Formation and Distribution of Marine Biogenic Halocarbons with Emphasis on Polar Regions

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Cover picture: The distribution of bromoform along a transect in the Arctic Ocean measured during the Beringia 2005 Expedition

Abstract

It is well-established that marine micro- and macroalgae form volatile halogenated compounds (halocarbons). Production occurs throughout the world ocean with strong regional sources in coastal areas. In the atmosphere, these compounds are converted to reactive inorganic halogen compounds, which degrade ozone. Biogenic halocarbons typically contain iodine or bromine, which have higher ozone depletion potentials than chlorine.

The main pathway of halocarbon formation involves haloperoxidases, which reduce hydrogen peroxide, formed during photosynthesis, by oxidation of halide ions. Therefore, this is a universal process in the oceans, but there are large spatial and temporal variations. Estimations of the oceanic source of these compounds rely on accurate assessments of production and degradation rates, as well as on air-sea flux calculations.

In this work, the distribution of biogenic halocarbons in the ice-covered central Arctic Ocean, and in the Pacific sector of the Southern Ocean, was investigated. Elevated concentrations were found under the sea ice, and even higher concentration in the ice. The production, attributed to sea ice algae, was highly variable. Degradation was also observed with half-lives as short as 1 day. Production was also found in snow, which could be attributed to biological activity. The studies were performed in a period when the sea ice was melting, and low nutrient levels indicated that a previous bloom had now been followed by heterotrophic activity. The fast degradation, presumably biotic since known abiotic reactions are much slower, showed the importance of this parameter when studying natural populations, as compared to culture studies.

The highest concentrations in surface water and sea ice brine in the Arctic Ocean coincided with high concentrations of dissolved organic matter (DOM) carried by river water from the Russian rivers. It was hypothesized that this is a key parameter for the production of halocarbons in this region, as an organic substrate is needed for halocarbon production.

In the Southern Ocean it was found that large regions may act as a sink for bromoform. This was highly dependent on the wind direction. When air was transported from coastal regions, under-saturation was measured in open ocean regimes. This has implications for the estimation of local sources to the atmosphere in the Southern Ocean, as the net air-sea flux may be lower due to these nearby sinks.

Keywords: volatile biogenic halocarbons, Arctic Ocean, Southern Ocean, sea ice, snow, air-sea exchange, cyanobacteria

Part A

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Research Papers:

Papers included in this thesis, referred to in the text by Roman numerals:

Paper I: Karlsson, A., Auer, N., Schulz-Bull, D. and Abrahamsson, K. (2008), Cyanobacterial blooms in the Baltic - A source of halocarbons, *Marine Chemistry*, *2008*, 110(3-4), 129-139, doi:10.1016/j.marchem.2008.04.010

Paper II: Karlsson, A., Theorin, M., Snoeijs, P. and Abrahamsson, K. (2012), Volatile Halogenated Organic Compounds in Pack-ice and Snow in the Central Arctic Ocean, *Manuscript*

Paper III: Karlsson, A., Theorin, M. and Abrahamsson, K. (2012), Distribution, transport and production of volatile halocarbons in the upper waters of the ice covered high Arctic Ocean, *submitted to Global Biogeochemical Cycles*

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

Paper V: Mattsson, E., Karlsson, A. and Abrahamsson, K. (2012), Regional Sinks of Bromoform in the Southern Ocean, *submitted to Geophysical Research Letters*

Contribution Report:

Paper I: Responsible for planning, conducting experiments, interpretation and writing

Paper II: Responsible for planning, conducting experiments, interpretation and writing

Paper III: Responsible for planning, conducting experiments, interpretation and writing

Paper IV: Participated in planning, interpretation and writing.

Paper V: Participated in planning, interpretation and writing.

Populärvetenskaplig sammanfattning

Tång och växtplankton producerar halogenerade flyktiga kolväten, halokarboner. Detta sker främst i samband med fotosyntes, och är ett sätt för organismen att göra sig av med syreradikaler som bildas under denna process. De halogenerade kolväten som alger bildar är framförallt sådana som innehåller brom eller jod, att jämföra med den industriella källan där ämnen med klor eller fluor är vanligast. Liksom dessa har de naturligt producerade bromerade och joderade en ozonnedbrytande effekt i atmosfären.

Den största källan för dessa ämnen är haven men vad som påverkar produktionen i olika delar av världshaven är osäkert. Den högsta produktionen lokalt sker i kustnära områden av olika arter av tång, men även i öppet hav är dessa ämnen generellt övermättade, relativt halterna i överliggande luft, och kan övergå till atmosfären. Då kustnära hav (grundare än 200m) utgör endast 7% av havsytan, så är öppet hav trots lägre produktion högst betydelsefullt.

Av särskilt intresse är polarområdena med tanke på de stora klimat/miljöförändringar som sker där. Den kanske mest spektakulära effekten av den globala uppvärmningen är den snabba minskningen av istäcket i Arktis. Utöver de direkta effekterna på ekosystemet där så har flertalet studier beskrivit mer långtgående konsekvenser, såsom ändrad havscirkulation och ändrade luftströmmar som paradoxalt nog skulle kunna ge ett kallare klimat i delar av norra hemisfären.

I polarområdena sker en snabb nedbrytning av ozon på våren när ljuset kommer tillbaka. Detta har visat sig vara starkt beroende av reaktivt brom i atmosfären, och biologisk bildning av bromerade kolväten i den arktiska oceanen är därför en viktig men inte speciellt välkänd parameter. Det är känt att de alger som lever i de vätskefyllda kanaler som finns i havsisen kan bilda halogenerade flyktiga kolväten men hur utbrett detta är och vad som styr denna produktion hade inte studerats tidigare. Under en expedition med isbrytaren Oden över den arktiska oceanen, från Alaska till Svalbard, så undersöktes fördelningen av flyktiga halogenerade kolväten i havsvattnet. Höga halter påträffades i isen och i vattnet under. Produktionsstudier visade att dessa ämnen kunde produceras såväl som brytas ned av mikroorganismerna i isen. Produktionen visade sig också vara beroende på organiskt material som härrörde från de stora ryska floder som mynnar ut i arktiska oceanen. Dessutom kunde produktion uppmätas i den snö som ligger på havsisen.

De halter som uppmättes i vattnet mitt i arktiska oceanen var mycket högre än vad som normalt brukar uppmätas så långt från kusten, och vi fann att den arktiska oceanen således är en potentiellt stor källa till atmosfären.

Även i Antarktis uppmättes förhöjda halter under och i isen, dock lägre än i Arktis. I stora delar av det öppna havet utanför havsisen i Antarktis visade sig vattnet vara undermättat, relativt halten i luften, av bromoform, det naturligt producerade halogenerade kolvätet som brukar hittas i högst koncentrationer. Undermättnaden kunde förklaras av på en hög löslighet i det kalla vattnet i kombination med att luften hade färdats nära kuster och då tagit upp höga halter av produktionen därifrån. En förhöjd havstemperatur skulle minska dessa områdens kapacitet som sänkor för bromoform vilket är intressant i ett klimatförändringsperspektiv.

1. Introduction

Volatile halogenated organic compounds (VHOCs), also referred to as halocarbons, are produced naturally in the world ocean by macro- and microalgae. Most common are methane derivatives with up to three halogen substituents, generally of which at least one is bromine or iodine. The dominating compound is bromoform, $CHBr_3$, for which the marine production is the primary global source. The reason, if any, why algae form these compounds is unclear. It has been suggested that halocarbons or their precursors, being toxic to many organisms, are produced as a defense against grazing or epiphytes. However, it is possible that they are produced just as byproducts from haloperoxidases, a class of enzymes that oxidize halides and reduce hydrogen peroxide, in a cycle to rid the cell of reactive oxygen species formed primarily during photosynthesis.

In the atmosphere, most bromo- and, especially, iodocarbons are very short lived (VSL) substances with estimated photochemical lifetimes ranging from 7 minutes for CH_2I_2 to 145 days for CH_2BrCl, with an intermediate lifetime of bromoform of 17 days [*Ordóñez et al.*, 2011]. The degradation yields reactive halogen species, which participates in the degradation of ozone. In the troposphere, ozone is a greenhouse gas and the primary precursor of atmospheric oxidation [*Simpson et al.*, 2007]. In the stratosphere, ozone absorbs harmful UVB-radiation. It was first thought that bromoform was degraded and "rained out" before reaching the stratosphere. However, it was found that bromoform could in fact be transported to these heights [*Sturges et al.*, 2000] and has been suggested to be an important carrier of bromine to the stratosphere [*Dvortsov et al.*, 1999]. An additional atmospheric influence is the involvement of iodocarbons in formation of marine aerosols [*O'Dowd et al.*, 2002], which in turn affects the radiative forcing.

Halocarbons are therefore interesting in a climate change perspective. Changes in species composition, productivity of algae, and in air-sea exchange driven by changes in sea-temperature, ocean surface film properties and wind, will have an effect on the halogen chemistry in the atmosphere.

Even if it is well-established that marine algae produce halocarbons, several key parameters, which are up to this date uncertain or even unknown, are needed to model the global circulation of these compounds. Parameters that control the production, the geographical variation, the air-sea flux, and microbial and abiotic degradation rates are all factors which require further investigation.

Of special concern are the Polar regions, which at the present undergo large-scale changes. The effect on formation and air-sea flux of biogenic volatile compounds in these areas is likely to be substantial. The knowledge of the halocarbon chemistry in the Arctic has been limited to a few measurements, generally at coastal sites. In the central Arctic Ocean and the Ross and Amundsen Seas in the Southern Ocean no measurements had previously been reported. This work has aimed to broaden the knowledge of biogenic volatile halocarbons in these remote areas (Paper II-V).

To understand what governs the production, connections to biology have been investigated (Paper II and IV). This has been done by correlating VHOCs to photosynthetic pigments, photosynthetic activity and nutrient concentrations.

Another issue which has been investigated deals with the formation of halocarbons by cyanobacteria (Paper I). Cyanobacteria are phototrophic prokaryotes and several species have the ability to fix nitrogen. They are widespread both on land and in the oceans. Regionally, often as a consequence of environmental forcing, these organisms may be the dominating species. One region where strong blooms of cyanobacteria have been observed is the Baltic Sea. Halocarbons production from cyanobacteria had not previously been seen.

In polar areas, sea ice has a high influence, both as a limiting factor for air-sea exchange, and because halocarbons are produced by sea ice algae. Since ozone depletions events (ODEs) are especially pronounced in the Polar regions, it is of importance to understand the ocean sinks and sources of halocarbons. The sea ice influence on halocarbon chemistry has been investigated in both the Arctic and the Southern Ocean (Papers II, III and IV). In the Southern Ocean, substantial focus has been to investigate the air-sea exchange, and the implications of the comparably high solubility in cold waters, and the spatial variability of halocarbon sources (Paper V).

1.1 Background

The field of volatile biogenic marine halocarbons was established forty years ago, when James E. Lovelock discovered that methyl iodide was produced by marine algae [*Lovelock et al.*, 1973]. At first, the monohalogenated methanes (CH_3Cl, CH_3Br and CH_3I) were considered. These compounds had previously been found in high concentrations in air, much higher than would be the case if the source was solely anthropogenic [*Lovelock*, 1975]. Soon thereafter, *Burreson et al.* [1975] discovered that the essential oil of the Hawaiian seaweed *Asparagopsis taxiformis* contained a range of polyhalogenated small organic compounds. The major constituent was found to be bromoform, which amounted to 80% of the essential oil [*Burreson et al.*, 1976].

