot} \tag{6}$$

$$\mathrm{O\cdot} + O_2 \longrightarrow O_3 \tag{7}$$

$$O_3 + hv \longrightarrow O_2 + \mathrm{O\cdot} \tag{8}$$

$$\mathrm{O\cdot} + \mathrm{O\cdot} \longrightarrow O_2 \tag{9}$$

3 Southern Ocean

3.1 Overview

The Southern Ocean is a vast ocean that surrounds the Antarctic continent. In contrast to the Arctic Ocean, it is not enclosed by continents, and is therefore not a formal geographic region, such as the Atlantic or Pacific Oceans. The Southern Ocean has its northern boundary defined by the subtropical front, which varies between latitudes 38°S and 60°S [*Alejandro H. Orsi et al.*, 1995]. Around the Southern Ocean, the Antarctic Circumpolar Current (ACC) flows (Figure 1). It is the world's largest ocean current [*Rintoul*, 2009], and it moves eastwards around the Antarctic Continent, and is driven by the strong westerly winds around the globe [*Trenberth et al.*, 1990]. The ACC connects the Atlantic, Indian, and Pacific Oceans by transporting deep and intermediate waters in-between their basins. The ACC plays a key role in the world's ocean deep water circulation and the global overturning circulation [*Alejandro H. Orsi et al.*, 1995], which has a large impact on Earth´s climate, its ecosystems and biogeochemical cycles.

Three continuous circumpolar fronts can be found within the ACC; the sub-Antarctic front, the polar front, and the southern ACC front (Figure 1). The Antarctic divergence can be found at the southern ACC front. There, upwelling of North Atlantic Deep Water (NADW) takes place. This newly formed surface water is diverted northwards until it reaches the Antarctic convergence at the polar front, where it sinks and forms Antarctic Intermediate Water (AIW). This process can at least partly be explained by a northward Ekman transport induced by wind stress on the surface of the ACC, and an opposite southward transport in the upper Circumpolar Deep Water (CDW) driven by eddies. Antarctic Bottom Water, AABW, is mainly produced in the Weddell and Ross Seas [*A. H. Orsi et al.*, 1999]. This water is formed when CDW mixes on the shelf slopes with newly formed bottom water coming of the shelves. The bottom water is formed in the process of sea ice formation, as the surface water becomes heavier due to ejection of brine when sea ice freezes.

The sea ice in the Southern Ocean has its maximum extent during September, and was 19.4 million km^2 in 2013. The smallest extent is found during February, (3.8 million km^2 2013). (http://nsidc.org/cryosphere/sotc/sea_ice.html). The sea ice in the Southern Ocean is mostly annual (> 80%) with a mean thickness of 0.5 – 0.6 m. The trend in the sea ice coverage is an increase of 1.2 % /10 year, contrary to the rapid decrease in the Arctic sea ice cover (-3.8 % / 10 year). Within the Southern Ocean, local anomalies can be found where the sea ice cover in the Ross Sea is increasing with 4.9 % /years, in contrast to the Amundsen and Bellingshausen sea ice, which is decreasing with 7.1 % / 10 years [*Thomas and Dieckmann*, 2010].

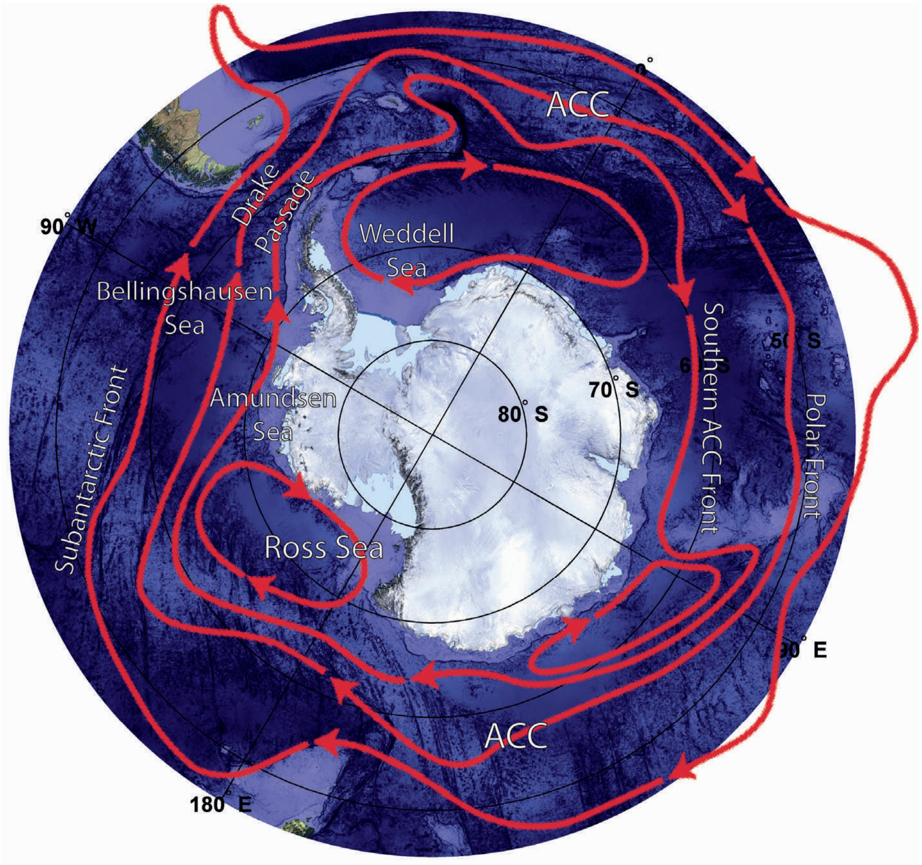


Figure 1. Southern Ocean frontal systems and surface currents.

3.2 Polynias

Two of the world's largest polynias can be found in the Southern Ocean, the Weddell Sea and the Ross Sea. The word polynia (UK spelling) originates from the Russian language and can be translated to "natural ice hole". A polynia, by definition, is an area of open water located in a place that would be expected to be covered by ice. Polynias are as such a winter phenomenon. During spring, when the sun returns, and the sea ice starts to melt, the polynias technically are no longer polynias, and are instead called post-polynias. These post-polynias are often the most biologically productive waters in the Southern Ocean.

Two types of polynias can be defined according to their physical properties, latent heat and sensible heat polynias. The Ross, Amundsen and Weddell Sea polynias are latent heat polynias. They are mainly formed by catabatic winds, blowing from the continent over the surface, pushing the ice away from the coast. As new ice forms in the open water of the polynia, the wind blows it to the leeward side of the polynia, keeping the windward side open and ice free. In this process, latent heat is released as the water freezes, and the surface water evaporates to the atmosphere. This continuous sea ice formation in the Ross and Weddell Sea polynias contribute with as much as 20-50 % (Ross polynia) and 5-10 % (Weddell polynia) of the total Antarctic sea ice cover [*Drucker et al.*, 2011]. Some sensible heat exchange occurs in the polynia, since the surface water temperature generally is warmer than the air above. Despite their relatively small areas, polynias play an important role in many physical and biological processes.

3.3 Ross Sea

The Ross Sea polynia (Figure 2) covers an area of ~20 000 km^2 in the winter and has a maximum summer extension of ~400 000 km^2. With a primary production of 47.9 ± 11.6 Tg C yr^{-1} (~ 150 g C m^{-2} yr^{-1}), the Ross Sea post-polynia is one of the biologically most productive polynias in the world [*K. R. Arrigo and van Dijken*, 2003]. The Ross Sea polynia produces roughly 20 % , e.g. 2 Sv [*Whitworth and Orsi*, 2006] of the AABW (~10 Sv)[*A. H. Orsi et al.*, 1999] in the Southern Ocean. This on-going process of sinking surface water together with the high primary production that consumes CO_2, enables more CO_2 to be taken up at the surface. Due to this process, the Ross Sea polynia has been suggested to be an important sink for CO_2. [*Kevin R. Arrigo et al.*, 2008]. Due to the high biological activity, surface nutrients are often depleted in the polynias, even though initial concentrations are high [*Kattner and Budéus*, 1997].

The biological production in the Amundsen and Ross Seas is primary limited by the supply of iron, and to a lesser extent by phosphate, nitrate or silicate [*Bertrand et al.*, 2011; *W O Smith et al.*, 2012].The different water masses of the Ross Sea are characterized by salinity, temperature, and neutral density (γ^N, kg m^{-3}) [*Jackett and McDougall*, 1997] (Figure 3). The water masses are mainly influenced by the cyclonic gyre found outside the shelf break, dominated by a ~ 2500 m mid depth layer of CDW, fed by the bypassing

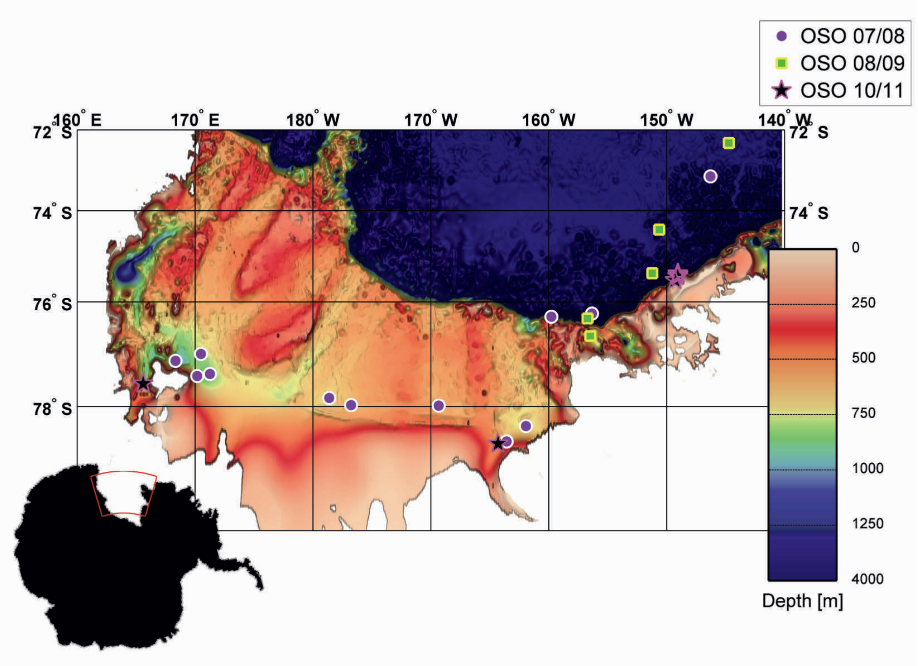


Figure 2. The Ross Sea

ACC. The shelf dynamics is to a large degree influenced by the deep water formation close to the Ross Sea Ice Shelf (RIS), in which dense saline Shelf Water (SW) is produced. Only thin layers of CDW can be found at intermediate depths above the outflowing SW. The CDW is a source of heat and nutrients, and consequently, the transport of CDW onto the shelf is critical to heat and salt budgets, the cycle of sea ice, and the biological primary productivity. AASW enters the Ross Sea in the eastern parts and continues westwards along the RIS. The circulation of the different water masses is topographically controlled, and the dense SW outflow occurs in several deep troughs that cut through the shelf in a north-south direction. Based on CFC measurements, it has been shown that the Ross Sea shelf waters rapidly ventilate, with a residence time of about 3.5- 8 years. The RIS is therefore vulnerable to changes in the temperature of the inflowing CDW, as this will affect the rate of basal melt [*Smethie Jr and Jacobs*, 2005; *Trumbore et al.*, 1991].

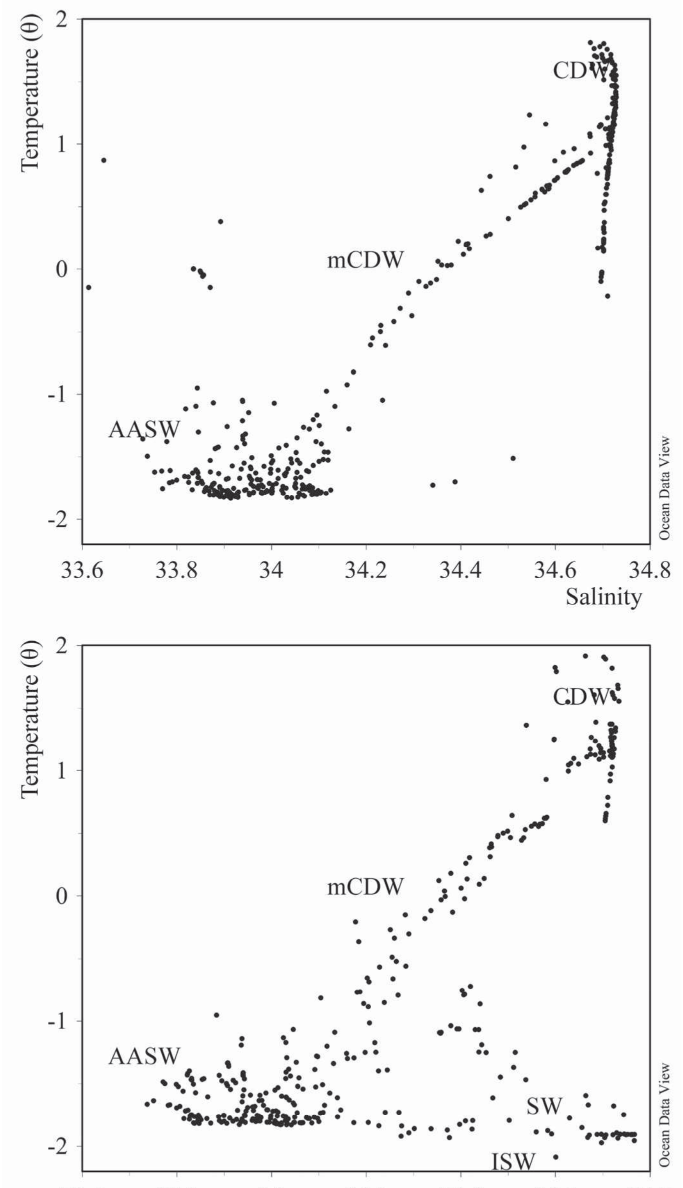


Figure 3. Temperature-Salinity relationship of waters in Amundsen and Ross Seas from 2007(bottom) and 2008(top).

3.4 Amundsen Sea

In the Amundsen Sea (Figure 4), two smaller polynias can be found- the Pine Island Bay polynia, and the Amundsen Sea polynia. Their extent varies in total between 5000 km^2 in the winter to 60 000 km^2 in the summer, where the Amundsen Sea polynia is the largest (~80 %) [*K. R. Arrigo and van Dijken*, 2003]. For simplicity, the two polynias will hereafter be treated as one. Few surveys have been conducted in the Amundsen Sea, hence very little is known about the biological, physical and biogeochemical processes acting in the Amundsen Sea compared to the more studied Ross Sea. The Amundsen Sea has been found to be as productive as the Ross Sea, with an annual primary production of 160.7 ± 36.9 g C m^{-2}. However, due to its smaller size, the total production of the whole sea becomes lower, ~ 6 Tg C yr $^{-1}$ compared to the Ross Sea [*K. R. Arrigo and van Dijken*, 2003].No deep water formation takes place in the Amundsen Sea, which is partly explained by its small winter polynia. The shelf-slope dynamics in the Amundsen Sea have been found to be different compared both to the Ross Sea and the Western Antarctic Peninsula (WAP). The WAP has been found to have inflows of the ACC in topographic depression, while in the Ross Sea, sharp frontal and current systems can be found due to the dense outflows from the shelf. The Amundsen Sea has none of the above mentioned dynamics, instead, it is suggested that small parts of the ACC that pass the eastern parts of the Amundsen shelf break, induces an Ekman transport of CDW onto the shelf, a case of "slippery" Ekman layer dynamics [*Wåhlin et al.*, 2012].