Already in 1908, the catalytic degradation of ozone by chlorine in the presence of light was discovered [*Weigert*, 1908]. These processes were later shown to occur in the stratosphere with the anthropogenic chlorofluorocarbons, CFCs (commonly known as Freons, the DuPont brand name), as primary carriers of chlorine [*Molina and Rowland*, 1974].

It was of course intriguing that there may be a biogenic source of atmospheric halogens, i.e. a natural regulation of ozone levels. In addition, bromine was suggested to be more efficient in degrading ozone than chlorine, and marine $CHBr_3$ was indicated as an important source [*Wofsy et al.*, 1975]. *Solomon et al.*

[1994] suggested that iodine may be involved in stratospheric degradation of ozone. However, the general consensus has been, and still is, that compounds carrying iodine are too short lived in the atmosphere. Even if iodine has a high ozone depletion potential, its contribution to ozone degradation at altitudes above the troposphere is negligible [WMO, 2011]. Model calculations of the inventory of short-lived halocarbons in the atmosphere has revealed that the required oceanic source of brominated compounds should be ~500 Gg year^{-1} for $CHBr_3$, 70 Gg year^{-1} for CH_2Br_2, and 90 Gg year^{-1} for CH_2BrI [*Ordóñez et al.*, 2011]. Other brominated compounds were estimated to contribute less. It should be noted that CH_3Br is another important source of bromine in the atmosphere. However, it is not a short-lived compounds (photolytic lifetime ~1.6 years [*Ordóñez et al.*, 2011]) and it also has a significant anthropogenic source.

Table 1. List of compounds

Formula	Name
Biogenic Compounds[a]	
$CHBr_3$	Tribromomethane (bromoform)
$CHBr_2Cl$	Dibromochloromethane
$CHBrCl_2$	Bromodichloromethane
CH_2Br_2	Dibromomethane
CH_2BrCl	Bromochloromethane
CH_3Br	Bromomethane (methyl bromide)
CH_2I_2	Diiodomethane
CH_2BrI	Bromoiodomethane
CH_2ClI	Chloroiodomethane
CH_3I	Iodomethane (methyl iodide)
CH_3CH_2I	Iodoethane (ethyl iodide)
$CH_3CH_2CH_2I$	1-iodopropane (propyl iodide)
CH_3CHICH_3	2-iodopropane (isopropyl iodide)
$CH_3CH_2CH_2CH_2I$	1-iodobutane (butyl iodide)
$CH_3CH_2CHICH_3$	2-iodobutane (*sec*-butyl iodide)
Anthropogenic Compounds	
CCl_4	Tetrachloromethane (Carbon tetrachloride)
CH_3CCl_3	1,1,1-trichloroethane (Methyl chloroform)

[a] Some of the biogenic compounds also have anthropogenic sources

1.2 General Description of the Arctic Ocean

The Arctic Ocean is a mediterranean sea, i.e. mostly enclosed by land. In the center, deep oceanic basins are found. Broadly, the basins can be divided in the Eurasian basin and the Amerasian basin, which are separated by the Lomonosov Ridge. These basins are surrounded by vast continental shelf areas. The circulation patterns (Figure 1) have been extensively researched and the present knowledge has been summarized by *Rudels et al.* [2012]. Generally, upper Atlantic water enters the Arctic Ocean through Fram Strait, west of Svalbard, and over the Barents Sea. This water moves along the Eurasian continental shelf, and gradually, during the transport, enters the surface layers of the oceanic basins. Additionally, Pacific water enters the Arctic Ocean through Bering Strait. Main circulation patterns in the central Arctic Ocean are the Beaufort Gyre, and the wind-driven Transpolar Drift. The sea ice basically follows the surface water circulation, and the main outflow is through the Fram Strait, east of Greenland.

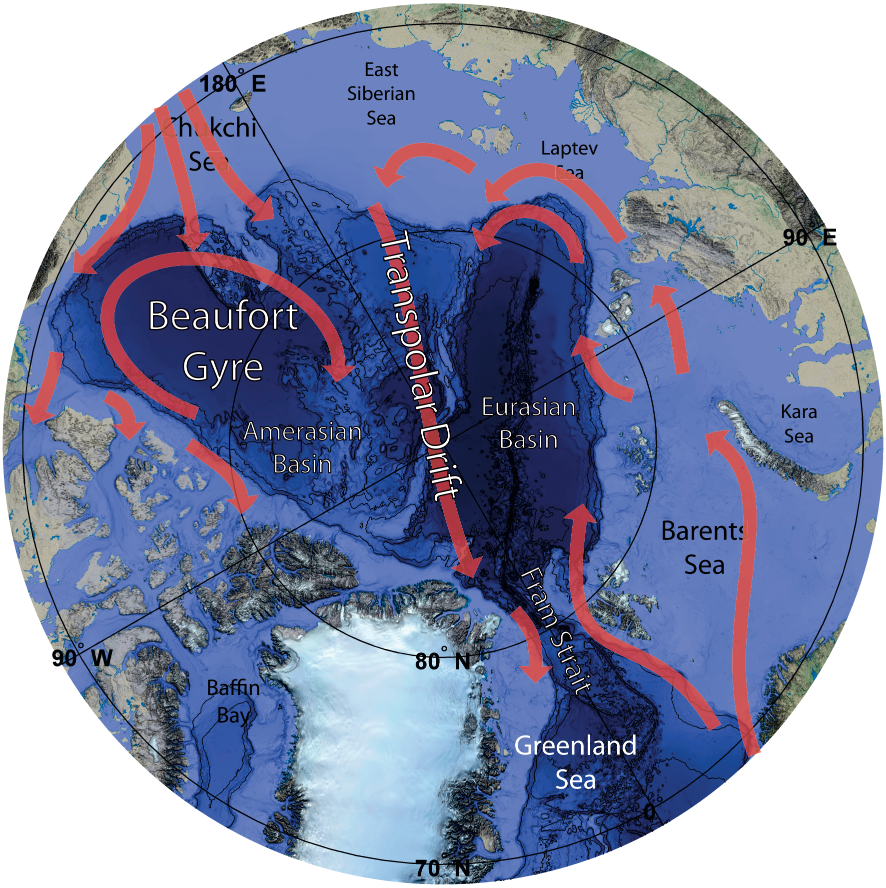

Figure 1. General pattern of surface water circulation in the Arctic Ocean. Depth contours correspond to depth intervals of 1000m.

There are several large rivers, mainly on the Russian side, which have their outflow in the Arctic Ocean. The discharge from the six largest Eurasian rivers is ~1900 km^3 yr^{-1}, and since 1936 a trend of increasing river flux has been observed [*Peterson et al.*, 2002]. The river water contains large amounts of terrestrial dissolved organic matter (DOM). The total flux of organic carbon from rivers to the Arctic Ocean has been estimated to 25-36 Tg C yr^{-1} [*Raymond et al.*, 2007].

The river water freshens the Arctic Ocean surface water, and is involved in forming the steep halocline below the surface mixed layer. As sea ice is formed, high salinity brine is rejected and sinks due to its higher density, and when it melts, water of low salinity accumulates at the surface. The halocline is a pronounced feature in the Arctic Ocean, and it prevents heat flux from underlying water, thereby keeping the surface water cool.

During the past decades, the Arctic Ocean has undergone large-scale changes. For the modern satellite era, starting in 1979, a steady decrease in sea ice extent has been shown. Recently there have been indications that the decrease accelerates [*Wang and Overland*, 2009]. As the sea ice cover decreases, the albedo decreases, and the surface water is heated. A warmer Arctic Ocean will have consequences for global ocean circulation, since this is a region of deep water formation. Also, the load of terrestrial DOM from rivers is likely to increase due to disintegration of permafrost [*Gruber*, 2004]. The results from Paper III show that this may affect the production of halocarbons in the Arctic Ocean.

1.2 General Description of the Southern Ocean

The Southern Ocean is the region surrounding the Antarctic continent (Figure 2). Compared to the Arctic Ocean, it is not enclosed by other continents, and therefore, it is no formal geographic region. A northern boundary can be defined by the Subtropical front, which varies between latitudes of 38°S – 60°S [*Orsi et al.*, 1995]. Around the Southern Ocean, the Antarctic Circumpolar Current (ACC) flows. This is the largest ocean current [*Klinck and Nowland Jr*, 2001], and it moves eastward around the Antarctic continent driven by the world's strongest westerly winds [*Trenberth et al.*, 1990]. The ACC connects the Atlantic, Indian and Pacific ocean, transporting deep and intermediate waters between these oceans, and plays a key role in the world ocean deep-water circulation [*Orsi et al.*, 1995]. Deep water is formed when circumpolar deep water mixes on the slopes with newly formed bottom water coming of the shelves. The bottom water is formed in the process of sea ice formation, when brine is ejected into the surface water. Deep water formation occurs mainly in the Weddell and Ross Sea [*Orsi et al.*, 1999]

Two of the world's largest polynyas can be found in the Southern Ocean, the Weddell Sea polynya, and the Ross Sea polynya. They are mainly driven by catabatic winds, blowing from the continent. The Ross Sea polynya has a maximum summer extent of ~400 000 km^2, and is thought of as the biologically most productive polynya in the world (100–200 g C m^{-2} yr^{-1}) [*Arrigo and van Dijken*, 2003]. Sea ice formation in the Ross and Weddell polynyas can be as high as 20-50% (Ross polynya) and 5-10 % (Weddell polynya) of total Antarctic sea ice cover [*Drucker et al.*, 2011]. The sea ice extent in the Southern Ocean has been found to increase with an average of 1.2% per decade with large regional anomalies. In the Ross Sea an increase of 4.9 % per decade has been observed, whereas sea ice in the Bellingshausen and Amundsen Sea has been found to decrease with -7.1% per decade. [*Thomas and Dieckmann*, 2010].