Water masses close to the glacial tongues reaching down into the Amundsen Sea have a pronounced layers of a melt water mixtures derived from the mixing of glacial melt water and modified CDW [*Wåhlin et al.*, 2010; *Wåhlin et al.*, 2012] . The inflow of CDW on the shelf takes place mainly in three deep troughs that cut through the Amundsen shelf. Recent findings show that the warming of CDW has increased the basal melt of the West Antarctica Ice Sheet in the Amundsen Sea [*Arneborg et al.*, 2012; *Pritchard et al.*, 2012; *Walker et al.*, 2007; *Wåhlin et al.*, 2010]. On the shelf, two main water masses can be found; Antarctic Surface Water (AASW) and modified CDW (mCDW). The east-west separation of waters of the Amundsen Sea is mainly attributed to a central 300 m high ridge, which divides the

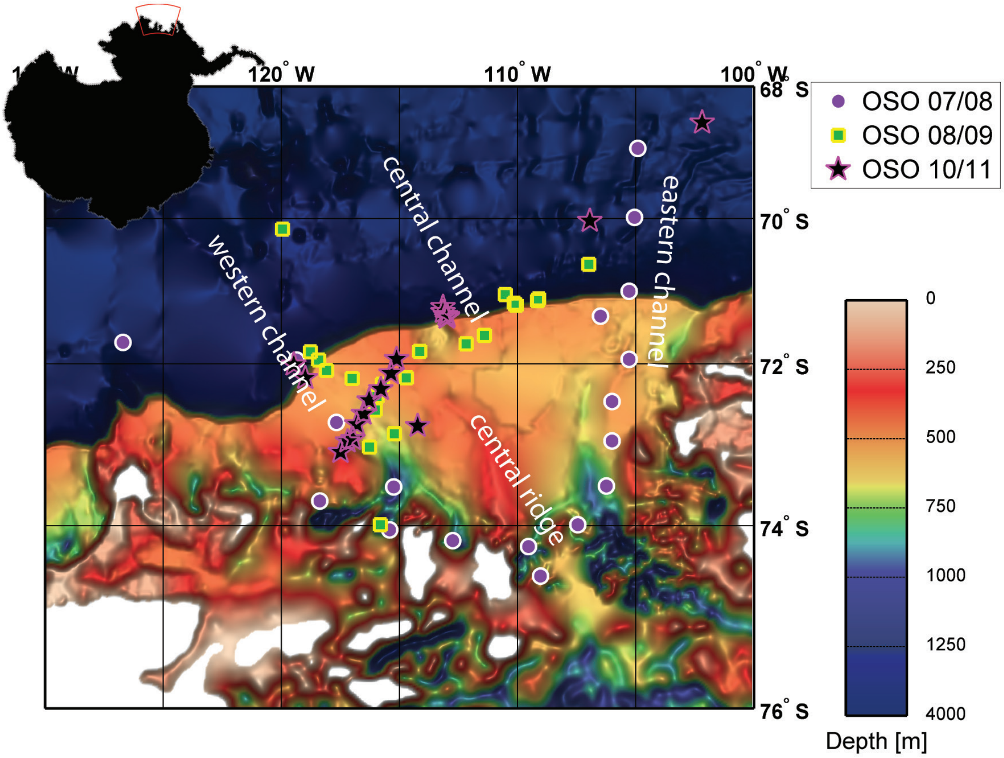


Figure 4. Bathymetric map of Amundsen Sea. Bathymetric data from [Timmermann et al., 2010]

Amundsen Sea into two main basins. Generally, the eastern basin is warmer and more saline compared to the western basin. The layer of AASW is deeper in the western parts of the Amundsen Sea, ~400 m, compared to the eastern parts, ~200 m. The water mass at 1000 m depth is about 0.3 °C warmer and 0.1 g kg^{-1} less saline in the west compared to the east [*Wåhlin et al.*, 2010].

4. Formation of Halocarbons

4.1 Enzymatic formation

The enzymatic production of halocarbons in marine algae is not fully understood, and several mechanisms have been suggested. *Theiler et al.* [1978] found that $CHBr_3$and CH_2Br_2 could be produced by the enzyme bromoperoxidase in the process of removing hydrogen peroxide. They suggested that the mechanism responsible for the formation could be explained by a subsequent stepwise substitution reaction, where the oxidized bromine reacts at α-position of ketones, such as β-keto-acids (3-oxooctanoic, 3-oxohexanoic acid), which finally yield bromoform. The intermediate steps in the mechanism suggest that the oxidized bromine, Br^+, is bound to the enzyme throughout the whole reaction. The release of bromoform from the formed bromoheptanone was suggested to be a non-enzymatic process as it was found to be pH dependent [*Burreson et al.*, 1976; *Theiler et al.*, 1978].

The mechanism suggested by *Deboer and Wever* [1988]. They found that bromoperoxidases in the brown algae *Ascophyllum nodosum* could produce HOBr, Br_2 or Br_3^+ by reduction of H_2O_2 and oxidation of Br^- (Eqn. 10). The brominating activity was suggested to take place in a second step (Eqn. 11), where HOBr rapidly reacts with the nucleophilic acceptor (AH), preferably a ketone, which forms the brominated product, ABr. They also found that the reaction rate of the brominating activity was independent of the choice of substrate, which indicates that there is no enzyme-bound halogenating intermediate present in the reaction.

$$H^+\text{-Enz} + H_2O_2 + Br^- \rightarrow [H^+\text{-Enz-}H_2O_2\text{-}Br^-] \rightarrow \text{Enz} + HOBr + H_2O \qquad (10)$$

$$HOBr + AH \rightarrow ABr + H_2O \qquad (11)$$

The mechanism found by *Deboer and Wever* [1988] was later supported by *Wever et al.* [1991], who showed that HOBr was released into the surrounding media by several macro algae. They concluded that addition of organic molecules and H_2O_2 under light conditions resulted in a bromination, and suggested that the bromoperoxidases were located on the thallus surface of the macro algae. *Wever et al.* [1993] addressed the possibility of at least two pathways in the formation of bromoform, and they concluded that extracellular formation via HOBr and dissolved organic matter would be the most probable pathway. This mechanism would be analogous to the enzymatically bound Br^+ suggested by *Theiler et al.* [1978] Theiler, and it would give rise to several subsequent intermediates (Eqn. 12 – 14) such as:

$HOBr + R\text{-}CO\text{-}CH_2\text{-}COOH \rightarrow R\text{-}CO\text{-}CH_2Br + CO_2 + H_2O$ (12)

$R\text{-}CO\text{-}CH_2Br + HOBr \rightarrow R\text{-}CO\text{-}CHBr_2 + H_2O$ (13)

$R\text{-}CO\text{-}CHBr_2 + HOBr \rightarrow R\text{-}CO\text{-}CHBr_3 + H_2O$ (14)

$R\text{-}CO\text{-}CHBr_3 + H_2O \rightarrow R\text{-}COOH + CHBr_3$ (15)

The last step (Eqn. 15) is decay due to the unstable $O\text{-}CHBr_3$ bond. The extracellular release of HOBr has been found in both micro and macro algae [*Hill and Manley*, 2009; *Manley and Barbero*, 2001]. This finding further supports the mechanism involving HOBr rather than the mechanism of enzymatically bonded Br^+. Substitution of other halides in the mechanisms would give rise to a range of mixed halocarbons, such as CH_2BrI, CH_2ClI, CH_2BrCl, and $CHBr_2Cl$. Haloperoxidases can therefore be categorized by their choice and use of halogens, where chloroperoxidases are able to use bromide, chloride or iodide, bromoperoxidases only bromide and iodide, and iodoperoxidase only iodide [*Wever and Hemrika*, 2001].

A different group of enzymes, perhydrolases, has been identified in bacteria [*Van Pée et al.*, 2000]. The enzymes were found to catalyse the production of peracetic acid from perhydrolysis of acetic acid serine ester. The formed peracetic acid could in turn oxidize halide ions, which form HOBr. HOBr could thereafter react as according to Eqn. 12 – 15. [*Van Pée and Unversucht*, 2003]. The enzymes were found to be different in their reaction centre compared to haloperoxidases, as they were lacking the prosthetic group (vanadium).

The biological formation of methylhalides has been found to be connected to a different type of enzymes, methyltransferases [*Itoh et al.*, 1997; *Manley*, 2002; *Wuosmaa and Hager*, 1990]. CH_3I, CH_3Br and CH_3Cl were reported to be formed according to

$X^- + \text{S-adenosyl-L-methionine} \rightarrow CH_3X + \text{S-adenosyl-L-homocystein}$ (16)

where methyltransferase transfers a methyl group from SAM (S-adenosyl-L—methionine) to the halide ion. This mechanism has been found in a range of different micro and macro algae, fungi, and higher plants [*Manley*, 2002; *Wuosmaa and Hager*, 1990]

Production of halocarbons by marine macro and micro algae has been found in several investigations [*Abrahamsson et al.*, 1993; *Baker et al.*, 1999; *Ballschmiter*, 2003; *Burreson et al.*, 1976; *Collen et al.*, 1994; *G. F. Cota and*

Sturges, 1997; *Giese et al.*, 1999; *Hill and Manley*, 2009; *Hughes et al.*, 2009; *Karlsson et al.*, 2008; *Laturnus*, 1995; *Manley*, 1994; *Manley et al.*, 1992; *Moore et al.*, 1995b; *Nightingale et al.*, 1995; *Scarratt and Moore*, 1998; *Schall et al.*, 1994; *Sturges et al.*, 1992; *Tokarczyk and Moore*, 1994]. For macro algae, where the haloperoxidases have been found on the thallus surface of the algae, halocarbon production has been suggested to be a protection against biofouling of bacteria and fungi, and as defence against grazers [*Wever and Hemrika*, 2001; *Wever et al.*, 1991].On the other hand, the production of halocarbons may just be a by-product of algae removing harmful hydrogen peroxide formed during photosynthesis.

4.2 Correlation to pigments

Efforts have been made to understand the relationship between halocarbon production and photosynthetic biomass (Paper I) [*Abrahamsson et al.*, 2004; *Karlsson et al.*, 2008; *Y Liu et al.*, 2013; *Quack et al.*, 2007; *Raimund et al.*, 2010]. Studies have shown that elevated concentrations of bromoform can be found in areas with high chlorophyll *a* (chl *a*) concentrations [*Carpenter et al.*, 2009; *Schall et al.*, 1997]. However, a direct relationship between halocarbon and chl *a* concentration in sea water has been difficult to prove, and is seldom statistically significant [*Hughes et al.*, 2009; *Y N Liu et al.*, 2011](Paper I). However, in studies of the upwelling region outside Mauritania, Quack et al. [2007] found positive correlations. The lack of correlation can possibly be due to other processes that influence the water contents, such as air-sea exchange, mixing of water, degradation and inter-species variations in production rates.

Halocarbons and pigments differ in their environmental half-lives. Bromoform, have been reported to have a half-life around 70 years in cold waters (~ 2 °C) [*Geen*, 1992], whereas phytoplankton loss processes (such as grazing or aggregate formation) in the Southern Ocean may act in timescales of a few days or weeks [*W O Smith et al.*, 2011]. Therefore, the brominated compounds found may have been produced solely by a different algae community rather than by an assemblage found during the time of sampling. The situation could be different for the iodinated compounds, since they are degraded on much shorter time scale: diodomethane degrades in ~10 minutes and chloroiodomethane degrades in ~10 hours in surface waters [*Jones and Carpenter*, 2005]. This might explain the correlations found between iodinated compounds and several pigments described in Paper I, since their measured values should reflect the active phytoplankton community.
It can be speculated that the physiological state of the algal blooms could affect the relationship between pigments and halocarbon distributions. The

amount of halocarbons produced has been shown to be related to the level of stress the algae experiences [*Collen et al.*, 1994; *Mtolera et al.*, 1996]. Stress induces an increase in the formation of reactive oxygen species, such as H_2O_2 whereby more halocarbons are formed. In the Ross polynia such stress could have been caused by iron limitation [*Fragoso and Smith*, 2012].

4.3 Abiotic formation

Abiotic formation of halocarbons may be an additional source in the ocean. Chlorination of water yields haloforms according to the haloform reaction

$$X_2 + H_2O \rightarrow XO^- + X^- + 2H^+ \quad \text{(where X = Cl, Br, I)} \qquad (17)$$

$$3XO^- + R\text{-}CO\text{-}CH_3 \rightarrow R\text{-}CO\text{-}CX_3 + 3\,OH^- \qquad (18)$$

$$R\text{-}CO\text{-}CX_3 + OH^- \rightarrow R\text{-}COO^- + {}^-CX_3 \qquad (19)$$

$${}^-CX3 + H2O \rightarrow CHX_3 + OH^- \qquad (20)$$

This reaction starts with the formation of hypohalite (Eqn 17). In the second step (Eqn. 18), the hypohalite reacts with methyl ketones. This reaction is followed by nucleophilic acyl substitution (Eqn. 19) which forms $CHCl_3$. This process is common in waterworks, and local anthropogenic sources can be found in densely populated regions. In addition, chlorination of sea water, for example when it is used as cooling agent in coastal power plants, has been found to produce substantial amounts of brominated halocarbons, such as bromoform. This abiotic production of bromoform was suggested to be coupled to the reaction of hypochlorite and bromide, which would produce hypobromite ions [*Fogelqvist and Krysell*, 1991].

Additional abiotic formation pathways have been identified in the surface layer of the ocean, such as photochemical formation of methyl iodide [*Happell and Wallace*, 1996; *Moore and Zafiriou*, 1994] and the recent finding of HOI formation from the reaction between iodide and ozone [*Martino et al.*, 2009]. The latter would give rise to a range of iodinated compounds in a similar way as the reaction of HOBr with dissolved organic matter (DOM) [*Manley and Barbero*, 2001].

5. Degradation and transformation of halocarbons

The most common pathwas for degradations or transformations of halocarbons are halide substitution, hydrolysis, photolysis (in the surface water), and microbial degradation. The resulting half-lives for these processes are still uncertain, which may lead to an overestimation of the ocean's source strength, as well as that of sea ice. Degradation and transformation processes affect the distribution of halocarbons in the ocean. It could therefore be possible to trace movements and age of water masses by utilizing the relationship between various halocarbons and the reaction products from the different degradation and transformation pathways. For the upper part of the ocean and its interactions with the atmosphere, knowledge of the different degradation pathways and the resulting environmental half-lives are crucial, since they may alter the direction of the flux over the air-sea interface.

5.1 Substitution of halides

The general nuchleophilic substitution reactions by chloride in seawater can be described as:

$$CHX_3 + Cl^- \leftrightarrows CHX_2Cl + X^- \quad \text{where } X = I, Br, Cl \tag{21}$$

$$CHX_2Cl + Cl^- \leftrightarrows CHXCl_2 + X^- \tag{22}$$

$$CH_3X + Cl^- \leftrightarrows CH_3Cl + X^- \tag{23}$$

The reaction rate vary with type of halogen that is substituted, e.g. substitution of iodine is faster than that of bromine. The reaction rates have also been found to be temperature dependent [*Elliott and Rowland*, 1993; *Geen*, 1992]. Few studies can be found about the nucleophilic substitution of halocarbons in the ocean [*Class and Ballschmiter*, 1988; *Karlsson*, 2012; *Moore and Tokarczyk*, 1993]. Equation 21 and 22 would for $CHBr_3$ result in the formation of $CHBr_2Cl$ and thereafter, $CHBrCl_2$. The final substitution would produce $CHCl_3$, but this has not been confirmed. *Geen* [1992] showed in laboratory studies that nucleophilic substitution of $CHBr_3$ with chloride could produce $CHBr_2Cl$ and $CHBrCl_2$, and that the rates for this process were relatively slow at low temperatures, resulting in a half-life of 74 years at 2 °C for $CHBr_3$.

Figure 5. $CHBr_3$, $CHBr_2Cl$ and $CHBrCl_2$ distribution in the Amundsen Sea.

Karlsson [2012] confirmed this finding in a study of the distribution of bromoform and its degradation products in the Arctic ocean. As a water mass ages, the ratio $CHBr_3/CHBrCl_2$ will chang. In Figure 5, the distribution of $CHBr_3$ and $CHBrCl_2$ is shown for the Amundsen Sea in austral summer of 2008/09 (Paper III). The enrichment of $CHBrCl_2$ in the bottom water indicates that the origin was most probably older CDW and not younger water formed on the shelf. *Moore and Tokarczyk* [1993] found a ratio of 0.6 for $CHBr_3/CHBr_2Cl$ in the water masses in the North West Atlantic, and attributed the increasing concentration of $CHBr_2Cl$ towards the bottom to an additional source, such as substitution by Cl^- or microbial production in the sediments.

5.2 Hydrolysis

Halocarbons are subjected to hydrolysis in the oceans. For methyl halides this process leads to the formation of methanol (Eqn. 24)

$$CH_3X + H_2O \rightarrow CH_3OH + X^- + H^+ \qquad (X = Br, I, or Cl) \qquad (24)$$

The reaction rate for CH_3Br is temperature dependent and the half-life has been estimated to be 100 days at a temperature of 20 °C, which can be compared with the much faster process of nucleophilic substitution by Cl^-, with a half-life of ~20 days [*Elliott and Rowland*, 1993].

The degradation of bromoform by hydrolysis is poorly known. Based on the reactivity constants in *Hine et al.* [1956], the half-life of bromoform due to hydrolysis would be 70 years at 25 °C and pH 8, and approximately 4000 years at 0 °C. The reactivity was found to be different between various halocarbons ($CHBrCl_2 > CHBr_2Cl \approx CHCl_2I > CHBr_3 > CHCl_3$). Since the rate constants where derived in a basic dioxane/water mixture, they should be treated as highly uncertain in ocean waters. Nevertheless, these estimates of hydrolysis rates can often be found in the literature.