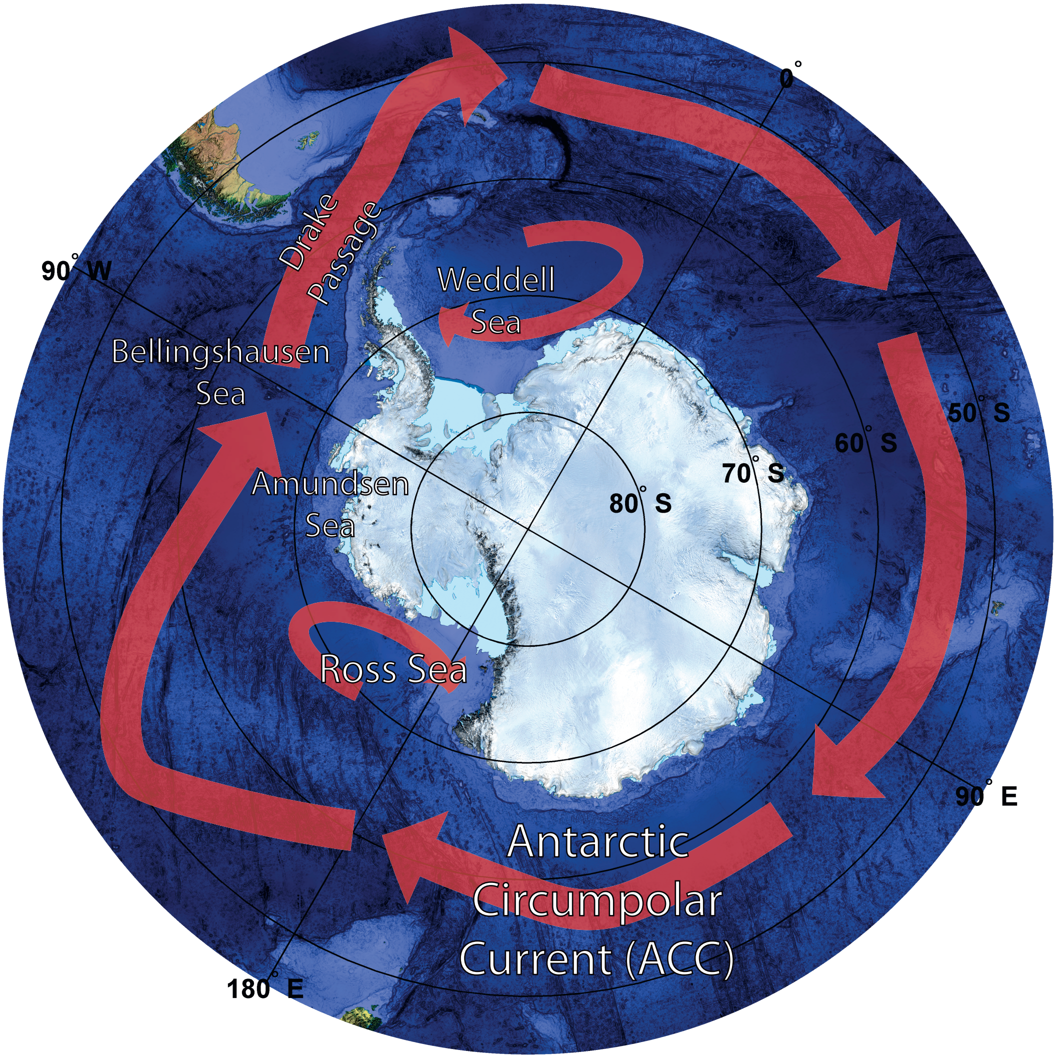

Figure 2. General pattern of water circulation in the Southern Ocean.

2. Formation

2.1. Mechanisms of formation

The first step toward an understanding of the enzymatic processes behind halocarbon production in algae was taken by *Theiler et al.* [1978] as they isolated a bromoperoxidase from the marine red algae *Bonnemaisonia hamifera*. It was shown that, in the presence of hydrogen peroxide, bromide and 3-oxooctanoic acid, $CHBr_3$ and CH_2Br_2 were formed. The organic substrate was chosen on the basis that bromoheptanones are major halogen-containing products in this alga. *Burreson et al.* [1976], in their study of *Asparagopsis taxiformis*, identified halogenated acetones as intermediates for a range of haloforms (1 carbon and 3 halogens) found.

Bromoperoxidases catalyse reduction of hydrogen peroxide, formed naturally during photosynthesis, to water by oxidation of bromide. The results indicated that subsequent stepwise substitution reactions of the oxidized bromine at the α-position of ketones, particularly β-keto acids, ultimately lead to formation of the brominated methanes (Figure 3). The release of bromform from the brominated ketone was shown to be highly pH-dependent [*Burreson et al.*, 1976; *Theiler et al.*, 1978], likely a non-enzymatic base catalyzed hydrolysis (Eq. 3) [*Beissner et al.*, 1981]. CH_2Br_2 would be the product if this reaction occurs after two bromine are added to the parent compound.

The corresponding reactions with iodine, which can also be a substrate for bromoperoxidase, were suggested. Subsequent substitution reactions with chloride of the brominated or iodinated compounds would give a range of mixed halogen compounds [*Theiler et al.*, 1978]. Chloride substitution of methyl iodide had previously been shown by *Zafiriou* [1975].

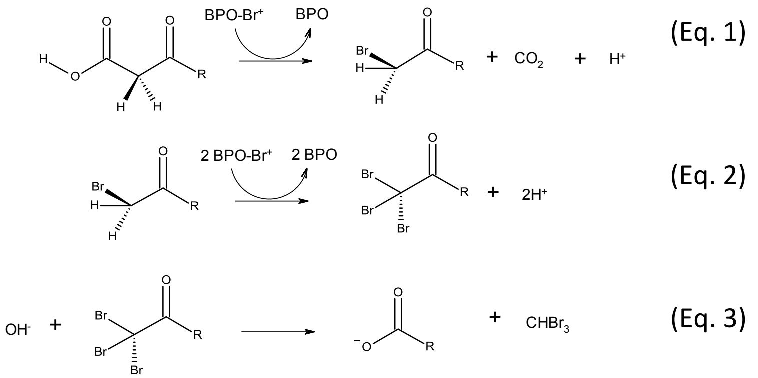

Figure 3. Early suggested mechanism for biogenic production of bromoform catalyzed by bromoperoxide (BPO) after oxidation of bromide. More recent studies indicate that HOBr, produced from haloperoxidase activity, may be the halogenating compound.

Further studies revealed that several other species of macroalgae contained bromoperoxidases, and produced halocarbons [*Gschwend et al.*, 1985; *Hewson and Hager*, 1980]. Although the efficiency of production was highly species dependent, halocarbon formation seemed to be a universal process in marine algae. The exact mechanism was, however, still uncertain. The kinetics, the location where these reactions occur, and which steps are catalyzed by bromoperoxidase were not known.

Already in 1926, it was shown that two red macroalga released HOBr and Br_2 in their seawater medium [*Sauvageau*, 1926]. It was later revealed that bromoperoxidases may be the source of HOBr [*de Boer and Wever*, 1988]. *Wever et al.* [1991] reported that, for a number of seaweeds, HOBr was released in the surrounding media, and that exogenous organic compounds were brominated. Possibly, bromoperoxidase would be located extracellular, on the thallus surface. They argued that it was in fact this mechanism that was responsible for the reactions forming halocarbons. It was speculated that the release of HOBr was part of a defense system against bacteria, fungi and grazing. The mechanism would be similar to the enzyme catalyzed reaction (Figure 3) but with HOBr replacing the enzyme bound activated bromine (Eq.4).

$$\mathrm{COOH\text{-}CH_2\text{-}CO\text{-}R + 3\ HOBr \rightarrow CHBr_3 + R\text{-}COOH + CO_2 + 2\ H_2O} \quad \text{(Eq.4)}$$

It is still not established which mechanism is correct, perhaps both occurs. Later research seem to support a mechanism where HOBr (or HOI) released from the algae reacts with DOM (dissolved organic matter) to give halocarbons [*Manley and Barbero*, 2001].

Haloperoxidases are generally accepted to be the singular most important enzymes for biogenic formation of polyhalomethanes. For larger halogenated organic compounds, several other enzymes have been identified [*Van Pée and Unversucht*, 2003], some of which potentially could give halogenated methanes as by-products. Although marine poly-brominated/iodinated methanes are mainly biogenic, there might be an anthropogenic source close to coastal population. Upon chlorination of water, haloforms are formed, analogously to the biogenic production, by the haloform reaction (Eq.5).

$$\mathrm{R\text{-}CO\text{-}CH_3 + 3\ X_2 + OH^- \rightarrow CHX_3 + R\text{-}COOH + 3X^- + 2H^+} \qquad \text{(Eq.5)}$$

For the monohalogenated methanes, methyl transferases have been suggested to be important [*Manley*, 2002; *Wuosmaa and Hager*, 1990]. These compounds, CH_3Cl, CH_3Br and CH_3I, have significant anthropogenic sources, e.g. as pesticides (fumigation), and formerly as flame retardants, and there have been reports that photochemical formation of CH_3I in the ocean should be considered [*Happell and Wallace*, 1996; *Moore and Zafiriou*, 1994; *Palmer*, 2010].

In soils and sediments, it has been shown that alkyl halides are formed during oxidation of organic matter (by reduction of Fe(III)) [*Keppler et al.*, 2000]. The importance of such reactions in the oceans is not known. From measurements close to the bottom in the Eurasian basin of the Arctic Ocean during the Beringia 2005 expedition, it was shown that sediment processes seem to occur even at large depths, >4000 m. The bottom waters are traditionally thought to be well mixed, but the distribution of halocarbons indicated that there may be a source of halocarbons in the sediments in the oceanic basins (Figure 4, left). -----------------
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----------------------------------Unpublished data--------------------------------------
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Figure 4. Depth profiles of $CHBr_3$ at two stations in the Eurasian basin. Station 47 left was located in the Amundsen basin, and station 49 on the Gakkel Ridge. Exact station locations can be found in Paper III.

Another recently discovered possible source of iodinated volatile compounds is reaction of iodide with ozone in seawater. Similar to the suggested action of haloperoxidases, HOI is formed which may then react with DOM, and form iodinated compounds [*Martino et al.*, 2009].

In the beginning of the 1990's there were several reports that also marine microalgae produce halocarbons [*Sturges et al.*, 1992; *Tokarczyk and Moore*, 1994], which was also indicated from the depth distributions in the Arctic Ocean

[*Krysell*, 1991]. Haloperoxidases were identified in several species of microalgae [*Moore et al.*, 1996], which indicated the same enzymatic pathways of formation as in macroalgae. Similar to macroalgae, extracellular release of HOBr and HOI have been shown for species of microalgae [*Hill and Manley*, 2009].

With progress in research the range of species that are found to produce halocarbons has increased, as has the range of compounds found to be produced. It is now known that not only bromo- and iodocarbons are biologically produced, but also strictly chlorinated volatile compounds such as $CHCl_3$, $CHClCCl_2$ and CCl_2CCl_2 [*Abrahamsson et al.*, 1995; *Nightingale et al.*, 1995].

2.2. Variability in production

The rates of production are species dependent. A general trend has been observed for macroalgae, where subtropical species are more productive than temperate ones, and that polar species are least productive [*Ekdahl*, 1997; *Laturnus*, 1996]. It was noted that this may be due to temperature and light conditions. For Arctic macroalgae, halogenating activity has been found to increase with temperature [*Mehrtens and Laturnus*, 1997]. A trend has also been observed for microalgae, where the smallest fraction, the picoplankton (0.4-2 µm), was shown to be most productive [*Abrahamsson et al.*, 2004].

A more specific assessment of the species variation has proven to be hard. Given the lack of consistency in units for reported production rates (pmol FW^{-1} h^{-1}, pmol DW^{-1} h^{-1}, pmol [µg chl *a*]$^{-1}$ h^{-1}, molecules $cell^{-1}$ h^{-1} etc.), and different incubations techniques, comparisons are uncertain, and may lead to the wrong conclusions. Progress in this field requires a standardized method for incubations and units.

Estimations of halocarbon production rates from individual species of micro- or macroalgae have generally been performed on cultures [*Manley and De La Cuesta*, 1997; *Scarratt and Moore*, 1996; *Tokarczyk and Moore*, 1994]. This allows identification of which species that are capable of halocarbon production and a relative measure in production efficiency compared to other cultures treated the same way. For mechanism studies, it is also the preferred approach. However, productions rates derived from culture studies do not translate well to the natural environment [*Venrick et al.*, 1977].

It is impossible to mimic natural conditions in a laboratory environment. Light conditions, concentrations of solutes and dissolved gases, water turbulence, and interaction with microorganisms are factors which are likely to influence the production. Also, a new surface, the container walls, is introduced, which may lead to adsorption of solutes and organisms. It has been indicated that DOM and different types of stress (oxidative, mechanical, temperature) are important parameters for halocarbon production [*Abrahamsson et al.*, 2003; *Manley and Barbero*, 2001; *Sundström et al.*, 1996]. This is normally not accounted for in culture studies were instead optimal growth conditions usually are sought. An indication of that many factors in addition to biomass govern the natural production of halocarbons in the oceans is that correlations between chlorophyll *a* and concentrations of halocarbons, which usually are strong in culture studies, are seldom seen in oceanic transects [*Abrahamsson and Ekdahl*, 1993; *Moore and Grozsko*, 1999; *Schall et al.*, 1997], except for regionally constrained areas (Paper IV). For global budgets it is therefore essential to do field measurements of concentrations and production rates. Incubations of natural seawater, brine or snow have been the approach in Paper I, II and IV. For the study on the cyanobacterial bloom (Paper I), incubations were performed in enclosed glass containers without headspace, which were put under running surface seawater and exposed to sunlight.

For the production studies in sea ice and snow (Paper II and IV), the natural conditions were harder to emulate. In order to study sea ice algae, traditionally, the ice is melted and salt is added to avoid osmotic shock. This procedure changes the composition of the sample, for instance DOM will be diluted. It takes surprisingly long time to melt sea ice, and halocarbons may both be produced and degraded during the procedure. The approach used in Papers II and Paper IV was to collect brine that seeped into sack-holes for incubation. Of course, this is not completely satisfactory, since micro-organisms can be attached to the ice. Incubation was done at -1°C to keep the snow from melting and the brine from freezing. The samples were exposed to artificial light.

The formation of halocarbons often shows a diurnal variation with highest production at mid-day (Paper I, [*Ekdahl et al.*, 1998; *Quack and Wallace*, 2003]). This is a natural effect of the dependence on hydrogen peroxide. During photosynthesis, in the Mehler cycle, superoxide radicals are formed and transformed to hydrogen peroxide by superoxide dismutase. Other sources of hydrogen peroxide are photochemical formation and mitochondrial respiration. The latter may explain that another production peak, although smaller than the mid-day peak, sometimes may be seen after sunset [*Abrahamsson et al.*, 2004]. In addition to haloperoxidases, several other enzymes exists that rid the cells from the toxic hydrogen peroxide, mainly catalase and ascorbate peroxidase [*Manley*, 2002]. The formation of halocarbons is therefore not only dependent on the amount of hydrogen peroxide in the cells, but, also, on the relative regulation of different enzymes that reduce reactive oxygen species.

In addition to marine micro- and macroalgae, haloperoxidases and other halogenating enzymes have been identified in bacteria [*Van Pée and Unversucht*, 2003]. This possible source of halocarbons has hardly been investigated. Haloperoxidases from bacteria seem to have a lower halogenating efficieny [*Van Pée and Lingens*, 1985], and in absence of photosynthesis, the concentration of hydrogen peroxide is low. Bacteria are, however, highly abundant in the ocean, and it is possible that part of the biogenic halocarbon production attributed to algae in fact originates from bacteria.

In contrast to heterotrophic bacteria, cyanobacteria are capable of photosynthesis. Given that they contain haloperoxidases, the potential of halocarbon production would consequently be higher. On the outset of the study of a cyanobacterial bloom in the Baltic Sea (Paper I), the presence of haloperoxidases in cyanobacteria had only been inferred from genome sequencing [*Kaneko et al.*, 1996]. *Schall et al.* [1996] had however suggested that cyanobacteria could be responsible for halocarbon production found in a melt pond in the Antarctic. The Baltic Sea late summer cyanobacterial blooms provided an opportunity for *in situ* studies of the ability of these organisms to form halocarbons. Several bromo- and iodocarbons were found to be formed, with a strong diurnal variation (Figure 5). Highest production rates was found for $CHBr_3$ which had a production maximum at mid-day of 0.3 pmol [µg chl *a*] h^{-1}.

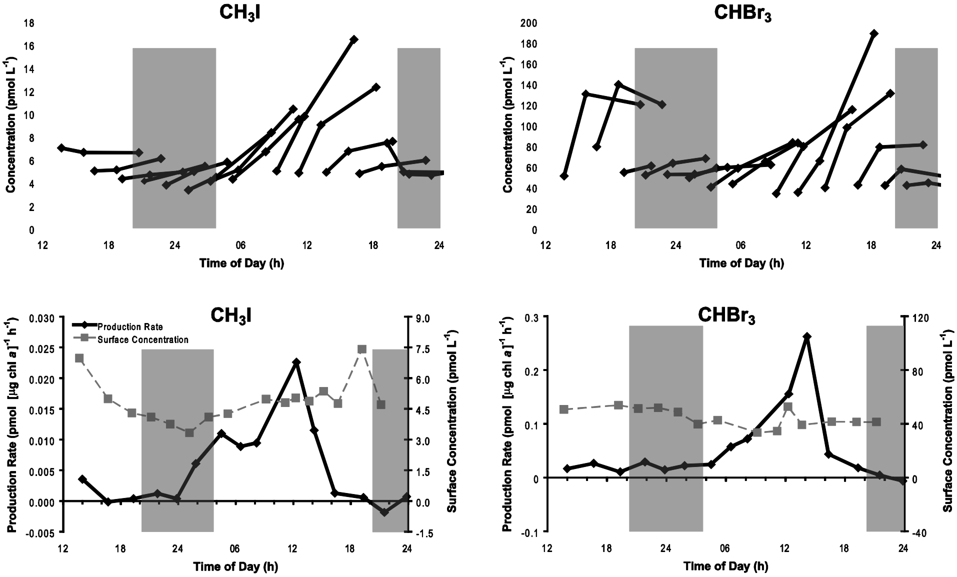

Figure 5. Concentrations of CH_3I and $CHBr_3$ in the incubated samples versus time (upper graph). Each incubation series is connected by lines. The shaded regions correspond to dark periods. In the lower graphs, the derived production rates from the incubations are shown together with the concentration in the seawater.

The investigated bloom was dominated by *Pseuanabaena limnetica*. To exclude production from smaller cells and abiotic reactions, halocarbon production from samples concentrated with a plankton net was compared to the variation in seawater concentration, corrected for fluxes from air-sea exchange and water mixing. Based on bloom period and coverage, and an average chlorophyll *a* concentration of 5 µg L^{-1}, this previously unknown source of bromoform in the Baltic Sea, was estimated to ~100 Mg yr^{-1}. For the other halocarbons found to be produced (CH_3I, CH_2Br_2 and $CHBr_2Cl$), the estimated annual production was 1-2 orders of magnitude lower.

More recently, the findings that species of cyanobacteria are capable of halocarbon production have been confirmed, as a bromoperoxidase, with halogenating activity, has been found in the cyanobacteria *Synechococcus* [*Johnson et al.*, 2011]. In addition, the Baltic Sea study confirmed previous results [*Abrahamsson et al.*, 2003], that brackish-water organisms may be efficient halocarbon producers, and that high salinity is not required for formation of halocarbons.

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3. Degradation

3.1 Halide substitution

Halocarbons are subjected to a range of degradation reactions in seawater. The high concentration of chloride causes nucleophilic substitution of bromine and iodine. This occurs for both mono- and polyhalogenated compounds.

$$CH_3X + Cl^- \rightleftharpoons CH_3Cl \qquad (X = Br \text{ or } I) \qquad (Eq.6)$$

$$CHX_3 + Cl^- \rightleftharpoons CHX_2Cl \qquad (X = Cl, Br \text{ or } I) \qquad (Eq.7)$$

The rate of reaction and the temperature dependence varies between different halocarbons. The reaction is faster for substitution of iodine than for substitution of bromine [*Elliott and Rowland*, 1993]. For bromoform, the degradation pathway by chloride substitution is $CHBr_3 \rightarrow CHBr_2Cl \rightarrow CHBrCl_2$, which is evident from depth profiles in the ocean (Figure 6), which typically show increased ratios of $CHBrCl_2$ and $CHBr_2Cl$ to $CHBr_3$ with depth (Paper III, [*Moore and Tokarczyk*, 1993]). If further substitution, to $CHCl_3$, occurs in seawater is unclear [*Class and Ballschmiter*, 1988].

For polybrominated compounds, determinations of halide substitution rates are few, and mostly rough estimates. From limited laboratory studies, *Geen* [1992] reported chloride substitution half-lives for bromoform of 5 years at 25°C and 74 years at 2°C. Substitution with chloride is thought to be the most important abiotic degradation pathway for bromoform in the oceans. This has, however, been hard to verify due to the long half-life in combination with other loss processes. In Paper III, it was shown that the degradation rate given by *Geen* [1992] fits well with other estimations of the age of the Arctic Ocean deep water, and the difference in age between the Amerasian and Eurasian basins [*Schlosser et al.*, 1997; *Tanhua et al.*, 2009].

A well determined degradation rate, with known temperature dependence, in absence of microbial degradation and photolysis, makes $CHBr_3$ a potential tracer in deep and intermediate waters. The temperature dependence, and relative ratio to $CHBr_2Cl$ and $CHBrCl_2$, should give information on both age and historical production. A pre-requisite would be to generate high resolution data even at larger depths, as in Papers III and IV.

Unpublished Data

Figure 6. Depth profiles of $CHBr_3$, $CHBr_2Cl$, and the ratios of $CHBr_3/CHBr_2Cl$ and $CHBr_2Cl/CHBr_3$, from the Arctic Ocean, over the Lomonosov Ridge.