5.3 Photolysis

Brominated, and especially iodinated, halocarbons can be degraded by photolysis in the surface layer of the ocean. Photolysis takes place in a few metres of the upper water column, since the incident light quickly dissipates in the water column. In a rough estimate of the photolytic rate of bromoform in the first metre of the surface layer, its half-life was estimated to ~30 days [*Carpenter and Liss*, 2000]. This can be compared to the air-sea exchange of bromoform, which was approximated to ~ 0.8 days [*Carpenter and Liss*, 2000]. Photolysis is therefore usually not taken into consideration when models of air-sea exchange of $CHBr_3$ are made. For iodinated compounds, such as CH_2I_2, the photolytic lifetime has been found to be much shorter, ~10 minutes [*Jones and Carpenter*, 2005], resulting in a close to zero air-sea flux of CH_2I_2 [*Martino et al.*, 2006]. The overall reaction can be written as

$$CH_2I_2 + hv + 2\ H_2O \rightarrow CH_2(OH)_2 + 2\ HI \qquad (25)$$

where photolysis of CH_2I_2 to $CH_2I\cdot$ and $I\cdot$ forms an isomeric form,CH_2I-I, which thereafter reacts with water to form methandiol and HI [*Li et al.*, 2003]. The same reaction has been found for $CHBr_3$, yielding HBr, instead of HI. When the reaction (Eqn 25) takes place in the presence of NaCl, CH_2ClI has been shown to be formed [*Guan et al.*, 2004] with yields of 35 % (±20 %) of the original CH_2I_2 concentration [*Jones and Carpenter*, 2005].

The photolytic lifetime of CH_2ClI was found to be much longer, ~10 hours, compared to CH_2I_2.There are only rough estimates of the photolytic degradation of brominated halocarbons. The end products might be more volatile compared to the original molecule, as has been shown for the photolytic formation of CH_2ClI from CH_2I_2 [*Jones and Carpenter*, 2005]. Therefore, in order to make the air-sea exchange models more accurate, the kinetics of these reactions should be determined.

5.4 Microbial degradation

Little is known about degradation of halocarbons due to microbial activity. *Goodwin et al.* [1997] investigated bacterial degradation of $CHBr_3$ and CH_2Br_2 in seawater surrounding kelp beds, and found degradation of CH_2Br_2 to CO_2, and estimated the rate of degradation to > 1 % of the algae production rate. The half-life of CH_2Br_2 was calculated to be approximately 20 days, indicating that the process was faster than hydrolysis but slower than volatilization. In a later study by *Goodwin et al.* [1998], the half-life of CH_2Br_2 during bacterial oxidation, was found to be as short as ~2 days. $CHBr_3$ was on the other hand found to be resistant to bacterial degradation, and no significant loss of $CHBr_3$ was found.

In Paper I, incubations studies of sea ice, brine, and snow were performed, and, net degradation was found for some of the halocarbons. Similar studies of halocarbons have been made in Arctic sea ice by *Karlsson* [2012], where degradation rates were found to be in the same order as in *Goodwin et al.* [1998].

Van Pée and Unversucht [2003] have suggested other microbial degradation and transformation processes, such as reactions catalyzed by methyltransferas, where the halogen in CH_3X (X = Br, I, Cl) could be exchanged by another halogen or substituted with a different functional group. Dehydrohalogenation, reductive dehalogenation, and oxidative dehalogenation are all catalyzed by enzymes found in bacteria [*Fetzner*, 1998].

6. Air-sea flux

The exchange of biogenic halocarbons between the ocean and the lower atmosphere is determined by the halocarbons' state of equilibrium. The saturation anomaly of the halocarbon can be calculated from the measured concentrations of halocarbons in air and surface water according to

$$Saturation\ anomaly = C_w - \frac{C_a}{H} \tag{26}$$

where H (C_a/C_w at equilibrium) is the compound specific temperature dependent Henry´s lawconstant, which for several halocarbons have been determined by *Moore et al.* [1995a]. The sign of the saturation anomaly determines the direction of the flux, F, between surface water and air, and the magnitude of the flux is determined by the transfer velocity, k, given in length per time. The flux can be estimated as

$$F = k \times \left(C_w - \frac{C_a}{H} \right) \tag{27}$$

The flux is an estimate based on the measured concentration in air and water, and the transfer velocity. The transfer velocity has been found to be highly dependent on the wind speed, and several parameterizations of the transfer velocity have been suggested [*Liss and Merlivat*, 1986; *McGillis et al.*, 2001; *Nightingale et al.*, 2000; *Wanninkhof*, 1992; *Wanninkhof et al.*, 2009]. Measurements of radioactive trace gases such as ^{222}Rn and $^{14}CO_2$, or tracers such as SF_6 and ^{3}He, have been used to study the wind dependence of the transfer velocity. In Table 2, different parameterizations of k have been used to calculate the air-sea flux of $CHBr_3$ (data from Paper II).

As evident in Table 2, large deviations arise in the results depending on which parameterization is used. One explanation to the diverging results is a constant that has been used in the different parameterizations compensating for the non-inertness of CO_2 [*McGillis et al.*, 2001; *Nightingale et al.*, 2000; *Wanninkhof*, 1992; *Wanninkhof et al.*, 2009]. The cubic parameterization of the wind also leads to higher transfer velocities at high winds speeds compared to the quadratic parameterization. There are still processes that have not yet been incorporated in the models, such as bubbles injected in the surface water from breaking waves, surfactants forming surface films in algal blooms, and turbulence in the surface layer. Additional uncertainties in flux estimations of halocarbons arise from the lack of data of diffusion coefficients, which instead are estimated from empirical models, [*Hayduk and Minhas*, 1982; *Wilke and Chang*, 1955]. In the Southern Ocean, the

Table 2. Comparison of the calculated flux of CHBr3 using different parameterizations of the transfer velocity(data from Paper II)

	Nightingale 2000	McGillis 2001	Wanninkhof 2009	Wanninkhof 1992
Transfer Velocity, k	$k_{600} = 0.333\, U_{10} + 0.222 U_{10}^2$	$k_{660} = 3.3 + 0.026\, U_{10}^3$	$k_{660} = 3 + 0.1 U_{10avg} + 0.064 U_{10avg}^2 + 0.011 U_{10avg}^3$	$k_{660} = 0.31\, U_{10}^2$
Mean (pmol dm^{-2} h^{-1})	-3.5	-5	-3.5	-4.5
deviation from Nightingale	0 %	43 %	1 %	30 %
Total variation (pmol dm^{-2} h^{-1})	-28 - 40	-55 - 46	-33 - 34	-38 - 50

concentrations of $CHBr_3$ in surface waters were found to be fairly constant, whereas the air concentrations were more variable in both time and space (Paper I, II and III). It was concluded that the flux was primarily governed by the concentrations in air. The origin of the air masses was investigated by the use of wind back trajectories, and it was found that other sources than the surface waters were involved, in this case sea ice and coastal regions[*Hughes et al.*, 2009] Paper I and IV). The flux, therefore, reflected the current meteorological conditions, as well as the sea ice extent, and possibly a reminiscence of a production at another occasion. To be able to follow these rapid shifts, high resolution measurements need to be performed alongside modelling of the air movements (Paper II).

The saturation anomalies and fluxes of bromoform for different geographical regimes have been summarized by *Quack and Wallace* [2003] (QW) and are presented in Table 3 together with data derived from Paper II, and data collected during cross-Atlantic transects (Karlsson et al. unpublished). The data is in fairly good agreement for all areas except for low latitudes. The calculated fluxes by QW were performed with an average background air concentration, which assigned the Southern Ocean as a source of bromoform. This is in contrast to the findings in Paper II, where this area was considered to be a net sink. This discrepancy is probably due to the use of a single air concentration in the estimates of the air-sea flux by QW, while our estimates were based on pair-wise measurements. Thereby, we could establish that the determining factor for the direction of the flux were the air concentrations.

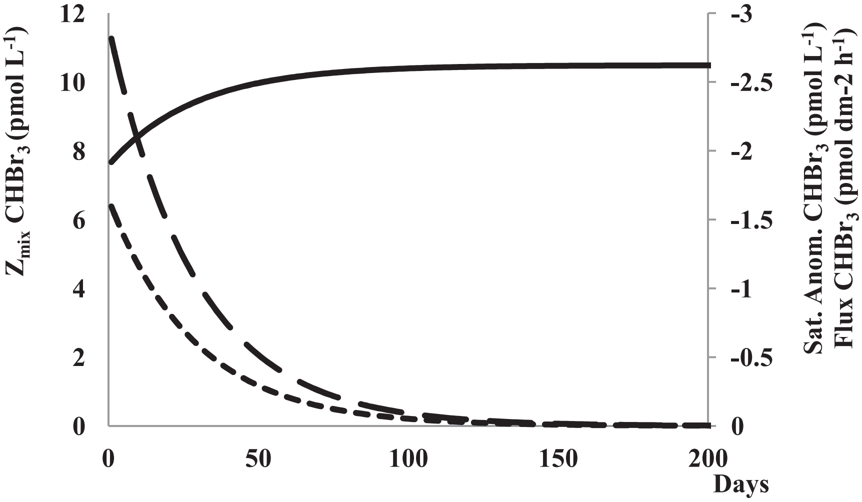


Figure 6. Concentration, (solid line, pmol L^{-1}), estimated flux (pmol dm^{-2} h^{-1}, ,long-dashed line), and saturation anomaly (short-dashed line) of $CHBr_3$ as a function of days in the mixed layer (Z_{mix}) of the Ross Sea.