3.2 Hydrolysis

Another abiotic degradation pathway is hydrolysis. For the monohalogenated methanes, this reaction is similar to chloride substitution (Eq. 6) except that the nucleophilic compound instead is water or hydroxide (Eq. 8).

$$CH_3X + H_2O \rightarrow CH_3OH + H^+ + X^- \quad (X = Cl, Br \text{ or } I) \quad \text{(Eq.8)}$$

For the haloforms, however, another hydrolytic mechanism seems to occur. Already in 1862 it was found that carbon monoxide and formate were formed from base catalyzed hydrolysis of chloroform, and it was suggested that the reaction goes through the intermediate CCl_2 [*Geuther*, 1862]. This was later revisited upon evidence that $CHCl_3$ was more reactive toward basic hydrolysis than CH_2Cl_2 or CCl_4. A mechanism for this reaction was later suggested by *Hine* [1950] and refined by *Robinson* [1961] (Eqs. 9-12).

$$CHCl_3 + OH^- \rightleftharpoons CCl_3^- + H_2O \quad \text{(fast)} \quad \text{(Eq.9)}$$

$$CCl_3^- \rightarrow :CCl_2 + Cl^- \quad \text{(slow)} \quad \text{(Eq.10)}$$

$$:CCl_2 + H_2O \rightarrow CO + 2HCl \quad \text{(fast)} \quad \text{(Eq.11)}$$

$$(CO + H_2O \rightarrow CO_2^-) \quad \text{(Eq.12)}$$

By this pathway, haloforms would not be transformed into other halocarbons, in contrast to the halide substitution reaction. The reactivity order of different haloforms by basic hydrolysis was found to be $CHBrCl_2$ > $CHBr_2Cl$ ~ $CHCl_2I$ > $CHBr_3$ > $CHCl_3$ in a 2:1 dioxane:water mixture [*Hine et al.*, 1956]. With the rate constants provided by *Hine et al.* [1956], and a normal pH of 8, the half-life would be ~69 years for $CHBr_3$ and ~14 years for $CHBrCl_2$ at 25.3 °C. The temperature dependence is strong and at 0°C the half-life would increase to ~4000 years for $CHBr_3$ and ~600 years for $CHBrCl_2$. It should be noted that these are highly uncertain values. They are measured in a dioxane/water mixture, and even if it was noted by *Mabey and Mill* [1978] that there was "a quite closely match" between hydrolysis rates for $CHCl_3$ in water and this solvent mixture, this is of course not ideal, especially since the medium of interest is seawater. Only the basic hydrolysis is considered and not neutral hydrolysis, which could be important at natural seawater OH^- concentrations. The rate constants from *Hine et al.* [1956] are still a common source for hydrolysis calculations of halocarbons, and often information of solvent, temperature as well as pH dependence is omitted (e.g. by *Vogel et al.* [1987]).

For the basis of air-sea flux this may seem unimportant as volatilization is a much faster process, but if transport and distribution in waters below the mixed layer are to be studied in warm waters, the hydrolysis kinetics, as well as halide substitution in seawater, should be better determined. In addition, seawater is a complex mixture of a wide range of solutes and several other degradation pathways are certainly possible from reactions with the intermediates in Eqs. 9-10. Basic hydrolysis may also be interesting in an ocean acidification perspective.

For iodinated compounds abiotic degradation in seawater may be important even on shorter time-scales. For some monoiodinated C1-C3 compounds *Jones and Carpenter* [2007] found half-lives, for substitution and hydrolysis combined, in the order of days at 30°C, and months at 0°C. Halide substitution was found to dominate at higher temperature, and hydrolysis at lower temperatures.

Other plausible degradation pathways are reaction with oxidizing species such as dissolved oxygen, ozone and reactive oxygen species. The rates of these reactions are unknown and typically not considered.

3.3 Photolysis

Brominated and, especially, iodinated organic compounds are subjected to photolysis in the ocean. Light of lower wavelengths dissipates fast in the water column, and photolysis mainly occurs in the first few meters from the ocean surface. *Carpenter and Liss* [2000] roughly estimated the photolytic rate of bromoform to be ~3% of the air-sea gas exchange rate. Consequently, and as photolysis in the atmosphere is faster, oceanic photolysis can rather be considered as an extension of the atmospheric photolysis sink, with small effect on the magnitude of the total air-sea flux. Generally, oceanic photolysis has not been much considered, but modeling efforts of halocarbon distribution in the oceans have started to address this [*Hense and Quack*, 2009], however, still with the rough estimates of photolytic rate from *Carpenter and Liss* [2000].

Photolytic degradation of halocarbons starts with homolytic cleavage of the C-X bond. In the atmosphere, the radical species then reacts with oxygen, which ultimately leads to formation of inorganic bromine, denoted Br_y (BrO, Br, $BrONO_2$, HOBr, BrCl, HBr) [*Hossaini et al.*, 2010].

In aqueous solutions another process may occur. It has been shown that, after dissociation of CH_2I_2 (Eq. 13), the molecules can recombine, assisted by a solvent cage, to form the isomeric CH_2I-I (Eq. 14). This compound is very short-lived, and may react by OH insertion/HI elimination to give CH_2IOH (Eq. 15) [*Li et al.*, 2003]. The corresponding reaction have also been shown for $CHBr_3$ [*Kwok et al.*, 2004]. In the last step, the halomethanol is degraded by reaction with water (Eq. 16).

$$CH_2I_2 + h\nu \rightarrow CH_2I\cdot + \cdot I \qquad \text{(Eq.13)}$$

$$CH_2I\cdot + \cdot I \rightleftharpoons CH_2I\text{-}I \qquad \text{(Eq.14)}$$

$$CH_2I\text{-}I + H_2O \rightarrow CH_2IOH + HI \qquad \text{(Eq.15)}$$

$$CH_2IOH + H_2O \rightarrow CH_2O + HI + H_2O \qquad \text{(Eq.16)}$$

In NaCl-solutions, CH_2ClI is also formed [*Guan et al.*, 2004], which has been confirmed to occur in seawater [*Jones and Carpenter*, 2005; *Martino et al.*, 2005]. *Jones and Carpenter* [2005] determined the yield of CH_2ClI from CH_2I_2 in natural sunlight conditions to be 35 ± 20%. They found that the photolytic rate increased in the order of $CH_2I_2 > CH_2BrI > CH_2ClI$. The photolytic lifetimes, normalized to 12 p.m. 1 July (at University of York, U.K.), were between ~10 minutes for CH_2I_2 and ~10 hours for CH_2ClI. Compared to the estimated value of ~30 days for bromoform in the top 1 meter of the ocean [*Carpenter and Liss*, 2000], this is much faster. However, the photolytic lifetimes of the iodinated compounds were based on small volumes of water (250 mL), i.e. the light penetration was high.

Oceanic photolysis clearly needs to be further investigated, both with the respect to air-sea exchange and to model halocarbon distribution in the ocean. There are certainly other mechanisms involved than in atmospheric photolysis, and a wide range of other products are viable given the complex composition of seawater. Reductive dehalogenation seems like a plausible reaction pathway. Some reactions will give non-halogenated and/or non-volatile compounds that will not be transferred to the atmosphere. Other products, such as CH_2ClI from photolysis of CH_2I_2, are still potential sources of atmospheric halogens, and may even enhance the flux as chloride substituted compounds are lighter and typically more volatile. For calm conditions (low transfer velocity) at high light intensity, photolysis of iodinated compounds may very well be the key parameter for the surface water concentration. In a modeling exercise, *Martino et al.* [2006] calculated that almost all CH_2I_2 may be photolyzed before reaching the ocean surface, i.e. the air-sea flux will be close to zero.

3.4 Microbial degradation

Even less understood than biogenic formation of halocarbons, is microbial degradation. For the monohalogenated methanes, methyl transferases, present in several aerobic and anaerobic bacteria, may exchange the halogen to either another halogen or to another functional group [*Van Pée and Unversucht*, 2003]. Enzymes that catalyze oxidative dehalogenation, dehydrohalogenation and reductive dehalogenation have shown to be widespread [*Fetzner*, 1998]. In natural water, these processes are masked by the measured biogenic production, and hard to isolate. Microbial degradation may be an explanation of fast decrease in concentrations, not explained by air-sea flux, that have been seen [*Abrahamsson et al.*, 2004; *Ekdahl et al.*, 1998].

Some studies have been made on the bacterial degradation of halocarbons. *Goodwin et al.* [1997] found that CH_2Br_2 was degraded by bacteria in seawater collected from a kelp bed. Degradation by methanotrophs and nitrifiers was excluded, and $CHBr_3$ was not found to be degraded. Compared to biogenic formation of CH_2Br_2 in the kelp bed, the microbial removal rate was slow, <1% of the formation. The rate was estimated to be faster than hydrolysis, but slower than volatilization. In a separate study, *Goodwin et al.* [1998] found that the half-life of CH_2Br_2, in seawater with respect to bacterial oxidation, may be as low as 2 days.

In the sea ice brine in the Arctic Ocean and the Southern Ocean (Paper II and Paper IV), high net degradation rates were found at some stations. In the Arctic Ocean, half-lives -- ----------------------------------Unpublished data-------------------------------------- ----------------------------.

These parallel processes of production and degradations that occur have implications for the assessments of source strengths. The high production rates of algal species shown in culture studies may in their natural environment, under certain conditions, be cancelled out by a high microbial degradation rate. It could also be speculated that this could lead to regional oceanic sinks of atmospheric halocarbons. If the degradation rate exceeds the production rate, there could be a shift from over-saturation to under-saturation with respect to the atmospheric concentration. As oceanic degradation is not particularly considered in global budget estimations, this could lead to significant over-estimates of source strengths.

4. Air-Sea Exchange

4.1 Air-Sea flux

To reach the atmosphere halocarbons, produced in the water column, need to be transferred to the surface and cross the sea-air interface. The first modeling attempts of this process was based on a film model [*Lewis and Whitman*, 1924], in which the air and water concentration profiles are thought to be uniform and the flux is determined by thin diffusive layers on both side of the air-sea interface. This was a highly simplified picture and with questionable basis in reality. A more general representation, is given by

$$F = k \times \left(C_w - \frac{C_a}{H}\right) \qquad \text{(Eq.17)}$$

where k is the transfer velocity (cm h^{-1}), C_w is the concentration in the surface water and C_a is the concentration in air. H is the compound specific temperature dependent Henry's Law constant (C_a/C_w at equilibrium), which for several biogenic halocarbons have been determined by *Moore et al.* [1995]. Transfer velocity is highly dependent on wind speed but parameterization has proven rather difficult.

The air-sea flux cannot be measured directly but has to be estimated. For this, different approaches have been used. Traditionally, flux estimation methods have been based on gaseous compounds with a known source on either side of the air-sea interface. From the near-surface depth profile, the rate of transport from or to the sea can be elucidated, and thereby the air-sea flux. These compounds must also be inert, or the degradation/decay rate must be known.

From a compound specific transfer velocity, the transfer velocity for any other gaseous compound can be determined. It has been shown that $k \propto Sc^{-n}$ ($n \approx 0.5$) [*Holmen and Liss*, 1984], the Schmidt-number (Sc) being the kinematic viscosity of seawater divided by the diffusion coefficient.

$$\frac{k_1}{k_2} = \left(\frac{Sc_2}{Sc_1}\right)^n = \left(\frac{D_1}{D_2}\right)^n \qquad \text{(Eq. 18)}$$

If the diffusion coefficient and transfer velocity of compound 1 (D_1 and k_1), and the diffusion coefficient of compound 2 (D_2) is known (Eq. 18), the transfer velocity of compound 2 can be determined.

For some time the radioactive trace gases ^{222}Rn and $^{14}CO_2$ [*Broecker and Peng*, 1974] were considered most useful to estimate k. ^{222}Rn is formed by decay of dissolved ^{226}Ra and ^{14}C is formed in the atmosphere by cosmic rays, or by nuclear bombs, and historically the $^{14}C/^{12}C$-ratio has been constant in the atmosphere. From the ocean depth profiles, the loss rate of radon from the mixed layer can be found, and also the decrease of $^{14}C/^{12}C$, which therefore gives the air-sea flux.

Alternatives for the radioactive tracers have been SF_6 [*Wanninkhof et al.*, 1985] combined with ^3He [*Watson et al.*, 1991], which are released in the ocean. The decrease in concentrations with time gives the transfer velocities from the equations:

$$\left(\frac{1}{R}\right)\left(\frac{dR}{dt}\right) = \frac{-(k_{He}-k_{SF_6})}{Z} \qquad \text{(Eq.19)}$$

$$\frac{k_{He}}{k_{SF_6}} = \left(\frac{Sc_{SF_6}}{Sc_{He}}\right)^n = \left(\frac{D_{He}}{D_{SF_6}}\right)^n \qquad \text{(Eq.20)}$$

where R=[^{3}He]/[SF_6] and Z is the depth. Other tracers, such as conservative bacterium spores [*Nightingale et al.*, 2000], and more recently, techniques that aim to more directly study the flux have been used. Eddy correlation methods are based on micrometeorological measurements combined with fast measurements of air concentration [*Baldocchi et al.*, 2001], and have been used, e.g., to measure air-sea flux of CO_2 [*McGillis et al.*, 2001].

By applying these different techniques, several suggestions of how k can be parameterized have been made from this empirical data. A reference height for wind speed (m s^{-1}) of 10 m has been chosen. Best fit to the data have been found for either linear, quadratic or cubic parameterization.

$$k_{600} = \begin{cases} 0.17\,U_{10} & (U_{10} \leq 3.6) \\ 2.85\,U_{10} - 9.65 & (3.6 < U_{10} \leq 13) \\ 5.9\,U_{10} - 49.3 & (U_{10} > 13) \end{cases} \qquad [\textit{Liss and Merlivat}, 1986]$$

$$k_{660} = 0.39\,U_{10_{avg}}^2 \quad \text{or} \quad 0.31\,U_{10}^2 \qquad [\textit{Wanninkhof}, 1992]$$

$$k_{600} = 0.333\,U_{10} + 0.222\,U_{10}^2 \qquad [\textit{Nightingale et al.}, 2000]$$

$$k_{660} = 3.3 + 0.026\,U_{10}^3 \qquad [\textit{McGillis et al.}, 2001]$$

$$k_{660} = 3 + 0.1\,U_{10_{avg}} + 0.064\,U_{10_{avg}}^2 + 0.011\,U_{10_{avg}}^3 \qquad [\textit{Wanninkhof et al.}, 2009]$$

The subscript in k denotes which Schmidt-number the transfer velocity is valid for. 660 and 600 are the Schmidt-numbers for CO_2 at 20°C in seawater and fresh water respectively. $U_{10,\,avg}$ refers to the average wind, which is an important distinction for the non-linear parameterizations.

All of these parameterizations are far from perfect (Figure 7). It has clearly been shown that wind speed alone cannot explain all processes that influence air-sea exchange. The effect on the transfer velocity from factors such as surface film properties influenced by macromolecules, bubble injection forming whitecaps, and atmospheric stability, need to be parameterized by other variables.

An additional uncertainty for transfer velocities of halocarbons are that their diffusion coefficients have not been measured, instead they have to be estimated from empirical models [*Hayduk and Laudie*, 1974; *Hayduk and Minhas*, 1982; *Wilke and Chang*, 1955]. These models often rely on the compounds molar volume at the normal boiling point, which is unknown for most biogenic halocarbons and also have to be estimated. This can be done by a group contribution method as described by *Sastri et al.* [1997], but introduces an additional error. The transfer velocity parameterizations are often optimized for CO_2 which is not inert in water. This chemical enhancement (assumed to be accounted for by the constant term in the equation by *Wanninkhof et al.* [2009]) does not occur for the halocarbons and the direct conversion between transfer velocities (Eq. 18) may not hold. Depending on which model is used to estimate the diffusion coefficient and which k-parameterization is used, large variations in the calculated air-sea exchange rate are obtained (Figure 7). The transfer velocity estimation is to be considered most uncertain. For a wind speed range of ~4-18 m, the parameterization that gives the highest transfer velocities is typically 100% larger than the lowest estimation. At low or high winds the difference is even larger.

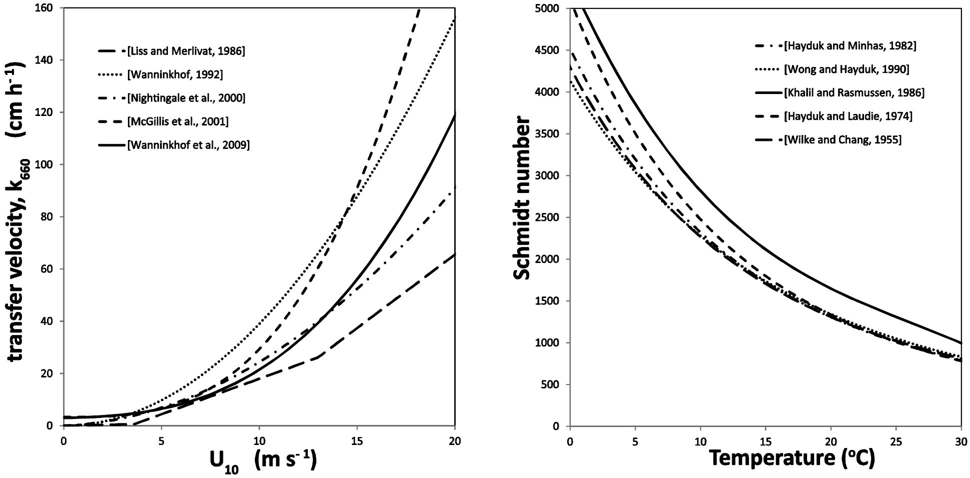

Figure 7. Different parameterization of the transfer velocity (left) and Schmidt numbers, for bromoform, derived from various empirical equations to estimate the diffustion coefficient (right).

Most biogenic halocarbons are very short lived in the atmosphere and have strong local sources related to primary production. This leads to high spatial and temporal variation in air and sea concentrations (Paper V). In contrast to gases with a relative uniform atmospheric concentration, such as CO_2, the high variability in air concentrations of halocarbons adds further uncertainty to flux estimations. Consequently, to estimate regional fluxes, high resolution measurements simultaneously in air and seawater are required. The diurnal variation, the seasonal variation and the wind direction are crucial parameters for the air-sea flux. The biogenic production is typically highest mid-day, which coincides with the highest photolytic degradation rate in the atmosphere. This needs to be accounted for in flux calculations. --Unpublished data---. Near-surface photolysis of especially iodinated compounds may also complicate the flux assessments as “surface concentration” often is measured at 5-10 m.

Unpublished Data

Figure 8. Air mixing ratio of CH_2ClI during an 18 days period going from 30°N, 17°W to 30°S, 48°W (days in UTC, with each day starting at 24.00) (Karlsson et al. unpublished data)

4.2. Geographical Variation

It has been shown that the ocean is not exclusively a source of volatile biogenic halocarbons to the atmosphere. Regionally, it can be under-saturated and act as a sink [*Quack and Wallace*, 2003]. Compared to anthropogenic and/or long-lived compounds, high regional and seasonal variability of the distribution of biogenic halocarbons in seawater and air can be found. Generally, highest concentrations are found in areas influenced by macroalgae, i.e. coastal zones (Figure 9). Reliable quantifications of the variations are limited by seasonal variations and lack of data. For $CHBr_3$, *Quack and Wallace* [2003] summarized the collective measurements in air and sea and estimated air-sea flux. *Butler et al.* [2007] merged pair-wise air-sea measurements and flux calculations of $CHBr_3$, CH_2Br_2 and CH_3I from 7 expeditions. The result from these studies indicated highest over-saturations over the equator and a stronger source of bromoform in the Pacific than in the Atlantic [*Butler et al.*, 2007]. --Unpublished data------------------------------.

Background levels of bromoform in air are ~0.5-1.5 pptv and regional maxima of >> 100 pptv have been found. In water, concentrations between 0.6 and 60 pmol L^{-1} (mean 18 pmol L^{-1}) have been found in the global open ocean, with 7.5 to 240 pmol L^{-1} in shelf regions (mean 72 pmol L^{-1}) and 36 to 2,800 pmol L^{-1} near-shore (mean 930 pmol L^{-1}). The total load of bromoform to the atmosphere from the ocean was estimated to 10 Gmol Br yr^{-1} [*Quack and Wallace*, 2003]. A range of 3 to 22 G mol Br yr^{-1}, corresponding to calculations based on the 25% and the 75% percentiles of the dataset, shows the high uncertainty in these estimations. *Warwick et al.* [2006] estimated global emissions of $CHBr_3$ of 5-7 Gmol Br yr^{-1}

Figure 9. Surface water concentration of $CHBr_3$ measured in October (Sweden)-December (Bellinghausen Sea) 2007 (partly shown in Paper V).

from an atmospheric 3D transport-model, but acknowledged the uncertainty. It was concluded that more comprehensive measurements of the oceanic flux were required, as well as further measurements in the troposphere and lower stratosphere. It should be noted that these air-sea flux estimations of bromoform differ considerably from global estimations of micro- and macroalgal sources of bromoform. *Carpenter and Liss* [2000] calculated a source from macroalgae of 0.4 – 2.7 Gmol Br year^{-1}, and *Quack and Wallace* [2003] a source from microalgae of 1.1 – 1.8 Gmol Br year^{-1}.

The implications of the high spatial and temporal variability of halocarbons on the air-sea flux were addressed in Paper V. -- --- --- --- --

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Unpublished Data

Figure 10. Saturation anomaly of $CHBr_3$,from 60°N to 80°S, for the transect shown in Figure 9 (partly shown in Paper V).

5. Polar Regions

Halogen chemistry in the Arctic has since the 1980's been in focus due to ozone depletion events (ODEs) at polar sunrise, and the connection to reactive halogen species. It was found that inorganic bromine, mainly BrO, in an autocatalytic process was highly involved in degrading ozone. This phenomenon is sometimes referred to as a "bromine explosion" [*Wennberg*, 1999]. *Barrie et al.* [1988] suggested that marine biogenic bromoform was an important source of the atmospheric bromine. This was supported by other studies, as boundary layer ozone was found to have a negative correlation to bromoform [*Sheridan et al.*, 1993; *Sturges et al.*, 1993]. More recent studies have, however, attributed the majority of the air-sea cycling of bromine to sea salts [*Simpson et al.*, 2007]. This assumption is uncertain as the halocarbon data from the Arctic Ocean is sparse.

It is known that Arctic macroalgae, as well as ice living algae, are potent producers [*Laturnus*, 1996; *Tokarczyk and Moore*, 1994], and high concentrations of halocarbons have been found in sea ice and snow [*Sturges*, 1997]. Halocarbon investigations in the Arctic have been confined mainly to coastal sites, where high concentrations have been found [*Schall and Heumann*, 1993], and to shorter transects [*Krysell*, 1991]. The horizontal and vertical distribution of halocarbons over the Arctic Ocean and factors that govern the production had not previously been investigated. This was studied in Paper II and III.

The biogeochemical cycling of halogens is likely to be influenced by a changing Arctic Ocean. Physical variables, such as the fact that warmer surface water decreases the solubility of halocarbons, and that less ice extent increases air-sea flux are relatively straightforward. The change in biogenic production is, however, not possible to assess given the current knowledge.