To evaluate the estimated fluxes from Paper II, a theoretical model can be constructed that simulates the uptake in the Ross Sea polynia. The input parameters that were used are as follows: area (400 000 km^2) of the polynia, a mixed layer depth of 40 m, the average wind speed (7.7 m s^{-1}), water temperature (-0.62 ºC), average concentration of $CHBr_3$ in the surface water (7.6 pmol L^{-1}) and the overlying air (1.5 pptv), the average estimated flux (-1.8 pmol m^{-2} h^{-1}), and the average saturation anomaly (-2.89 pmol L^{-1}(-28 %)). All parameters, except for the concentration in water, the saturation anomaly, and the flux, were held constant in the simulation.

The surface water concentration was allowed to increase (Figure 6) and the air concentration was held constant. The saturation anomaly was allowed to change according to the increasing concentration in the mixed layer due to the on-going flux. As the saturation anomaly increases (becomes less negative), the flux becomes lower, in accordance with Equation 27. The theoretical equilibrium concentration of $CHBr_3$ in the mixed layer would therefore be reached after approximately 100 days (Figure 6). In reality, after a period of hundred days, the sea ice would be in advancement and thereby decreasing the surface area of polynia, and hence the total flux. A modest interpretation of this result could be that the estimated fluxes in Paper II could be valid during this time of the year in this part of the Southern Ocean. In a recent model study by *Ziska et al.* [2013], the southern ocean was found to act as a sink of $CHBr_3$with a possible uptake of ~ 0.1 Gmol Br 100 days $^{-1}$, whereas the corresponding value from Paper II would be an average uptake of 0.04 Gmol days $^{-1}$ Br. The results are in good agreement, but it should be noted that the estimated flux could only be sustained as long as the surface waters are open and not covered by sea ice.

7. Sea ice

Sea ice and the overlying snow play an important role in the distribution of halocarbons, and they both affect the exchange of all gaseous compounds between the surface of the ocean and the lower parts of the atmosphere. When sea water freezes, the water molecules form a crystal lattice. The structure does not permit incorporation of any larger ions or molecules (fluorine and NH_4^+ and some gases can be incorporated or fitted in voids of the lattice), which leads to desalination of the sea water as it freezes. As the crystal lattice grows, part of the salts and other impurities, e.g. CO_3^{2-}, SO_4^{2-}, organic molecules, halocarbons, are retained as liquid inclusions in the solid matrix, creating channels and pockets in the microstructure. Most of this liquid, called brine, is rejected, which makes the ocean water saltier and heavier, but some is retained in the channels of the sea ice. The brine channels create a micro habitat for biota. Algae, bacteria, and grazers populate the channels and adapt to this extreme environment, and are subjected to limitations in light [*Glenn F. Cota*, 1985], salt and temperature stress [*Bayer-Giraldi et al.*, 2011], nutrient limitations[*R E H Smith et al.*, 1997], pH stress, and hypoxic conditions [*Gleitz et al.*, 1995; *Rysgaard and Glud*, 2004].

The knowledge of halocarbon chemistry in sea ice and the role of the sea ice plays in the biogeochemical cycle of halocarbons in the Southern Ocean is today elusive or non-existent. The first evidence of halocarbon production of Antarctic sea ice algae was presented by *Sturges et al.* [1993]. They concluded that pennate and centric diatoms, *Nitzschia stellata* and *Porosira pseudodenticulata,* living on the underside of sea ice, were able to produce several brominated halocarbons, and subsequently release them to the underlying sea water.

Production of the iodinated halocarbons CH_3I and CH_2CH_3I has been found in snow at the Greenland Summit. This was, however, assumed to be an abiotic formation, and the production was attributed to a photochemical formation [*Swanson et al.*, 2002]. Elevated concentrations of $CHBr_3$ and chl *a* in snowpack was found by *Sturges* [1997]. It was suggested that these concentrations could have originated from the underlying sea ice, which also had high concentrations of $CHBr_3$, but the findings were summarized as "puzzling". In Paper I, incubations of snow collected from sea ice showed a release of halocarbons, e.g. $CHBr_3$ 0.5 – 7 pmol L^{-1} d^{-1} and CH_2ClI, 0.1 – 1 pmol L^{-1} d^{-1}. This result is comparable to the findings of halocarbons production in Arctic snow[*Karlsson*, 2012]. As thick snow covers can be found on sea ice in the Southern Ocean, this could be a significant source to

Table 4. Measured concentrations in brine (Paper I)

Location	Amundsen						Ross
Latitude	-70.2	-71	-71.4	-72.7	-71.7	-71.8	-78.4
Longitude	-105.2	-105.2	-106.6	-117.9	-126.8	-132.6	-164.2
Brine depth (m)	2	0.6	0.7	1	1	0.6	0.7
Snow thickness (m)	1	0.2	0.6	0.5	0.2	0.3	0.1
Ice thickness (m)	3	1	>3.5	>3.5	1	1	1.2
CH_3I	3	3.7	3.8	4.9	2.6	1	5.1
CH_3-CH_2I	4.6	1.4	3.8	1.4	2.6	1.8	1.8
CH_3-CHI-CH_3	2.6	1.6	0.95	1.3	0.92	1.8	1.8
CH_2I-CH_2-CH_3	1	32	7.1	16	4.2	4.7	2.7
CH_2I-CH_2-CH_2-CH_3	3.2	2.7	1.4	2.4	0.95	0.9	1.2
CH_2I_2	1.9	1.2	3.8	5.4	7	9.5	8.6
CH_2ClI	20	2.1	29	7.8	0.56	1.3	0.29
CH_2BrI	1	0.29	0.24	2.5	0.34	0.31	0.46
$CHBr_3$	16	23	12	34	0.03	9.5	8.6
CH_2Br_2	17	32	7.1	16	4.2	4.7	2.7
CH_2BrCl	2.6	1.6	3.8	1.3	2.6	1.8	1.8
$CHBr_2Cl$	3.2	2.7	1.4	2.4	0.58	1.3	0.74
$CHBrCl_2$	2.7	32	7.1	16	4.2	4.7	2.7

the atmosphere, especially if the production occurs during wintertime, when the sea ice covers a much larger area of the Southern Ocean compared with summertime. The findings by *Sturges et al.* [1993] were confirmed in Paper I and IV, where the first results of halocarbon measurements in sea ice in the Amundsen and Ross Seas were presented. Sea ice was found to have a heterogeneous distribution of halocarbons (Table 4). With few exceptions, halocarbons concentrations were found to be elevated in brine compared to the underlying surface waters (Papers I and IV). A striking difference between iodinated and brominated halocarbons in the sea ice was the relative higher concentration of iodinated compounds in sea ice compared to sea water (Table 4, Papers I and IV). *Atkinson et al.* [2012] also found high concentrations of several iodinated compounds in sea ice brine. They suggested that iodine in the atmosphere probably had additional sources or cycling of iodine, since they found unexpected high concentrations of I_2 in the marine air above the sea ice together with depletion of iodate and iodide

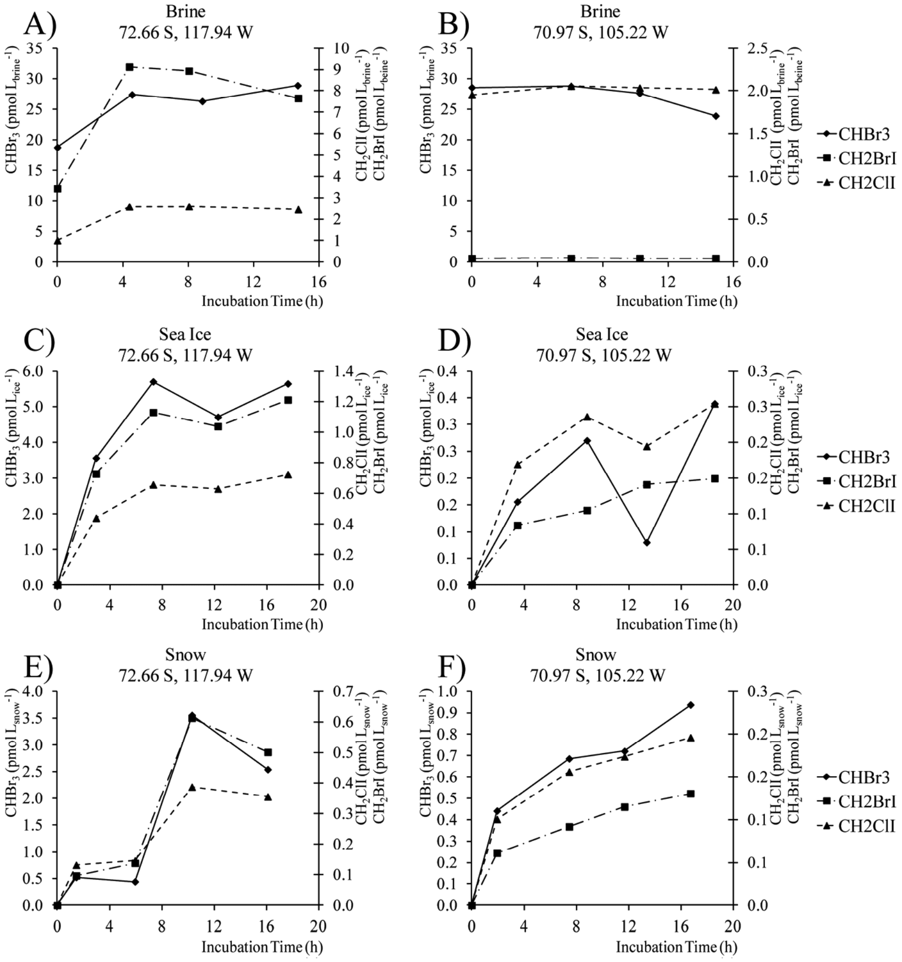


Figure 7. Sea ice, snow and brine incubations of collected samples in the Amundsen Sea. Concentration changes of $CHBr_3$, CH_2BrI and CH_2ClI of hours of incubation. Incubation procedures describe in Mattson et al. [2012]

in the sea ice. The underlying water also showed vertical profiles of increasing halocarbons, e.g. $CHBr_3$ and CH_2ClI,towards the overlying sea ice. This indicates that the sea ice was a source of halocarbons to the underlying sea water during this time of the year. The concentrations of $CHBr_3$ in brine were in the same range as *Karlsson* [2012] and *Theorin* [2002] reported from arctic sea ice, whereas CH_2ClI was found in approximately 10 times higher concentrations compared to the Arctic studies. *Nomura et al.* [2011] measured concentrations of 5.5 ± 2.4 pmol L^{-1} of $CHBr_3$ in flooded land fast ice in eastern Antarctica, which is lower compared to the results from Papers I and IV. The source of the elevated concentrations in sea ice and brine has also been investigated (Papers I and IV). Incubation experiments of unaltered sea ice (Paper I, Figure 7) and brine (Papers I and IV) were performed, and it was found that halocarbon could be produced in the brine. The production of halocarbons in sea ice and a possible release to the atmosphere were investigated in Paper IV. Halocarbon profiles showed that highest concentrations coincided with highest chl. *a.* concentrations in the middle of the sea ice, but correlations between halocarbons and chl. *a*. could only be established for iodinated compounds. The gradients in the profiles suggested that the decrease of halocarbons towards the surface and the bottom of the sea ice could be attributed to a transport out from the sea ice. The measured production rates in brine strengthen this theory. Similar production rates have been found by *Karlsson* [2012] and *Theorin* [2002] in arctic sea ice and brine experiments.

Few other studies have been performed in the Antarctic region; *Sturges et al.* [1992] measured production rates of bromoform from arctic ice algae and concluded that sea ice with an algal biomass of 0.35-3.5 g C m^{-2} could produce 43-430 nmol m^{-2} d^{-1} . This is comparable with the results from Paper I, i.e. two to twenty times higher production rates, since our incubations showed a production/release of bromoform in brine of -1.7- 19 pmol L^{-1} d^{-1}, e.g. if sea ice thickness is set to one meter, our production rates in brine becomes -1.7 – 19 nmol m^{-2} d^{-1}. The findings of elevated concentrations and production of several biogenic halocarbons in sea ice raised new questions concerning the biogeochemical cycle of halocarbons. Very little is known about the flux and the fate of halocarbons produced in the sea ice. *Granfors et al.* [2013] found the transport/diffusion of halocarbons inside newly frozen sea ice to be $D = 7.5 \times 10^{-5}$ cm^2 s^{-1}, which is approximately in the same magnitude which were found for O_2 *Loose et al.* [2011]. *Loose et al.* [2011] showed that the rate of diffusion of O_2 and SF_6 were somewhat higher compared to diffusion in the sea water. An explanation for this could be a gas-phase transport in the channels, which could enhance transport rate through the sea ice. Attempts have been made to estimate the transfer velocity in sea ice covered ocean. In a discussion paper by *Loose et al.* [2013], a transfer velocity, k_{eff} , have been estimated for air-sea exchange for sea ice covered ocean and it was found to vary between 1×10^{-5} m d-1 for areas with sea ice close to 100 %, to values exceeding $k_{eff} = 5$ m d^{-1} for areas with 40 % sea ice coverage.

An additional uncertainty in estimating the source strength of halocarbons is their large spatial heterogeneity in distribution and production rates (Papers I and IV, Figure 7). In Paper I, both net degradation and net production were found in sea ice. This is illustrated in Figure 7, where typical incubations often started with positive production/release, and thereafter reached a sort of steady-state. In some incubations, net degradation rates were also found. These findings illustrate the difficulty in establishing overall source strength from sea ice.

8. Analytical methodology

Several analytical aspects need to be taken into consideration when halocarbons are measured in the ocean and overlying air. The complex sample matrix of seawater, and the low concentrations of halocarbons typically found in the oceans (pmol L^{-1}) and in the atmosphere (pptv), require analytical methods that are both sensitive and offer selectivity. In addition, contamination due to sampling, storage and pre-treatment needs to be minimized.

8.1 Sampling and storage

Sample handling has always been a concern in the determination of halocarbons concentrations since there is a risk for cross-contamination from the surrounding air. Sampling needs therefore to be carried out rapidly, and care should be taken to avoid degassing and head-space in the sampling containers. Another concern is halocarbons sensitivity to photolysis and the possibility of biological production/degradation in the sample containers, which limits the possible storage time. In Papers I-IV, an auto-sampler was used in combination with a commercial purge and trap system. A performed investigation showed that water samples could be stored in glass vials with no head space for at least 100 h, both at 4 °C in the dark, and in the cooled auto-sampler [*Hagman*, 2013]. An example is given in Figure 8. Very small deviation from normalized concentrations of stored samples could be found for most brominated halocarbons. For iodinated compounds, a small increase in concentration was measured in stored samples. A method for storage of air and purged water is to use tubes filled with an adsorbent. This enables sampling in remote areas and the method was successfully used by *Hughes et al.* [2009].

8.2 Pre-concentration techniques

For analysis of halocarbons, a pre-concentration step is needed due to the low concentrations found in both sea water and air. Purge and trap techniques are most frequently used. They are dynamic head-space techniques that usually are fully automated and coupled to gas chromatographs. In Papers I-IV, a modified version of the custom-made purge and trap instrument described by *Anja Ekdahl and Katarina Abrahamsson* [1997] was used. The modification consisted of the integration of an automated system for semi-continuous surface water and air measurements and an upgrade to a different trap (VOCARB 3000, Supelco), which was insensitive to water vapour and therefore did not require any dry trap.

The main difference between the commercial Velocity XPT and the custom made system were that the compounds are trapped at ambient temperatures in the commercial system, whereas in the trap was cooled to 0 °C in the custom made system. The commercial system also employed rinsing steps with MQ water. Therefore, the quality of the MQ water is critical, especially for the determination of chlorinated compounds due to contamination.