In the Antarctic, ozone depletion, mainly in the stratosphere, is even more severe than in the Arctic. This has been attributed to that reactions occur on polar stratospheric clouds which are more prone to form in the colder Antarctic stratosphere [*Poole and McCormick*, 1988].

Like the Arctic Ocean, the Southern Ocean is vastly under-sampled for halocarbons. Measurements at coastal sites [*Hughes et al.*, 2009; *Hughes et al.*, 2012] and studies of Antarctic macroalgae [*Laturnus et al.*, 2000] show that regional sources certainly can be significant, but the source strength of the open ocean regimes, and the ice-covered areas is more uncertain. *Carpenter et al.* [2007] found high over-saturations, of several bromo- and iodocarbons, in the Weddell Sea. This was in the vicinity of sea ice, and the production was attributed to ice-algae liberated from the ice. However, these measurements were performed in coastal waters, and arguably, the high concentration could origin from macroalgae. In the Bellinghausen Sea, *Butler et al.* [2007] found concentrations of $CHBr_3$ and CH_2Br_2 that were slightly over-saturated at average, but also regions with under-saturated water was found. Given the limited data it is not possible to determine the source strength of halocarbons from the Southern Ocean.

In Paper IV and V, the first halocarbon data from the Amundsen and Ross Seas is presented.

5.1 Cryosphere

A main feature of the Polar regions is the sea ice and overlying snow. The ice cover limits air-sea exchange, and, the flux through sea ice is still uncertain. Compared to frozen freshwater, sea ice is highly porous with a network of brine filled channels. The apparent diffusion rates for O_2 and SF_6 through sea ice have been shown to be slightly larger than normal aqueous diffusion rates, with a possible explanation that gas-phase partitioning in partially gas filled pore spaces is responsible for the enhancement [*Loose et al.*, 2011]. It is also plausible that turbulence in the brine channels is created from wind stress, movement of underlying water, ice living organisms and freezing/thawing. For some C1-C3 iodocarbons, it was estimated that gas transfer velocities for ice-covered regions at -3°C was at least ~60 times lower compared to transfer velocities over polynyas or leads [*Shaw et al.*, 2011].

Another concern is the halocarbon production from sea ice algae (Figure 11). Cultures of microalgae typically found in sea ice have proven to form several halocarbons [*Tokarczyk and Moore*, 1994], and bromoform production has been seen in suspensions of organisms from sea ice, presumably ice-algae [*Sturges et al.*, 1992].

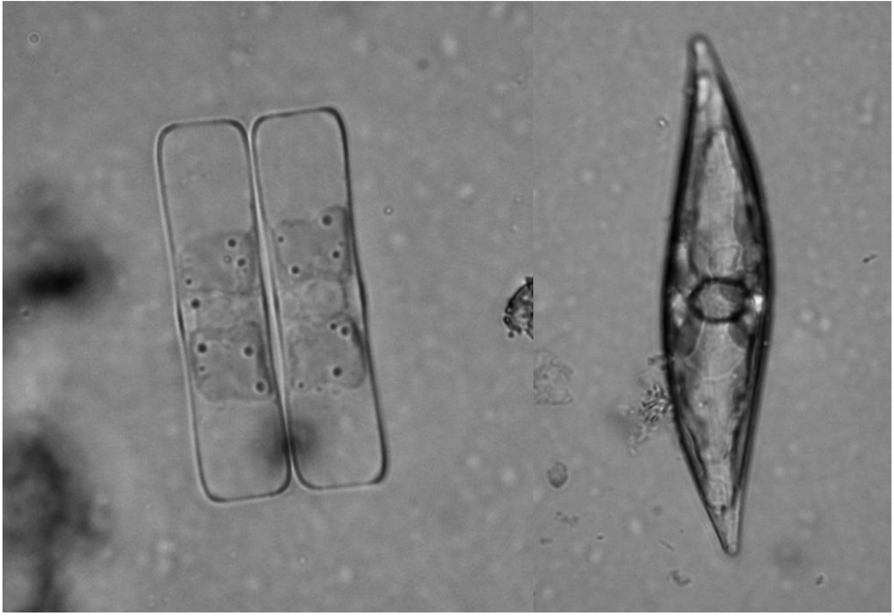

Figure 11. Microalgae found in sea ice brine in the Arctic. On the left, a chain-forming diatom, *Navicula cf. granii*. On the right, a motile diatom, *Gyrosigma* / *Pleurosigma* spp. (courtesy of Pauline Snoeijs).

In snow, production of CH_3Br, CH_3I and C_2H_5I, has been shown. This was, however, attributed to photochemical formation as it was argued that the dry and cold conditions at the site (Summit, Greenland) excluded the possibility of a biological production [*Swanson et al.*, 2002]. Elevated concentrations of bromoform in snow was found by *Sturges* [1997], who also found chlorophyll *a* in the snow. Nevertheless, the high concentrations were described as a "mystery" and attributed to flux from sea ice or abiotic processes with a similar reasoning as *Swanson et al.* [2002].

The results from Paper II showed for the first time that halocarbon production in
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Production in unaltered sea ice brine samples was investigated in the Arctic Ocean (Paper II), and the Southern Ocean (Paper IV). The distribution in the underlying water was also investigated (Paper III-IV), and it was shown that the concentration was higher than in open water, and that the concentration increased toward the sea-ice interface. The concentration in brine (normalized to seawater salinity) was elevated compared to seawater, i.e. the sea ice clearly was a source of halocarbons.

Compared to normal surface waters over deep water basins (global open ocean mean ~18 pmol L^{-1} [*Quack and Wallace*, 2003]), the concentrations in the ice-covered central Arctic Ocean --
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--. As air-sea flux is limited by the ice, halocarbons may become over-saturated in the water. It is not clear what the fate of halocarbons produced in the sea ice is, but they may be transferred to the atmosphere through leads in the ice or through diffusion, or be transported with the surface water to ice-free regions and thereby transfer to the atmosphere. Also, microbial degradation could occur. -------------------------
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Figure 13 shows the surface water concentration of $CHBr_3$ in the Arctic Ocean measured during the Beringia 2005 Expedition (Paper II-III), together with other surveys from 1991-2002 (Abrahamsson et al., unpublished data). ---------------
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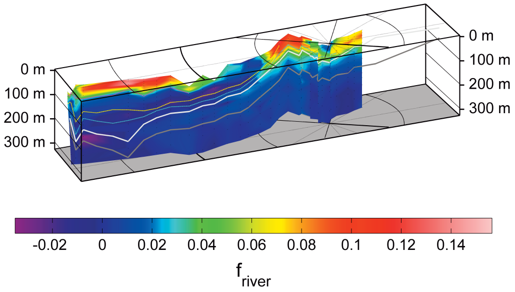

Figure 12. The CDOM signal, the river water fraction (se Paper III) and the bromoform concentration in the Upper Waters of the Artic Ocean from the Beringia 2005 expedition. On top of the depth distribution, the concentrations in seawater just below the ice, in brine from two depths, and in melt ponds are shown. Also, the signals of Alaskan Coastal Water (ACW), winter Bering Strait Water (wBSW) and summer Bering Strait Water (sBSW) are indicated.

Figure 13. Surface water concentrations (mean 30m) of bromoform compiled from data from the expeditions Oden Arctic Ocean 1991 (diamonds), Hudson 1992 (triangles), Swedish-Russian Tundra Expedition1994 (stars), ARKXI 1995 ("H"), ARK XII 1996 (pentagrams), AO-02 (crosses), 2002 (Abrahamsson et al. unpublished.) and Beringia 2005 (circles). The ice-cover shown is the mean sea ice extent at the time of the Beringia 2005 cruise, i.e. it does not apply to the other expeditions.

The large-scale changes that have been seen to occur in the Arctic are likely to affect the emission of halocarbons. The result from Paper III showed that a ---Unpublished data---.

To investigate what factors are important for the production from sea ice algae, production rates were determined and compared to pigment composition, photosynthetic activity and concentration of nutrients (Paper II). --Unpublished data--

cultures studies to the natural environment. In cultures with high biomass, degradation processes are likely to be slow, and negligible, compared to production rates. This may not be true in nature. In the presence of other micro-organisms these parallel processes of production and degradation may at times be in the same range. Previous estimations of the Arctic ice-algal emission of bromoform, of 4.7-70 Gg year^{-1} [*Sturges et al.*, 1992], which have not accounted for microbial degradation, may therefore be too high.

Table 2. Concentration in brine in the Southern Ocean (Amundsen and Ross Seas) in Dec-Jan 2007/2008 and over the central Arctic Ocean in Aug-Sep 2005. All samples are from melting ice with brine salinity lower than in the underlying seawater.

Compound	*Arctic Ocean*^{a}		*Southern Ocean*^{b}	
	average pmol L^{-1}	range pmol L^{-1}	average pmol L^{-1}	range pmol L^{-1}
CH_3I			3.4	(1 - 5.1)
CH_2ClI			8.7	(0.29 - 29)
CH_3CH_2I			2.5	(1.4 - 4.6)
$CH_2ICH_2CH_2CH_3$			1.8	(0.9 - 3.2)
CH_2BrCl			2.2	(1.3 - 3.8)
CH_2Br_2			12	(2.7 - 32)
$CHBrCl_2$			9.9	(2.7 - 32)
$CHBr_2Cl$			1.8	(0.58 - 3.2)
$CHBr_3$			15	(0.03 - 34)

[a] n=33

[b] n=7

6. Analytical Considerations

To measure halocarbons in the atmosphere and in the ocean is not without difficulties. Complicating factors are:

- Volatility
- Short-lived (e.g. photolysis)
- Production/Degradation by microorganisms
- Low concentrations
- The sample-matrix (seawater)
- Sample through-put

The volatility issue is handled by sampling quickly, but gently, to avoid outgassing, and the sampling containers are filled without headspace. Typically, we have sampled with 100 mL gas-tight glass syringes, which are used to directly inject the sample in the instrument. Alternatively, 40 mL vials with Teflon lined septa have been used.

The short-lived nature, e.g. sensitivity to photolysis, microbial degradation processes, and the fact that microorganisms may continue to produce halocarbons after sampling, limits storage possibilities. *Hughes et al.* [2009] has, however, shown that purged samples may be stored for at least 16 months in adsorbent tubes. This is an important finding, which allows for more compact systems, and makes sampling possible in areas where no analysis instrument can be brought. Still, because of the increased uncertainty, it is preferable to perform the analysis directly after the samples are taken. Regarding the depth profile samples (Paper III and IV), all samples from a station were analyzed within ~20h and stored cool (around 0 °C), in darkness, during that time.

The low concentrations, typically fmol L^{-1} to pmol L^{-1} in the oceans, and often less than 1 pptv in air, require sensitive methods. Seawater is a highly complex sample matrix and selectivity is needed. The technique of choice is pre-concentration by purge-and-trap, separation by gas chromatography (GC) and quantification by an electron capture detector (ECD). Alternatively, with proper tuning, mass spectrometers (MS) can be used as detectors. They are generally less sensitive than ECD for halocarbons and certainly less adapted for field-work (in Paper II-V, ice-breaker expeditions). For this work, MS has, however, been used at the university laboratory to confirm the identity of the chromatographic peaks.