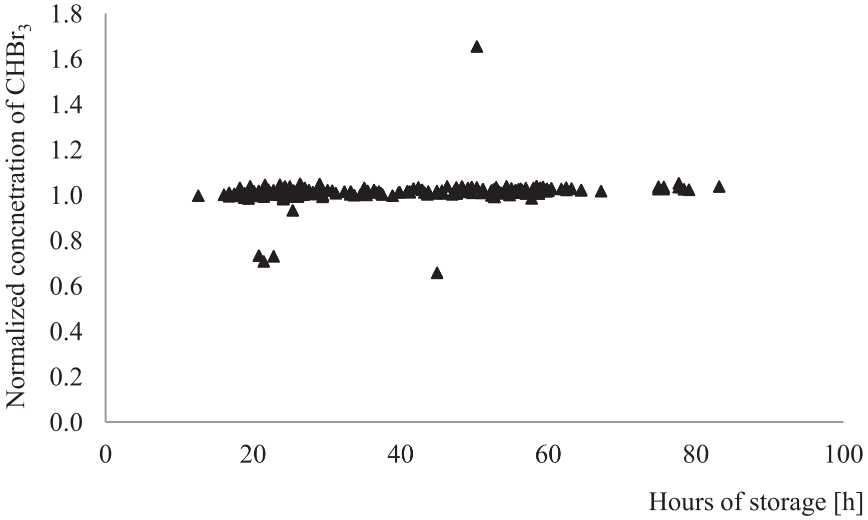


Figure 8. Normalized concentrations of $CHBr_3$ *for stored water samples in both dark and light conditions at 4 ℃. The deviation in concentration from* T_0 *on y axis is derived by* C_h / C_0*, where* C_h *is measured concentration after storage.*

Equilibrators have been used instead of pre-concentration with purge and trap [*Butler et al.*, 2007; *Lobert et al.*, 1997; *Lobert et al.*, 1995]. These instruments measure the partial pressure of the halocarbons in the seawater. This can be an advantage when saturation anomalies shall be established, since no solubility data will then be needed in the calculations [*Johnson*, 1999]. The main drawback of this technique is the time it takes to reach equilibrium, which can vary from minutes to hours, depending on the volatility of the compounds measured. An additional problem is the eventual deviation from equilibrium, which infers a constant (ε) to the calculations. This disequilibrium constant needs to be evaluated for each measured compound, due to their different solubilities. Careful monitoring of the temperature deviations in the head-space and the water is also needed since the equilibrium is temperature dependent.

Traditional solvent/solvent extractions, such as water/pentane, have also been used in analysis of halocarbon in seawater [*Abrahamsson and Klick*, 1990; *Fogelqvist and Krysell*, 1986]. This has several drawbacks compared to the other techniques since extraction yields need to be determined, and random errors are likely to occur even if an internal standard is used. Also, the most volatile halocarbons are difficult to extract since they also participate in the gas phase during the extraction.

8.3 Quantification

In principal two detectors are used for quantification of halocarbons, the electron capture detector (ECD) and mass spectrometers (MS). The invention of the ECD in 1958 by James. E. Lovelock [*Lovelock*, 1958] made it possible to detect low concentrations of halocarbons in a gas flow from a GC. Since then, the ECD has been one of the most frequently used detectors in halocarbon measurements [*Abrahamsson and Klick*, 1990; *Eklund et al.*, 1978; *Fogelqvist et al.*, 1986; *Lovelock et al.*, 1973; *Manley et al.*, 1992; *Rasmussen et al.*, 1982; *Reifenhauser and Heumann*, 1992; *Sturges et al.*, 1993]. The ^{63}Ni source of electrons makes it sensitive for all electronegative compounds, especially halocarbons. Today, the ECD technique has been refined and detection limits can be as low as fmol L^{-1}[*A. Ekdahl and K. Abrahamsson*, 1997].
Mass spectrometers have also been used[*Carpenter et al.*, 2007; *Groszko and Moore*, 1998; *Lobert et al.*, 1995; *McFiggans et al.*, 2000; *Mead et al.*, 2008; *Moore et al.*, 1996; *Sturges et al.*, 2000]. The advantage with MS compared to ECD is its capability to more accurately determine the identity of the compounds. However, the detection limit (pmol L^{-1}) is somewhat higher compared to an ECD, which makes MS less useful in investigations of the deeper oceans, where (pmol L^{-1}) concentrations low are usually found. Usually, a larger volume of water is purged (1-10 L) compared to the ~30 mL needed for ECD measurements. This leads to longer analysis times, which will influence the sample throughput.

Recently mass spectrometers have been used in studies of the origin (anthropogenic or natural) of halocarbons. Isotopic measurements of halocarbons ^{12}C/^{13}C and ^{35}Cl/^{37}Cl as well as ^{79}Br/^{81}Br have been performed [*Auer et al.*, 2006; *Horst et al.*, 2011], and the success of these measurements relies on the amount of sample (typically in ng) that is available.

Liquid or gas standards are used in calibrations of halocarbon measurements in sea water and air. For the anthropogenic CFCs, gas standards have been proven to be stable over long periods of time. However, for the biogenic, more short–lived halocarbons, the possible transformation of the initial compounds, such as the inter-conversion of $CHBr_3$ to $CHBr_2Cl$ and CH_2I_2 to CH_2ClI, has been shown to constitute a problem. This is somewhat of a disappointment, since preparation of gas standards from batch solutions would increase the robustness of halocarbon measurements in the research community.

An obstacle for the use of liquid standards is the lack of commercially available halocarbon-free solvents. In addition, halocarbon standards prepared in ultra pure methanol will, even if they are stored in dark glass vials at -18 °C in the dark, degrade after some months. In this work four individual stock standard solutions were prepared in methanol, each containing approximately 8 different halocarbons, chosen so that the possible inter-conversion and eventual contamination from the methanol itself could be detected. The final addition to seawater was made in such way, that the final amount of methanol was the same in each sea water standard. This was done to avoid any interferences of the methanol in the final sea water calibration standard.

In an inter-calibration study by*Jones et al.* [2011], six laboratories measured $CHBr_3$, CH_2Br_2 and CH_3I in sea water. The results indicated that the different working procedures and instrumental setups gave rise to large spreads in the results (relative standard deviations of 33 %, 41% and 25 % for CH_3I, $CH2Br_2$ and $CHBr_3$, respectively). It was, however, concluded that the large deviations in the measurements were outweighed by the much larger spread in the estimates of the global budgets of the different compounds. In this work three instruments have been inter-calibrated on each cruise. A number of samples, with concentrations varying from around the limit of quantification to some 50 pmol L^{-1} were analyzed on the three instruments at every occasion. We found that the pre-concentration step was the most crucial part of the determinations. The two custom-made purge and trap systems were similar, while the commercial system, with its rinsing steps, could experience problems with the background. The difference between the instruments in 2010 where e.g. < 3 %, 2 % 3 %, 8 % for CH_3CCl_3, $CHBr_3$, CH_2Br_2, and CH_2ClI respectively.

9. Concluding remarks

The work presented in this thesis has brought new insights in the biogenic formation of halocarbons in the Southern Ocean. Even though the polynias of the Amundsen and Ross Seas showed high primary productivity, halocarbon concentrations were comparably low. Instead, a strong coupling between the halocarbon distribution and the extent of sea ice was found, where elevated concentrations were encountered under the sea ice. The production of halocarbons by ice living organisms was shown, and concentration gradients indicated a possible transport of halocarbons to both the atmosphere and the surface water.

Earlier findings have indicated that Antarctic waters could act as a source of halocarbons to the atmosphere. However, the Amundsen and Ross Seas were found to be undersaturated for bromoform. This was consistent between the years, which indicate that the Southern Ocean may be a sink for bromoform. The studies of the distribution of halocarbons with depth showed that the deep water formation in the Ross Sea was an additional sink of halocarbons. Also, in the CDW, the relationship between $CHBr_3$ and its degradation products, as well as CH_2ClI was found to co-vary. This finding was used in T-OPLS models in order to trace water masses on in the Amundsen Sea.

10. Outlook

With this work, new insights have been gained regarding the biogenic halocarbon distribution in the Southern Ocean. The discrepancies found in measurements, not only in Antarctic waters, but also on a global scale, indicate that our knowledge of the processes that govern production and degradation is not sufficient. I suggest that one way to extend our knowledge is to study the mechanisms behind the formation and consumption on different spatial and temporal scales. Development of imaging optical sensors for studies of changes in pH, ammonium, and oxygen has proven to be useful in a broad range of biological studies. An intriguing idea would be to develop similar types of sensors for halocarbons to use in studies of, for instance, how environmental stressors, such as ocean acidification, effects the halocarbon production. With an improved knowledge of what governs the production, new proxies could perhaps be found that explains the distribution of halocarbons in surface waters. Sensor development could also facilitate studies of air-sea exchange and sea ice processes, and may enable investigations of sediments both in shallow waters, but also in deep basins if they are mounted on remote operated vehicles (ROV).

The studies of halocarbons have exclusively taken place during the austral summer. The biological productivity at this time of the year is at its maximum, and the sea ice is retreating. To fully understand the biogeochemical cycle of halocarbons in ice-covered oceans, knowledge of the formation and distribution during other seasons need to be investigated.

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