6.1 Instrumental setup

Two different types of purge-and-trap systems have been used in this work. One of these is a custom-made system that has been modified from an earlier version described by Ekdahl and Abrahamsson [*Ekdahl and Abrahamsson*, 1997]. One modification was the addition of a gas sample loop that allowed measurements in air. Two commercial systems were also used.

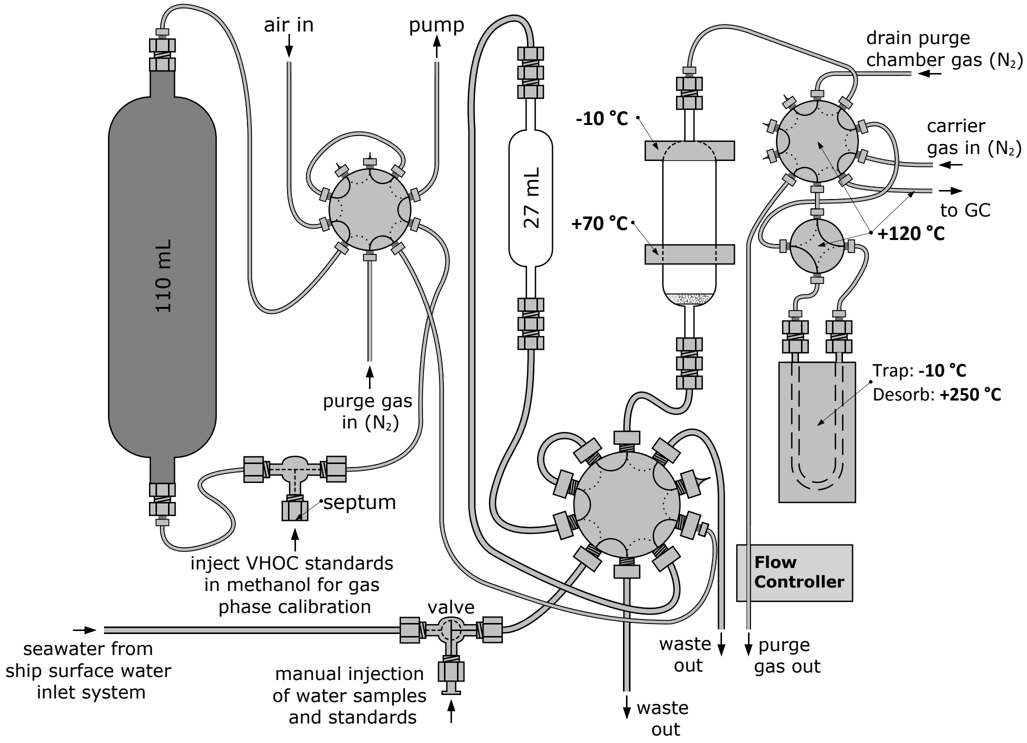

Figure 14. The custom-made purge-and-trap system used in this work.

The basic outline of the purge-and-trap system is shown in Figure 14. To optimize extraction yields, the bottom part of the purge chamber was heated (60-70 °C), and in order to minimize chromatographic and trapping issues due to water, the upper part was cooled (-10 °C). It was shown that for 27 mL samples, 9 minutes of purging at 100 mL min^{-1} gave extraction yields close to 100%.

There are a number of traps that can be used to adsorb halocarbons. In paper I and II, the traps were filled with Porapak, and cooled with a cooling bath to -10°C. When this adsorbent was used, the gas stream was dried with anhydrous $MgClO_4$, which had to be replaced regularly. This decreased the sample through-put as a "system blank" had to be run after replacement. In Paper III, IV and V, the trap contained the commercial adsorbent VOCARB-3000 (Supelco), which is a multi-bead adsorbent that contains Carbopack-B (Graphitized Carbon Black), Carboxen-1000 and Carboxen-1001 (Carbon Molecular Sieve). For this trap, the drying step after the purge chamber could be omitted.

The system has been extensively optimized to give high purge efficiency, high reproducibility, low carryover, and adequate separation, all in reasonable time (~30 minutes total analysis time). This involved selection of lengths and internal dimensions of valves and tubings to avoid bottle-necks, and choice of materials to avoid wall-reactions and adsorption. The timing of each step in the purge-and-trap system and the temperature in the heated zones, as well as purge-gas flows and bake-out flows, have also been tested at different settings before finalizing the method. The GC-temperature programming is important given the high number of peaks in a typical seawater chromatogram. For carrier gas flow, 3mL min^{-1} was used which is a trade-off, as the highest separation efficiency for the column used (DB-624, ID 0.32 mm) is lower. The higher flow was necessary for desorption and injection of the samples.

During expeditions, sample through-put is a major obstacle when simultaneous measurements of air and water are to be conducted, or high resolution depth profiles both vertically and horizontally are collected. Therefore, two or three instruments have been used. The inter-calibration procedure showed that there were no systematic errors in either system, and ensured high quality data. Figure 15 shows depth profiles from the Arctic Ocean (station 42, Paper III) where all three instruments were used.

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Data

Figure 15. Depth profiles of $CHBr_3$ and the anthropogenic CH_3CCl_3 in the Amundsen Basin of the Arctic Ocean (89.5°N, 167°E), where three different systems where used for the measurements.

6.2 Calibration

As recognized by the research community [*Butler et al.*, 2010], and revealed by an UK inter-laboratory calibration study [*Jones et al.*, 2011], it is not straightforward to calibrate the instruments for these volatile short-lived compounds. Traceability is important, since merged datasets are used in modeling of global budgets of these compounds. It was suggested by *Butler et al.* [2010] that gas standards are preferred, due to less interferences, and less possible reactions than in liquids. Stability of, especially, iodinated compounds in gas cylinders was, however, noted as uncertain. It could be speculated that there are additional uncertainties from gas standards, such as leakage and contamination, which may be less of a problem for liquid standards if precautions are taken.

For this work liquid standards were used, and all standard substances were stored as pure compounds in darkness at +4°C. Prior to calibration, these were diluted several steps in methanol (purge-and-trap grade) at -20°C. This was done in vials, through septa, to ensure that no loss or contamination occurred. The possibility of losses was further decreased by the cold solution. Dark vials were used to exclude photolytic reactions. Both solvent and solutes were gravimetrically determined with a high-precision scale. This allowed exact determination of the w/w ratio of each halocarbon in the final solution, i.e. without dependence on volumetric measurements, which would introduce large errors. Generally, mixed standards, with about 8 compounds per solution, were used. The syringes used were thoroughly cleaned, in several steps with methanol, between additions of different compounds, and different syringes were used for each dilution step. The mixtures were chosen so that compounds that could be suspected to, potentially, be interconverted, such as CH_2I_2/CH_2ClI or $CHBr_3$/$CHBr_2Cl$, were not in the same solution.

To avoid possible contamination from methanol, three different mixed standards were added to the final seawater standard solutions in varying proportions, and the methanol concentration was kept the same. Four-point calibrations were used, and from additions of varying proportions of the different halocarbon mixtures, inter-conversion or cross-contamination issues would be easily spotted from the calibrations curves. The mixed halocarbon methanol standard solutions could also be used to calibrate for the air measurements (Figure 14). The solution (1-3 μL) was readily volatilized and trapped with no heating of the injection port required.

It was found that these standards (stored at -20°) could be used at least for the duration of an expedition (<4 months). No reason was found why liquid standards would be inferior to gas standards if properly prepared and handled. Rather, possibilities of leakage, contamination or wall reactions in gas cylinders are uncertainties which indicate that liquid standards instead may be preferable.

7. Concluding remarks

This work has brought new insight to the biogenic formation of volatile halocarbons in Polar Regions. In both the Arctic Ocean and the Southern Ocean, sea ice and overlying snow was shown to be sources that should be considered in global models. In the sea ice and underlying water, concentrations in ranges which typically are found only in coastal regions were encountered. The strong sea ice dependence was obvious in the ice-covered regions near polynyas in the Southern Ocean. Even though the primary productivity of pelagic algae was much higher in the polynyas, the highest concentrations of halocarbons were found under the ice. Regions surrounding the sea ice were also under-saturated compared to overlying air which had been travelling over ice-covered areas. This indicates that the sea ice is the main source of halocarbons in this region. Estimations of the oceanic emissions of halocarbons to the atmosphere generally exclude the sea ice and instead assume a source from the open ocean correlated to pelagic primary production. The results presented in this work show that, in the polar regions, this is not appropriate.

In the Arctic Ocean, river water which carried high loads of terrestrial dissolved organic matter (DOM) from the large Russian rivers was shown to be a key factor for the high concentrations of brominated compounds found in the sea ice. As the load of DOM has been hypothesized to increase due to climate change, this could potentially have a dramatic effect on the production of halocarbons, both in ice and in the surface waters. To assess the net effect of climate change on halocarbons emission in the central Arctic Ocean is however not straightforward. Less formation of ice would, given the results in this work, presumably lead to less formation of halocarbons, even if pelagic primary production would increase. On the other hand, a higher seawater temperature would lead to less solubility and a smaller ice-cover to a larger area open to air-sea exchange which could increase the sea to air flux.

Another factor which previously had not been seen is the high post-bloom degradation of halocarbons that could be found in several sea ice brine samples. The rates indicated microbial degradation. It could be speculated that more rapid summer ice melt would release the halocarbons produced in the ice-algal blooms faster, which would decrease this sink.

In addition to these polar studies, it was also shown that cyanobacterial blooms in the Baltic Sea is a source of halocarbons. It was estimated that this source is in the range of 100 Mg yr^{-1} of bromoform.

8. Future Outlook

There have been several attempts to estimate the global oceanic load of halocarbons. Different approaches have been used, such as extrapolation of culture studies, net global air-sea flux from observed saturation anomalies at different regions ("bottom up" methods), and from atmospheric transport models ("top down" methods). These estimates are uncertain as has been shown in this thesis in a number of respects; poor seasonal and spatial coverage, accurate assessments of degradation rates still missing, common protocols for measurements of production rates not in place and parameterization of factors influencing air-sea flux not solved. In addition, the short atmospheric life-times make the air-mixing ratios dependent on wind patterns, which to a large extent influence the air-sea exchange.

One approach could be to investigate what affects the production. Ideally, this would be parameters which can be derived from remote sensing. It is clear that chlorophyll *a* alone is not a good enough proxy, since correlations to concentration or production, at least over larger areas, seldom is seen. With advances in remote sensing, estimations of a range of compounds, and even different types of algae, can be made. With satellite data it is possible to study the distribution of CDOM, which has been shown to influence halocarbon production.

A seemingly unnecessary uncertainty in flux calculations is that basic parameters such as the diffusion coefficients of biogenic halocarbons have not been determined, and have to be estimated. These should be measured, as well as rates of reactions of known abiotic degradation processes, to improve future modeling efforts.

Specific regions which require further investigations are the Polar regions. The investigations in this work have been performed in the summer seasons, which is typically the case given the inaccessibility in other seasons. Studies at other times of year are required to be able to quantify the production from sea ice algae. Also, the vast continental shelf regions could be suspected to be a significant source of halocarbons, which should be investigated. --Unpublished data--. The significance of this source can however not be determined without measurements in this region.

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